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Photoinduced Transparency of a Suspension of Onion-Like Carbon Nanoparticles

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Abstract—We have observed the phenomenon of photoinduced transparency in a suspension of onion-like carbon (OLC) nanoparticles in N,N-dimethylformamide (DMF) under the action of high-power laser radiation (λ = 1064 nm). The OLC particles were prepared from detonation nanodiamonds (NDs) by means of high-temperature annealing in vacuum and then ultrasonically dispersed in DMF. Upon exposure to laser radiation, the optical density of the suspension significantly decreases in the visible and near-infrared range, but increases in the range of wavelengths below 400 nm.

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In recent years, much attention has been devoted to the investigations into nonlinear optical properties of suspensions of various carbon nanoparticles (soot, fullerenes, single- and multiwall nanotubes, etc.) in various liquid media [1–7]. These investigations are of interest, in particular, for the creation of laser radiation power limiters intended for protecting light sensors and human eye against the risk of optical damage. Another topical issue is the development of nonlinear optical self-bleaching gates for passive mode-locked lasers operating at various wavelengths [8–10]. The number of experimental investigations of the nonlinear optical properties of onion-like carbon (OLC), which is another form of carbon nanoparticles, is rather restricted (see, e.g., [11]). In this context, it was of interest to study features of the interaction of high-power laser radiation with OLC suspensions. This Letter presents the results of such investigations.

The OLC samples were prepared by the high-temperature (1800 K) annealing of detonation nanodiamonds (NDs) in vacuum [12]. The primary ND particles had an average size of about 4.5 nm and formed aggregates with dimensions of about 100–200 nm. During the vacuum annealing, each ND particle exhibits graphitization and converts into an OLC particle, while the presence of bonds between the primary ND species leads to the formation of closed, curved grapheme sheets. These sheets comprise several OLC particles bound in agglomerates with dimensions close to those of the primary ND aggregates.

The OLC powder was ultrasonically dispersed in N,N-dimethylformamide (DMF). It was established that OLC suspensions with a concentration of about 1 mg/ml are stable in time (with insignificant precipitation detected only 9 months after preparation). According to the photon correlation spectroscopy data (Nicomp 380ZLS, Particle Sizing System Co.), OLC agglomerates had an average size of ~170 nm.

The experiments were performed with a passively Q-switched single-mode YAG:Nd^{3+} laser operating at a wavelength of λ = 1064 nm with a pulse duration of 20 ns. The optical scheme is described in detail elsewhere [13]. A 1-mm-thick glass cell containing the OLC suspension was placed at the focus of a collecting lens with a focal distance of 100 mm. The size of the focal spot in the waist zone was about 100 μm. The laser pulse energies at the input (ϵ_{in}) and output (ϵ_{out}) of the measuring tract (involving the collecting lens and the optical cell) were measured using an automated multichannel system for laser pulse detection [14], which allowed the transmission coefficient $\tau = \epsilon_{out}/\epsilon_{in} \times 100\%$ of the cell with a suspension to be determined for each laser pulse. The laser operated at a pulse repetition rate of 1 Hz.

The experiments showed that the OLC/DMF suspensions exhibit the phenomenon of photoinduced transparency, according to which the region of suspension interacting with laser radiation becomes almost completely transparent after a certain critical number N_{cr} of laser pulses. This is illustrated by the τ versus N curve in Fig. 1a. It was established that N_{cr} depends on the laser pulse energy ϵ_{in} at the cell input and on the distance z from the cell input to the beam waist (z = 0) along the optical axis. For example, Figs. 1a and 1b show the $\tau(N)$ curves obtained for the same ϵ_{in} = 0.5 mJ

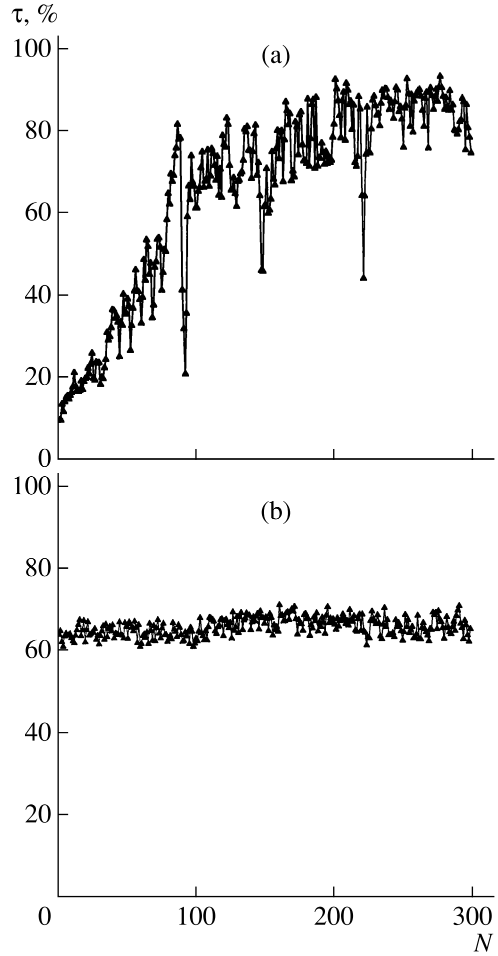

Fig. 1. Plots of the transmission coefficient τ versus number N of laser radiation pulses for a 1-mm-thick cell with the OLC/DMF suspension measured at (a) $z = 0$ and (b) $z = 23$ mm for a fixed primary laser pulse energy of $\epsilon_{in} = 0.5$ mJ.

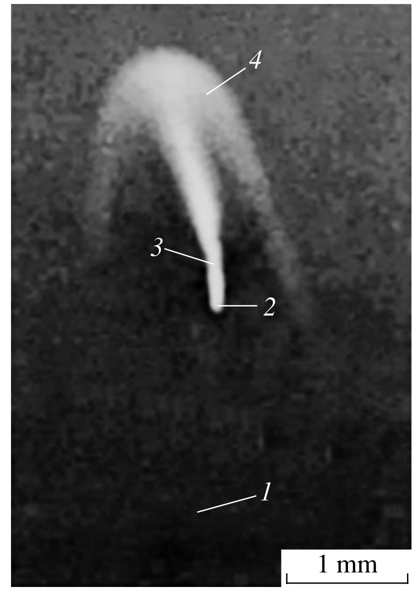

Fig. 2. Photographic image of a bleached zone of the OLC/DMF suspension: (*1*) intact suspension; (*2*) zone of interaction between focused laser radiation and the suspension (laser beam propagates perpendicularly to the figure plane); (*3, 4*) bleached fraction of suspension rising up and expanding due to thermal convection.

and different z (i.e., different laser radiation power densities). As can be seen, at a large distance from the focus ($z > 20$ mm), that is, at a low radiation intensity (Fig. 1b), the transmission coefficient amounts to about 65% and remains almost constant during the action of multiply repeated laser pulses. At a high radiant power density (~300 MW/cm^2) corresponding to the cell being placed at the focus ($z = 0$), the initial laser pulses are subject to optical limiting and lose more than 80% of their energy (Fig. 1a). On a qualitative level, this behavior agrees with the experimental data on the optical limiting in aqueous OLC suspensions [11]. As the number N of laser pulses in our experiment is increased, the transmission coefficient τ grows so that the optical limiting at $N > 80$ changes to clarification (bleaching) and the suspension in the zone of laser action becomes almost transparent. Thus, laser action on the same zone of a cell with the OLC suspension leads to the almost complete clarification of the absorbing medium. It should be noted that the curve in Fig. 1a contains regions of random sharp decrease in τ, which are followed (within several laser pulses) by regions of increasing transparency.

Figure 2 shows an image of the bleached zone of the suspension, which was obtained after 900 laser pulses (within 15 min) using a Canon EOS 20D camera with an EFS (f/2.8) Macro USM objective. As can be seen, the bleached fraction of the medium appearing at the zone of interaction between laser radiation and the suspension (point *2*) rises up due to thermal convection at a very low velocity (~2.2×10^{-3} mm/s) and expands to acquire a mushroom shape with time. Therefore, the clarified fraction is stable, which implies that the observed laser-induced bleaching substantially differs from a short-time bleaching of the medium that is possible, for example, in silicon nanocrystals suspended in glycerin [10] or in a fullerene-containing medium as a result of the action of two sequential laser pulses [14]. It should be emphasized that an increase in the amount of bleached suspension is due to the continuous supply of fresh suspension to the interaction zone *2*. Note also that, at a certain height of the cell, the bleached suspension expands both in lateral directions and downward. Apparently, the random sharp drops in τ observed in Fig. 1a can be related to a nonuniform supply of fresh portions of the suspension to the zone of laser action.

It was of interest to elucidate the mechanism of laser-induced bleaching of the OLC suspension. A possible approach to solving this task is based on a comparison of the optical densities of the initial suspension

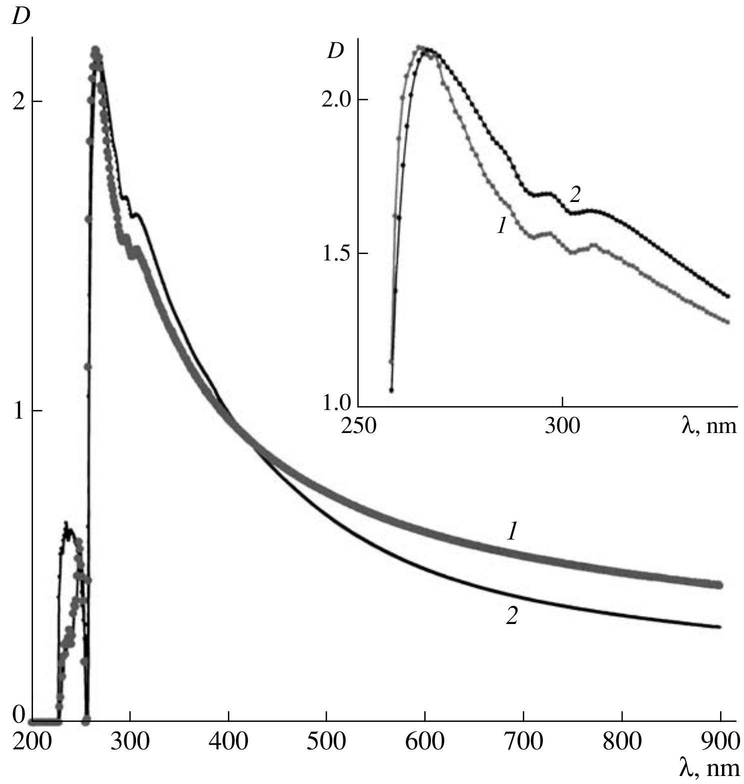

Fig. 3. Plots of the optical density *D* versus wavelength λ for the (*1*) initial and (*2*) laser-treated OLC/DMF suspensions measured in a 2.09-mm-thick quartz cells.

and the products formed under the action of multiply repeated laser pulses. For this purpose, the cell with initial suspension was exposed to focused laser radiation for several days with constant stirring of the interaction products. Then, the absorption spectra of the initial and laser-treated suspension were measured on a scanning double-beam UV spectrometer (Lambda 650, PerkinElmer Co.) in 2.09-mm-thick quartz cells. The reference quartz cell of the same thickness was filled with pure DMF.

The results of measurements are presented in Fig. 3 where curves *1* and *2* are plots of the optical density *D* versus wavelength λ for the initial and laser-treated suspensions, respectively. It should be noted that the band of strong absorption by DMF is observed at $\lambda <$ 260 nm. An interesting feature of the measured absorption curves is the presence of several intersection points. The most significant of these is observed at $\lambda_0 = 414$ nm. As can be seen, curve *1* lies above curve *2* in the region of $\lambda > \lambda_0$ and is mostly below curve *2* at $\lambda < \lambda_0$. This fact implies that the laser action on the OLC/DMF suspension leads to an increase in the transparency in the visible and near-infrared (VIS–NIR) range. At the same time, the modified fraction of the suspension is characterized by increased absorption in the blue-violet and ultraviolet range. Thus, the action of focused laser radiation produces bleaching of the suspension in the VIS–NIR range, in agreement with the results presented above (Figs. 1a and 2). Another interesting feature is that the absolute maxima of curves *1* and *2* are almost the same, while their positions are shifted by 2 nm (seer the inset in Fig. 3). In addition, the absorption band of the suspension in the wavelength interval of 245–252 nm exhibits broadening and shifts toward shorter wavelengths. All of these features indicate that the laser action significantly modifies the optical properties of the OLC/DMF suspension.

It might be suggested that the thermal field of high-power laser radiation could result in the partial precipitation of carbon nanoparticles. However, our experiments did not show evidence for this precipitation (Fig. 2). In addition, the precipitation would not be accompanied by an increase in optical absorption in the blue range and by its decrease in the red range (Fig. 3). Probably, the high-power laser radiation might produce disintegration of agglomerated particles to smaller species. This can lead to significant changes in the absorption spectrum and, in particular, to an increase in transmission in the VIS–NIR range. It is also not excluded that laser-stimulated chemical reactions can lead to the formation of products with the optical product different from those of the initial suspension. In particular, the laser action can lead to the local heating of OLC particles and stimulate their chemical reactions with DMF, for example, leading to hydrogenation of the OLC surface. This reaction was observed for laser-irradiated C_{60}

fullerene and led to formation of C_{60} dehydro- and tetrahydrofullerenes [15]. Chemical reactions can lead to functionalization of the surface of graphene sheets with the formation of substituted polyaromatic fragments and the resulting decrease in the conductivity. A decrease in the conductivity can account for the bleaching of the OLC/DMF suspension in the visible range, while the formation of functionalized aromatic fragments can lead to increased absorption in a wavelength range of 300–400 nm.

In conclusion, we demonstrated that high-power nanosecond pulsed laser radiation at $\lambda = 1064$ nm can produce irreversible bleaching of an OLC/DMF suspension in the VIS–NIR range.

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