

PACS numbers: 78.67.Bf; 42.70.Gi
DOI: 10.1070/QE2009v039n04ABEH013855

Optical limiting and bleaching effects in a suspension of onion-like carbon

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***Abstract*. We have studied the effect of nanosecond laser pulses ($\lambda = 1064$ nm) on the optical properties of onion-like carbon (OLC) prepared by high-temperature vacuum annealing of detonation nanodiamond and dispersed in N,N-dimethylformamide (DMF). The results demonstrate that, under low-intensity irradiation, the OLC suspension displays optical limiting behaviour. Increasing the incident intensity leads to bleaching of the suspension in the visible and near-IR spectral regions.**

Keywords: *optical limiting, optical bleaching, suspensions, onion-like carbon.*

1. Introduction

The interaction of laser radiation with suspensions of various carbon nanoparticles is of interest for the development of effective laser power limiters intended to protect light sensors and human eyes from optical damage [1 – 5]. Broadband optical limiters based on carbon nanoparticles have been the subject of many reports (see, e.g., the review by Chin et al. [6]). In contrast to fullerene solutions [7], aqueous suspensions of onion-like carbon (OLC), consisting primarily of nested closed fullerene-like shells, have a broad absorption band [8]. This makes such suspensions potentially attractive for the development of broadband optical limiters. Aqueous OLC suspensions are, however, known to be insufficiently stable. At the same time, our experiments have shown that OLC suspensions in N,N-dimethylformamide (DMF) are sufficiently stable. It is therefore of interest to characterise in detail the interaction of laser radiation with such suspensions, which is the subject of this study.

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Received 25 March 2008; revision received 10 July 2008
Kvantovaya Elektronika **39** (4) 342 – 346 (2009)
Translated by O.M. Tsarev

2. Experimental

OLC samples were prepared by annealing detonation nanodiamond particles in vacuum at 1800 K [9]. The particles were on average ~ 4.5 nm in size and formed 100- to 200-nm aggregates. Annealing leads to nanodiamond graphitisation and conversion to OLC. Bonding between the parent nanodiamond particles results in the formation of curved closed graphene shells which keep several carbon onions together to form agglomerates close in size to the parent nanodiamond aggregates.

The OLC powders were dispersed in DMF by sonication. The suspensions with an OLC concentration of 1 mg mL^{-1} were found to be stable (with little precipitation over a period of nine months). The average size of the OLC agglomerates was ~ 170 nm as determined by photon correlation spectroscopy (PSS Nicomp 380/ZLS instrument).

Figure 1 shows transmission electron microscopic (TEM) images (JEOL JEM-4000EX, 0.18-nm resolution) of the OLC sample studied. TEM specimens were prepared by ultrasonic spraying of an OLC suspension onto a holey amorphous carbon film supported on a copper grid.

Initially, the purpose of our experiments was to study optical limiting. To this end, we used standard open aperture z-scan measurements [10, 11] with 20-ns pulses at 1064 nm from a passively Q-switched single-mode Nd : YAG laser [12]. The suspension was held in a 1-mm-thick quartz cuvette, which was translated along the optical axis near the focus of a converging lens with a focal length of 100 mm. The laser pulse energies at the input (ε_{in}) and output (ε_{out}) of the measuring system (converging lens and optical cuvette) were measured with an automatic multichannel laser pulse detection system [13]. In this way, the transmittance of the cuvette containing the suspension, $\tau = \varepsilon_{out}/\varepsilon_{in}$, was determined as a function of the distance z from the cuvette to the beam waist ($z = 0$), produced by the lens. The pulse repetition rate was 1 Hz.

3. Experimental results

Experimental $\tau(z)$ curves were expected to have a minimum near the beam waist at any values of ε_{in} because of optical limiting. In our experiments, however, we observed optical bleaching: after a certain number of laser shots, $N = N_{cr}$, the irradiated zone became essentially transparent, as illustrated by the curve in Fig. 2a. According to our

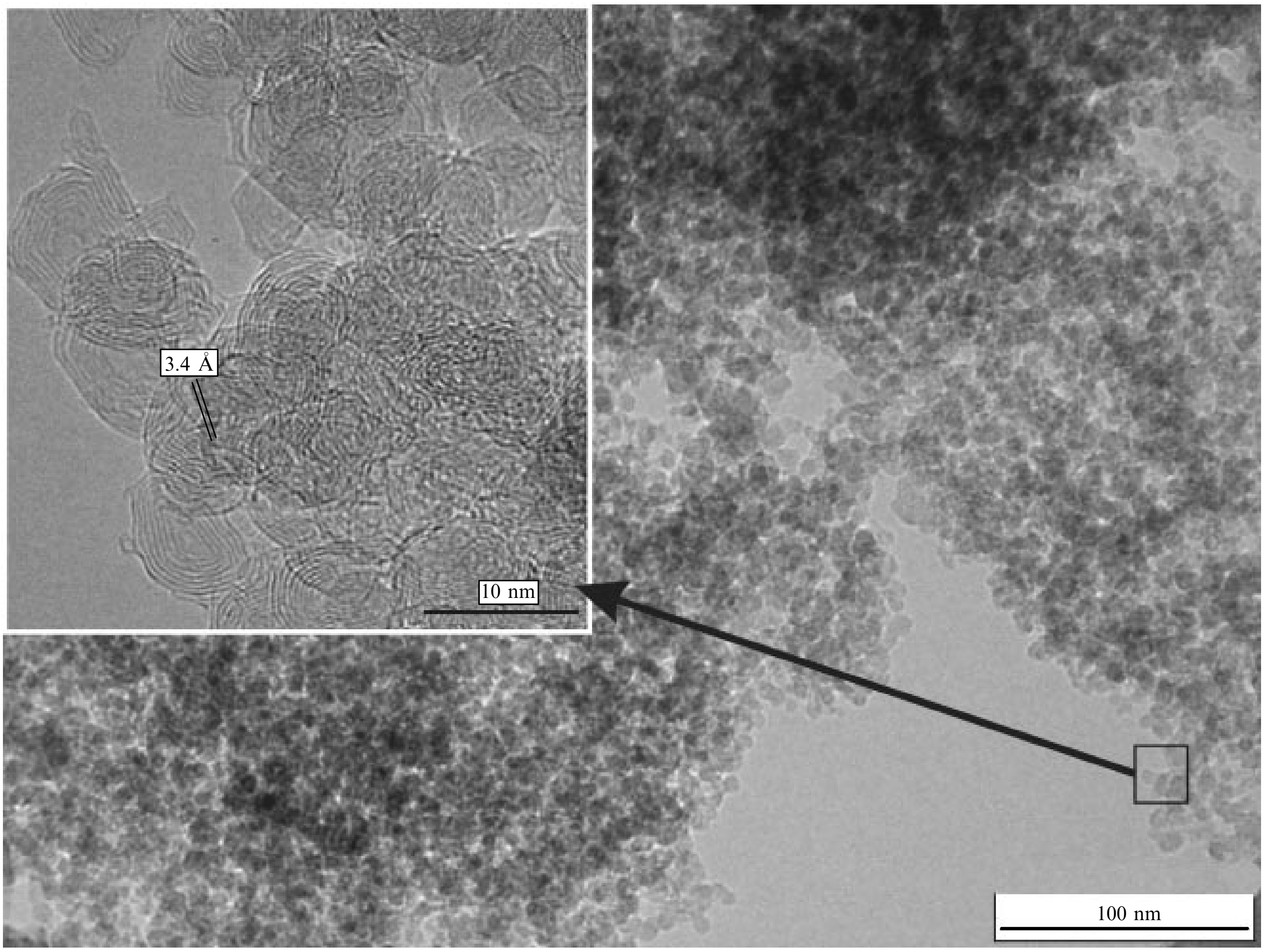

Figure 1. TEM images of the OLC sample. The dark lines represent projections of graphene shells perpendicular to the image plane.

experimental data, N_{cr} depends on the laser pulse energy at the cuvette input ε_{in} and distance z. As an example, Fig. 2 shows the $\tau(N)$ curves obtained at the same energy $\varepsilon_{in} = 0.5$ mJ and two values of z. Away from the beam waist, at $z = 23$ mm (Fig. 2b), the transmittance of the suspension is $\sim 65\,\%$ and is unaffected by multiple laser pulses. At the same time, when the cuvette containing the suspension is placed at $z = 0$, the first laser pulses experience optical limiting, with more than 80 % of their energy lost (Fig. 2a). With increasing N, the transmittance τ rises, and for $N > 80$ optical limiting gives way to bleaching: the irradiated zone of the suspension becomes essentially transparent. Thus, laser irradiation of a zone in the cuvette containing the suspension leads to an almost complete bleaching of the suspension. Of special note are 'dips' in τ in Fig. 2a, which give way to a rise in τ after several shots.

Figure 3 is an image of a bleached zone produced by 900 shots. The photograph was taken using a Canon EOS 20D camera with a macro lens (EF-S 60 mm f/2.8 Macro USM). The suspension bleached by laser radiation (zone *2*) was found to slowly (2.2×10^{-3} mm s^{-1}) rise by virtue of thermal convection, taking on the shape of a mushroom. Thus, the bleached suspension is stable, which distinguishes this type of optical bleaching from transient bleaching, e.g. in silicon nanocrystals immersed in glycerol [10] or in a fullerene-containing medium in response to two consecutive laser pulses [14]. It should further be noted that the volume of the bleached liquid increases owing to the gradual ingress of the suspension into the zone under irradiation (*2*). It is remarkable that, at a certain height, the bleached suspension begins to spread in all directions, in particular, downwards. Based on the above, the random dips in τ (Fig. 2a) are attributable to a nonuniform ingress of the unbleached suspension into the zone under irradiation.

To eliminate the effect of optical bleaching, the laser pulse energy in our optical limiting studies was kept below 0.1 mJ, and the measurement results were averaged over no more than five shots, after which the suspension was stirred. Figure 4 presents z-scan results for two values of ε_{in}. Note that the power density of the 1064-nm laser radiation was 0.04 MW cm^{-2} away from the focus of the converging lens and 19 MW cm^{-2} at the beam waist ($z = 0$). As seen in Fig. 4b, the transmittance of the suspension drops by a factor of 1.5 as the beam waist is approached. Thus, OLC suspensions in DMF are capable of optically limiting the laser beam power, just like aqueous OLC suspensions [8].

It is of interest to understand the mechanism of optical bleaching. To this end, we examined the effect of multiple laser shots on the absorption spectrum of the suspension. The suspension was placed in an optical cuvette and exposed to a focused laser beam for several days with constant stirring. The absorption spectra were measured with a PerkinElmer LAMBDA 650 double-beam UV/Vis spectro-

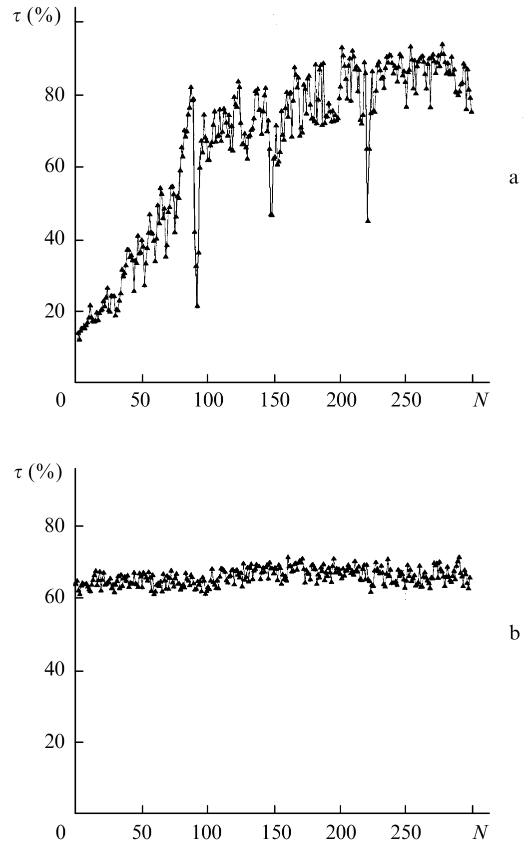

Figure 2. Transmittance τ of the OLC suspension in DMF as a function of N at $z = 0$ (a) and 23 mm (b) at a fixed laser pulse energy $\varepsilon_{in} = 0.5$ mJ (1-mm-thick quartz cuvette).

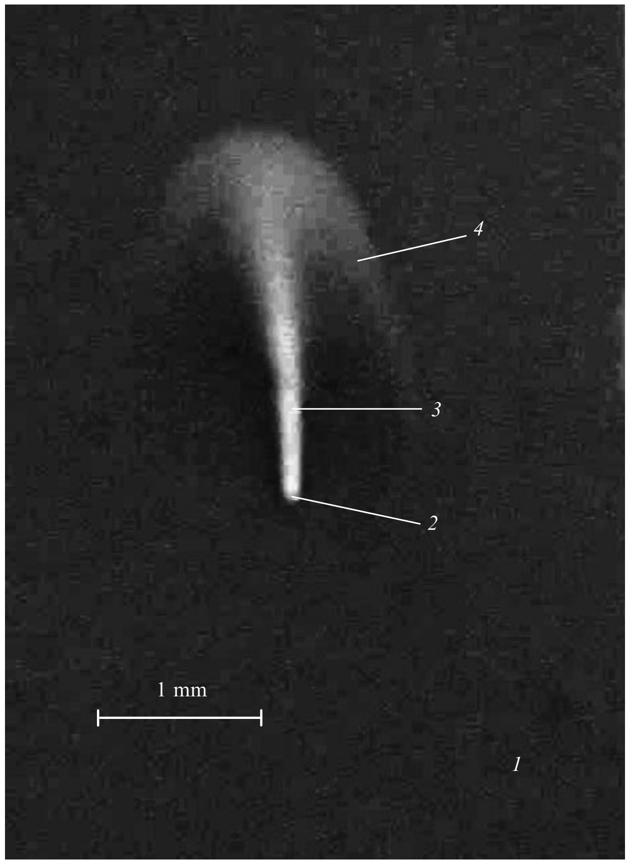

Figure 3. Photograph of the bleached zone: (*1*) suspension, (*2*) zone under irradiation (a focused laser beam was perpendicular to the image plane), (*3, 4*) bleached suspension spreading upwards by virtue of thermal convection.

photometer. As a reference cuvette, we used a 2.09-mm-thick quartz cuvette filled with DMF. The sample cuvettes had the same thickness.

Figure 5 shows the absorption spectra of the suspension before [spectrum (*1*)] and after [spectrum (*2*)] the laser irradiation. It is worth mentioning that the strong absorption band of DMF lies at $\lambda < 260$ nm. A noteworthy feature of the data in Fig. 5 is that the spectra intersect at a few points, the most significant of which is the intersection point at $\lambda_0 = 414$ nm: spectrum (*1*) lies above spectrum (*2*) for $\lambda > \lambda_0$ and below it for $\lambda < \lambda_0$. This means that laser irradiation increases the transmittance of the OLC suspension in DMF in the near-IR to visible range. At the same time, irradiation increases the absorption in the suspension in the blue-violet and UV spectral regions. Thus, focused laser radiation leads to bleaching of the suspension in the visible and near-IR spectral regions, in accordance with the above results (Figs 2a, 3). Another important feature is that the spectra in Fig. 5 are very close in peak height but differ in peak position by 2 nm (Fig. 5, inset). In addition, laser irradiation markedly shifts the absorption band of the suspension in the range 245–252 nm to shorter wavelengths and broadens it. All this demonstrates that laser irradiation has a significant effect on the optical properties of the OLC suspension in DMF.

4. Discussion

High-power laser irradiation might be expected to lead to local heating of the suspension, causing some of the carbon nanoparticles to precipitate. In our experiments, however, no precipitation was detected (Fig. 3). Moreover, precipitation would not raise the absorption in the blue spectral region and reduce it in the red (Fig. 5). It may be that high-power laser irradiation reduces the size of the carbon structures. Clearly, this may have a strong effect on the absorption spectrum of the suspension, e.g., leading to bleaching in the near-IR to visible spectral region.

Also possible are laser-induced chemical reactions, whose products may differ in optical properties from the reactants. In particular, laser irradiation may lead to local heating of the OLC particles and initiate chemical reactions between the OLC and DMF, e.g. surface hydrogenation of the OLC, much like irradiation of C_{60} fullerene (the formation of di- and tetrahydro[60]fullerenes [15]). Such reactions may result in surface functionalisation of graphene shells and the formation of substituted polyaromatic species with reduced electrical conductivity. A reduction in conductivity might account for the bleaching of the OLC suspension in DMF in the visible range, and the formation of functionalised aromatic species might be responsible for the rise in absorption between 300 and 400 nm.

5. Conclusions

The present results demonstrate that high-power nanosecond laser pulses at 1064 nm have a significant effect on the absorption spectrum of OLC dispersed in DMF: the

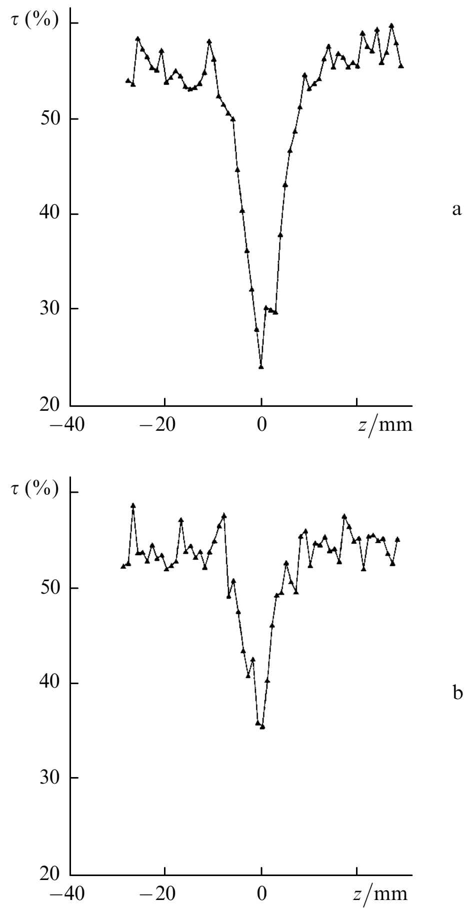

Figure 4. z-Scan results for the OLC suspension. A 1064-nm laser beam was focused by a lens with a focal length of 100 mm; $\varepsilon_{in} = 90$ μJ (a) and 30 μJ (b).

suspension becomes transparent in the long-wavelength portion of the visible spectrum, whereas its absorption in the blue-violet spectral region increases.

Acknowledgements. The authors gratefully acknowledge the assistance of V.V. Aksenova in the spectroscopic measurements. This work was supported by the Siberian and Ural Branches of the Russian Academy of Sciences (joint research programme) and in part by the RF Ministry of Education and Science (Grant No. RNP.2.1.1.1604), INTAS (Grant No. 06-100013-9225) and NATO (Grant No. SfP-981051).

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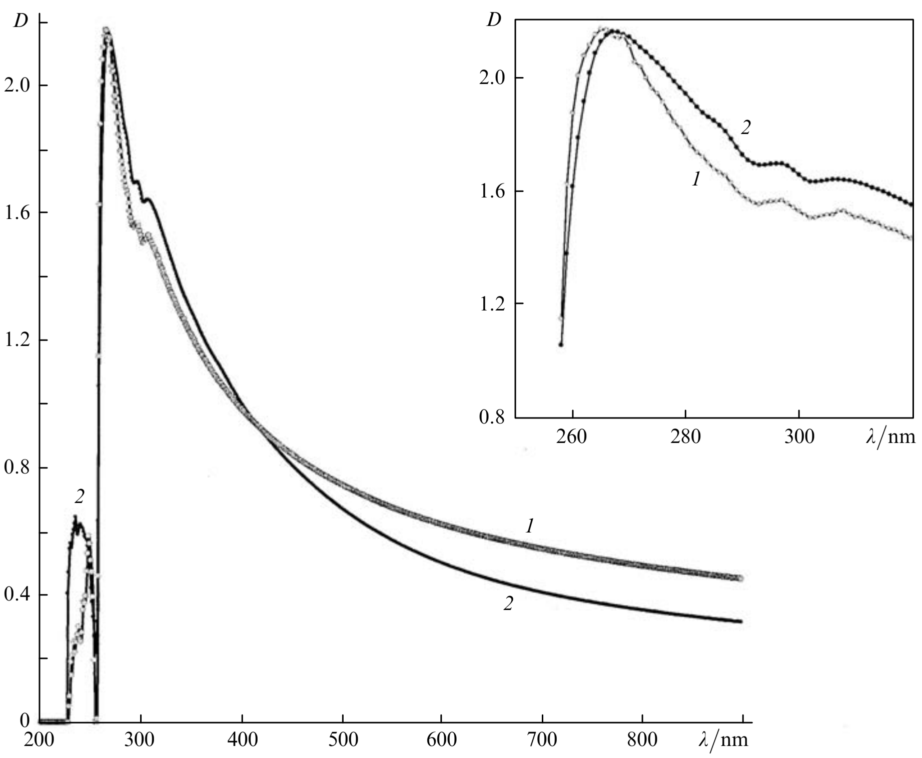

Figure 5. Absorption spectra D of the OLC suspension in DMF (*1*) before and (*2*) after laser irradiation (2.09-mm-thick quartz cuvette).

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