# Production of carbon nanoclusters supported on a graphite foil by laser ablation under supercritical conditions

**Sergei I. Kudryashov,* Sergei G. Ionov and Nikita B. Zorov**

*Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax: +7 095 932 8846; e-mail: serge@laser.chem.msu.ru*

The most probable size of carbon nanoclusters produced under supercritical conditions by pulsed laser ablation from a graphite foil covered by a glass plate gradually decreased from 40 to 10 nm as the laser power density increased from 0.05 to 1.6 GW cm$^{-2}$.

Nanostructured materials consisting of nanoclusters less than 10 nm in diameter are expected to be different from common polycrystalline materials in the elastic, optical, magnetic and electrical properties.[1–3] These cluster-assembled materials are usually produced by physical deposition using various sources of clusters (laser vaporisation, sputtering of solids by ion and electron beams or electric discharges).

In this work, a new technique for the production of refractory nanocrystalline materials is proposed. It is based on clustering (spinodal decomposition) of a thermodynamically unstable (labile) liquid phase with near-critical parameters.[4] The characteristic size of charged carbon nanoclusters that were generated from a polycrystalline graphite under laser-induced spinodal decomposition and detected in a gas phase by real-time electrostatic probe technique[5] varied within the range $10^4$–$10^6$ atoms per cluster (the diameter of clusters varied from 6 to 30 nm at a liquid carbon density of about 2 g cm$^{-3}$).[6] However, the preparation of nanocrystalline materials using this phenomenon has not been studied experimentally.

In this work, carbon nanoclusters were produced from a low-density ($\rho$ = 0.7 g cm$^{-3}$) graphite foil, which was extensively studied earlier.[7–10] Low bulk density and high porosity (near 70%) of the sample resulted in the black body absorbance (0.9) of visible light by a subsurface layer (100 nm) of the foil, very slow propagation of ultrasonic waves ($V_{us} \approx 450$ m s$^{-1}$)[8] in the sample and low thermal diffusivity. Quasi-equilibrium laser evaporation of the subsurface layer of the sample occurred in pores with an average size of 10–20 nm (comparable to a free path length under conditions of intense evaporation) and was followed by subsequent formation of critical and supercritical states of carbon[9,10] due to a relatively high bulk density of the foil sample ($\rho > \rho_{crit}$, where the critical carbon density $\rho_{crit}$ is equal to 0.64 g cm$^{-3}$).[11] A considerable energy (about 70 kJ mol$^{-1}$) released under laser irradiation of the graphite foil due to thermal annealing of non-equilibrium thermally and chemically induced defects (vacancies *etc.*) in graphite crystallites decreased the laser power density required for the generation of a supercritical carbon phase to 0.006 GW cm$^{-2}$.[9,10]

A sample of the graphite foil (size of 1×1 cm, thickness of 0.06 cm) used for preparing carbon nanoclusters was placed on a square linear translation stage, which can be moved in the horizontal plane with a step of 5 μm. The surface of the low-density sample was accurately covered with a transparent glass plate to avoid any interface cavities. This glass plate also allowed laser irradiation of the target and prevented the removal of the material. The second harmonic output of a Q-switched Nd:YAG laser [wavelength 532 nm, pulse energy 4.5±0.3 mJ, pulse width (FWHM) 25±2 ns, angular divergence 0.6 mrad, pulse repetition rate 12.5±1.5 Hz] attenuated by neutral calibrated filters by factors of 2.5, 5, 13.5 and 32 was chopped and focused by a lens ($F \approx 28$ cm) through the covering glass plate at the surface of the graphite foil sample with a focal aperture of the laser beam of about 160 μm. Fresh spots of the sample translated horizontally with a step of 150 nm were irradiated by 1–2 laser pulses. After irradiation, the sample was examined using a commercial JEM-2000FX scanning electron microscope (SEM) with a LaB$_6$ cathode (the maximum magnification of the microscope was 800000, and the accelerating voltage of the electron beam was 200 kV). The instrument was operated in the mode of detecting of secondary electrons scattered at the right angle to the surface of the graphite foil sample. SEM images of the modified surface of the graphite foil irradiated with the laser power densities $I_0$ 0.05, 0.12, 0.3, 0.64 and 1.6 GW cm$^{-2}$ were obtained.

**Table 1** Experimental and calculated parameters of laser-induced modification of a graphite.

| Power density/ GW cm$^{-2}$ | Thickness of heated layer/μm | Density of deposited energy/ kJ cm$^{-3}$ | Molar energy/ kJ mol$^{-1}$ |
|---|---|---|---|
| 0.048±0.005 | 0.31±0.05 | (3.4±0.8)×10$^1$ | (6±2)×10$^2$ |
| 0.12±0.01 | 0.5±0.1 | (5.6±1.7)×10$^1$ | (9±3)×10$^2$ |
| 0.31±0.03 | 1.0±0.2 | (7±2)×10$^1$ | (12±4)×10$^2$ |
| 0.64±0.06 | 2.0±0.5 | (7±2)×10$^1$ | (12±4)×10$^2$ |
| 1.6±0.2 | 5±1 | (7±2)×10$^1$ | (12±4)×10$^2$ |

Laser-induced modification of the covered graphite foil surface proceeded as an isochoric ‘autoclave’ process in the subsurface foil layer with the thickness $X$ of 0.3–5 μm, as measured by SEM (Table 1) [the initial depth of light absorption $\alpha^{-1}$ (532 nm) in the foil sample was equal to only 0.3 μm]. That is,

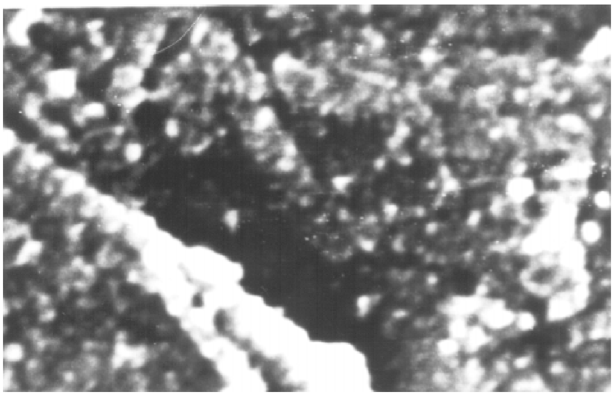

**Figure 1** SEM image of carbon nanoclusters at the surface of a graphite foil sample irradiated with a laser power density of 0.05 GW cm$^{-2}$ (magnification ×100000).

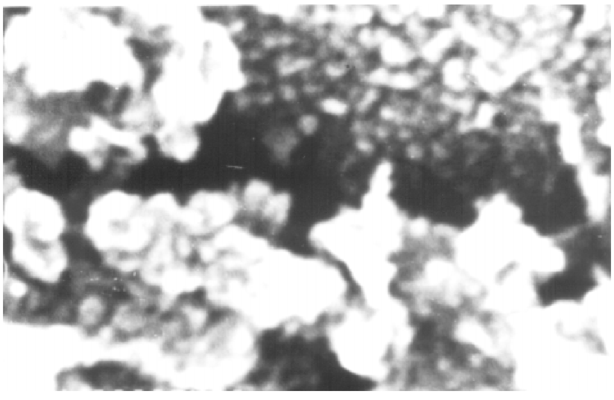

**Figure 2** SEM image of carbon nanoclusters at the surface of a graphite foil sample irradiated with a laser power density of 1.6 GW cm$^{-2}$ (magnification ×100000).

the pressure and temperature of the substance in the layer gradually increased during a laser pulse with the power density. Acoustic off-loading of the laser-heated layer with a thickness of 0.3–5 μm takes less than 10 ns at the velocity of ultrasonic waves $V_{us} \approx 450$ m s$^{-1}$. Thus, the main step of the graphite foil transformation occurs under quasi-static thermodynamic conditions of the 'bath'. The volume density of the energy $E_{dep}$ deposited in the laser-heated layer of the sample was calculated on the assumption that the absorbance $A$ of the sample is constant (0.9) during a laser pulse:

$$E_{dep} = A\min(\alpha, X^{-1})\int I(t)dt \qquad (1)$$

where $I(t)$ is the current laser power density with the peak value $I_0$, $\min(\alpha, X^{-1})$ is the effective absorption coefficient of the laser-heated layer. The molar energies corresponding to the volume densities of deposited energy 30–70 kJ cm$^{-3}$ are equal to 600–1200 kJ mol$^{-1}$ (Table 1) and increase as the laser power density increased from 0.05 to 1.6 GW cm$^{-2}$. These calculated values of the molar energy deposited in the laser-heated subsurface layer of the graphite foil are considerably higher than the enthalpy of formation of critical carbon (about 270 kJ mol$^{-1}$ as was estimated from the data[12]). This fact provides support to the conclusions of papers[9,10] related to generation of a supercritical carbon state at a free (uncovered) surface of the same graphite foil ($\rho > \rho_{crit}$) under the same conditions of laser ablation ($I_0 = 0.006$–$1.6$ GW cm$^{-2}$).

Carbon nanoclusters sized from 10 to 40 nm (Figures 1 and 2) were observed by SEM on the irradiated spots of the graphite foil surface. According to the calculations of a molar energy deposited in a laser-heated layer of the graphite foil, these particles were generated by laser ablation under supercritical conditions. It is assumed that this expanding supercritical fluid of carbon was quenched due to high porosity of the graphite foil and hence exhibited a microstructure of supercritical density fluctuations.

The most probable size (diameter) of carbon nanoclusters generated (Figure 3) gradually diminishes with increasing molar energy deposited in a laser-heated layer of the graphite foil (Figure 4). This tendency is consistent with the current theory of supercritical fluids,[4] which predicts a temperature-dependent decrease of the correlation radius as $T^{-2/3}$ and thus provides a real opportunity to control the size of laser-generated nanoclusters by choosing proper operation conditions.

Thus, carbon nanoclusters of size 10–40 nm were generated from a refractory material (graphite) through an intermediate laser-induced supercritical state of carbon.

This work was supported in part by the Russian Foundation for Basic Research (grant no. 98-03-32679).

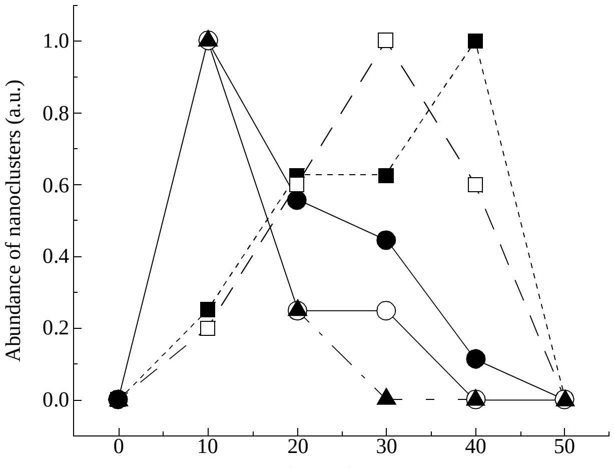

**Figure 3** Abundance of carbon nanoclusters (5 measurements, RSD < 25%) at the laser power densities (GW cm$^{-2}$): ■ 0.05, □ 0.12, ● 0.3, ○ 0.64 and ▲ 1.6.

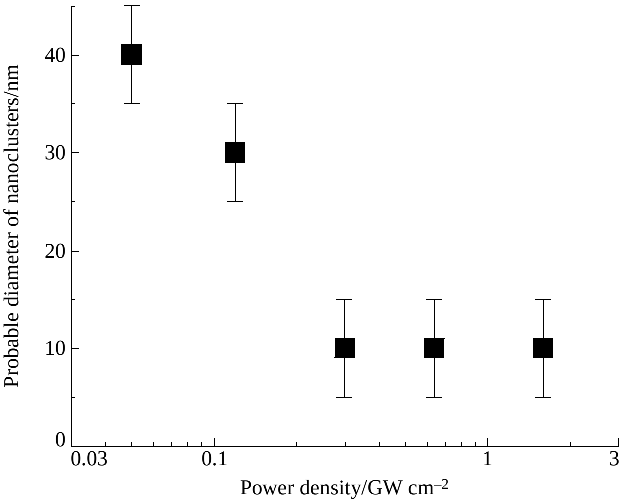

**Figure 4** The most probable diameter of carbon nanoclusters *versus* laser power density.

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*Received: Moscow, 15th July 1998*
*Cambridge, 26th October 1998; Com. 8/05584J*