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Structural Transformations of Technical Carbon under the Action of Nanosecond Laser Radiation

M. V. TRENIKHIN[1], O. V. PROTASOVA[1], G. M. SEROPYAN[2] and V. A. DROZDOV[1,3]

[1]*Institute of Hydrocarbons Processing, Siberian Branch of the Russian Academy of Sciences, Ul. Neftezavodskaya 54, Omsk 644040 (Russia)*

E-mail: tremv@ihcp.ru

[2]*Dostoevsky Omsk State University, Pr. Mira 55A, Build. 1, Omsk 644077 (Russia)*

[3]*Omsk Scientific Centre, Siberian Branch of the Russian Academy of Sciences, Pr. K. Marksa 15, Omsk 644024 (Russia)*

Abstract

The structural features and morphology of the particles (globules) of technical carbon (TC) samples, both initial and those treated with pulsed laser radiation, were studied by means of high-resolution transmission electron microscopy. Measurements were carried out; the average distances between graphene layers (d_{002}), length and curvature of graphene layers in TC globules were calculated. Results of the investigation of structural transformations in TC samples irradiated with nanosecond laser pulses are presented. Changes of the average diameter of globules in TC samples determine the essential difference in the morphology of irradiated nanoparticles and in the lattice parameter d_{002}.

Key words: technical carbon globules, extension and curvature of graphene layers, transmission electron microscopy, laser irradiation

INTRODUCTION

One of the major tasks in the area of carbon nanotechnologies is connected with the creation of new methods and development of available ones for the formation of nanoparticles with required size, predictable structure and properties. The methods used to synthesize carbon nanomaterials (CNM) include chemical vapour deposition [1], arc discharge [2, 3], ion [4], electron irradiation [5] and laser irradiation [6].

The latter method is widely used due to a number of advantages. Laser irradiation allows achieving higher rates of carbon ablation and the formation of CNM in comparison with other known methods. Laser beam provides direct energy transfer to the material under irradiation, which excludes the danger of contamination of the products. Finally, the energy of laser beam may vary within a broad range, so that it becomes possible to control temperature action on the material under irradiation.

Laser irradiation involves the processes of rapid heating of primary particles to the temperature typical for vaporization and partial evaporation of the carbon material, as well as rapid cooling accompanied by the crystallization into graphite-like nanostructures. For example, the first samples of fullerenes were obtained through evaporation of graphite during laser irradiation [7]. It is also known that the action of millisecond pulsed laser radiation on carbon black, depending on experimental conditions and pulse power, leads to the formation of onion-shaped, graphite-like particles or nanodiamonds [8].

It was demonstrated in [5] that technical carbon (TC) may serve as the initial material for obtaining ordered graphite-like structures. In this situation, TC is well characterized: comprehensive information on specific surface, globule and aggregate size, their structuring for several ten grades of TC were described in scientific and technological literature [9, 10]. However, such parameters of TC as average distance between graphene layers, extension and curvature of graphene layers have been determined and investigated not completely.

One of the most informative methods of CNM investigation is high-resolution transmission electron microscopy (HRTEM). It is urgent not only to obtain the information on the morphology of primary particles and structural changes occurring at the atomic level during the synthesis of CNM but also to obtain statistical data on the extension and thickness of graphene clusters, curvature degree of separate graphene layers *etc.* [11]. These investigations were carried out by the authors of [12] for carbon samples obtained from benzene, ethanol and acetylene.

On the basis of analysis of electron diffraction patterns and Fourier transforms of electron microscopic images, it is possible to determine the degree of CNM crystallinity. Further treatment of the Fourier transform images allows one to obtain the data characterising not only the distance between graphene layers but also the size of graphene clusters in TC globules. In addition, it is possible to estimate the thickness of graphene packing in such structures as carbon nanocapsules or nanobaskets [13].

In the present work we carried out the analysis of the structural parameters of initial TC globules and presented the results of their investigation after irradiation with nanosecond laser pulses.

EXPERIMENTAL

The samples of fine TC obtained using the furnace-based method (globule diameter 10–30 nm) and low dispersed TC obtained using furnace-based and thermal methods (globule diameter 100–300 nm) [9, 10] were studied.

To irradiate TC samples, we used a Nd:YAG laser with the wavelength of 1064 nm, pulse duration 16 ns, pulse-repetition frequency 10 Hz. Energy density was varied from 1200 to 6300 J/cm^2 with the use of focusing lens. Laser irradiation process is shown schematically in Fig. 1.

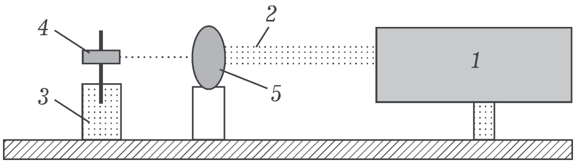

Fig. 1. Scheme of the set-up for laser irradiation of TC: *1* – source of pulsed laser radiation, *2* – laser beam, *3* – sample holder, *4* – sample, *5* – focusing lens.

The analysis of the structure and morphology of globules was carried out using transmission electron microscope JEM-2100 JEOL (Accelerating voltage 200 kV, resolution 0.145 nm).

Computer processing of the electron microscopic images, determination of the distance between graphene layers (d_{002}), length (L) and curvature of graphene layers (K) was carried out using the Digital Micrograph Gatan software package. The value of d_{002} was determined after the treatment of electron diffraction patterns through plotting the profiles of radial intensity according to the procedure presented in [13].

The value of K was determined as a distance between its ends measured along the straight line (A) and divided by the total length of this layer (L) (Fig. 2).

RESULTS AND DISCUSSION

According to HRTEM data, TC is composed mainly of spherical particles; low degree of ordering of the structure of graphene clusters comprising globules is observed (Fig. 3). The distance between graphene layers varies within the range 0.36–0.40 nm for fine TC and 0.36–0.37 nm for coarse TC. Electron diffraction pat-

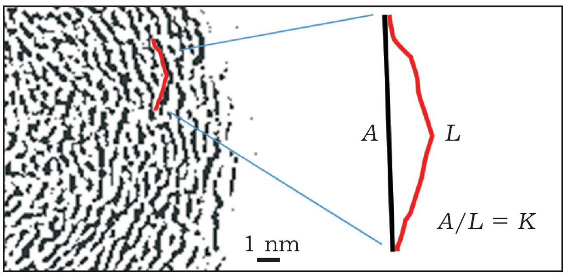

Fig. 2. Electron microscopic image of the fragment of TC globule structure and determination of K parameter (curvature of graphene layer).

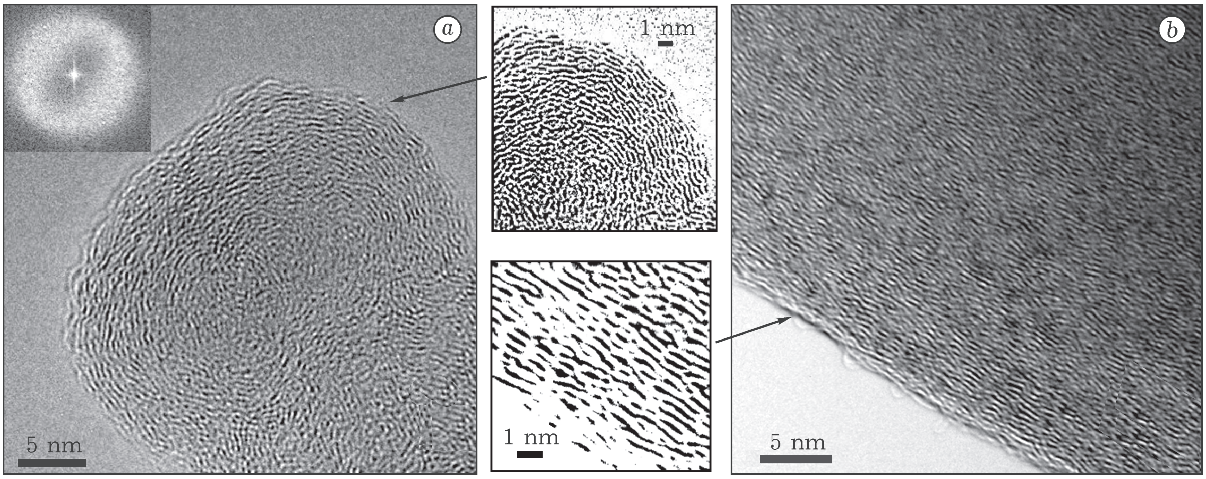

Fig. 3. Morphology of the globules of fine (*a*) and coarse (*b*) technical carbon.

terns obtained by means of Fourier transform from electron microscopic images of graphene layers have the appearance of two diffuse rings, which is another evidence of not very high degree of structural ordering.

Coarse TC is characterized by the presence of longer graphene layers in comparison with fine TC (Fig. 4). In this case, measurements were carried out within the range 0.4–3.0 nm. According to the statistical data, layers with the length up to 1 nm dominate in the globules of fine TC (see Fig. 4, *a*), while a broader length distribution is characteristic of coarse TC (see Fig. 4, *b*); layers 1–2 nm long are observed with the same frequency as the layers shorter than 1 nm.

The curvature of graphene layers (K) in the globules of fine TC differs substantially from this parameter for coarse TC. Computer processing of electron microscopic images shows that the maximum of K distribution for fine

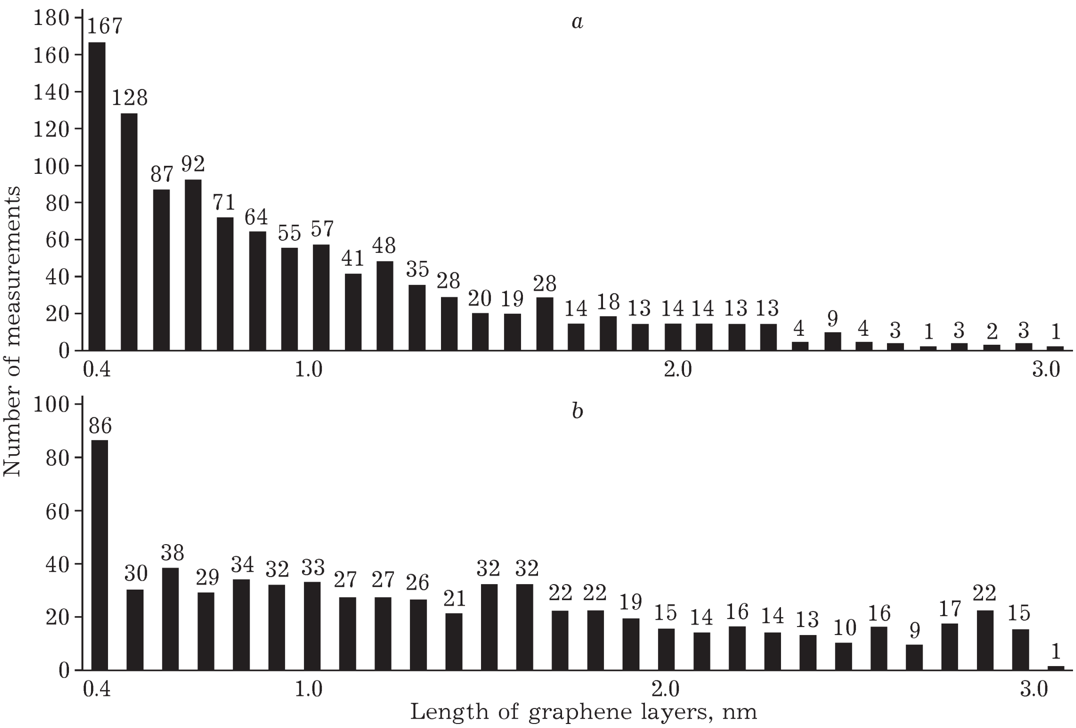

Fig. 4. Histograms of the length of graphene layers for fine (*a*) and coarse (*b*) technical carbon.

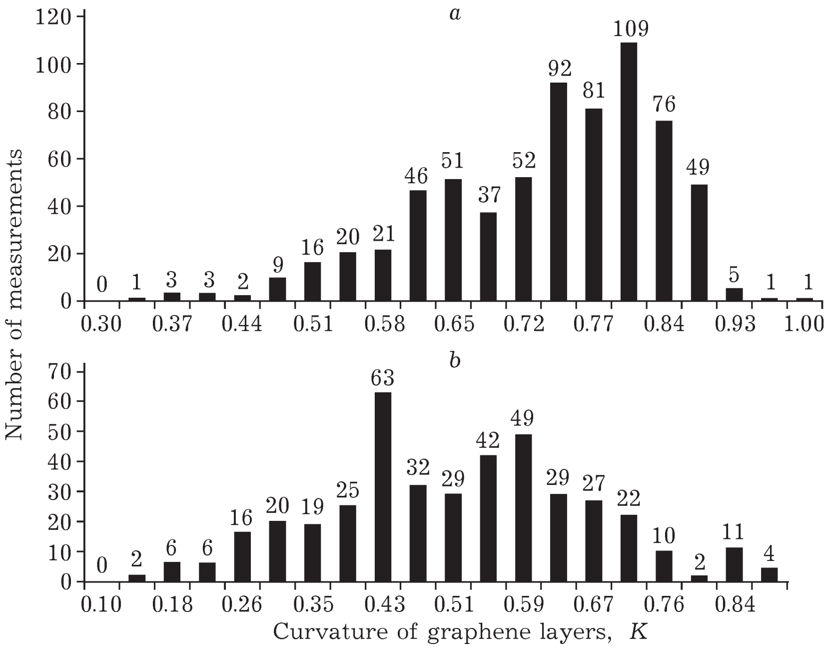

Fig. 5. Curvature of graphene layers of fine (*a*) and coarse (*b*) technical carbon.

TC fits within the range 0.75–0.85, while in the case of coarse TC 0.4–0.6 (Fig. 5).

Electron microscopic studies of the samples of fine TC subjected to laser irradiation with energy density of 1200–6300 J/cm^2 provide evidence of the formation of spheroidal particles 10–30 nm in diameter with the shell composed of 5–10 graphene layers. Carbon particles with this morphology were called hollow spheres or capsules [14]. The average distance between graphene layers in these particles, measured in electron diffraction patterns, is 0.355–0.363 nm.

After irradiation of coarse TC, a deep structural rearrangement of carbon material is observed. The formation of globular structures 100 to 500 nm in diameter composed of the rows of parallel extended graphene layers was observed by means of HTTEM (Fig. 6, *b*–*d*). In turn, the layers are united into carbon shells embedding one another and having a definite volume of empty space between them. These

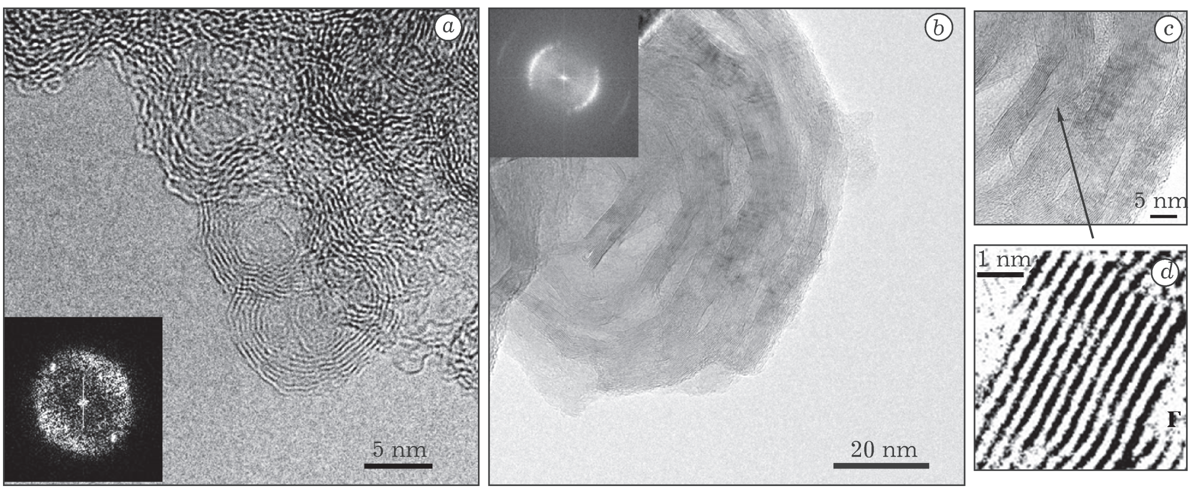

Fig. 6. Morphology of the globules of technical carbon after irradiation: *a* – finely dispersed sample; *b*, *c* – coarse dispersed samples; *d* – image of the structure of graphene layers.

structures generally do not form spheres similarly to initial TC but often have fractured geometry over a circle. After irradiation we often observed the groups of such particles embedded into a common shell. In the case when the density of radiation density was 6300 J/cm^2, average distance between the layers measured from electron diffraction patterns was (0.344±0.002) nm. A decrease in the density of energy to 3500 J/cm^2 caused an increase in d_{002} value to 0.335–0.360 nm. In electron microscopic images the morphology of these particles resembles a section of rose bud (see Fig. 6, *b*). The particles of this morphology were obtained and studied by the authors of [15]. The particles of this kind were synthesized using a setup generating conical converging shock waves.

The presence of several rather clear rings is characteristic of the electron diffraction pictures of rose-shaped particles, which allows one to speak of the substantial increase in the degree of structural ordering of graphene layers forming these particles in comparison with initial globules.

Analyzing the results we may conclude that two types of CNM are formed as a result of laser irradiation of TC, depending on the diameter of primary particles and the features of their structure (curvature and extension of graphene layers). Irradiation of globules with the diameter of 16–30 nm leads to the formation of nanocapsules, while irradiation of TC particles 100–300 nm in diameter gives rose-shaped particles. Taking into account literature data [16, 17], we may assume that regular concentric packing of carbon layers is most probably formed during laser irradiation due to rapid heating (~15 ns) to a temperature of 3500–4000 K and the transition of the initial substance of globules into the vaporized state, followed by crystallization of carbon into nanocapsules and rose-like particles.

A similar investigation of the characteristics of irradiated samples by means of TEM is connected with the fact that these materials may be promising for fuel elements of new generation. At present, attempts are known to use these structures in lithium ion batteries where carbon nanospheres 100–200 nm in diameter were used as negative electrodes [18].

CONCLUSION

So, on the basis of the results of electron microscopic studies, the information on the average distance between graphene layers, extension and curvature of graphene layers in the globules of technical carbon was obtained. The distance between graphene layers varies within the range 0.36–0.40 nm for fine TC and 0.36–0.37 for coarse TC.

The possibility to use pulsed nanosecond laser radiation with high energy density for structural transformations of the particles of technical carbon with the formation of new modifications of nanostructured carbon was demonstrated.

An increase in the spatial extension of graphene layers and change of the morphology of the globules of technical carbon provide evidence of substantial rearrangement of these layers.

Depending on the size of primary carbon globules, the formation of nanocapsules and rose-like particles occurs during laser irradiation.

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