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Concentration dependence of the optical limiting and nonlinear light scattering in aqueous suspensions of detonation nanodiamond clusters

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ABSTRACT

Optical limiting (OL) is observed for detonation nanodiamond clusters (ND) suspended in water with mass concentrations of 3–0.01%. By using nanosecond *Z*-scan measurements at 1064 nm we demonstrate that the nonlinear light scattering strongly contributes to the OL in a wide range of ND concentrations. Moreover we show that the ratio of the nonlinear and linear extinction that can be seen as figure of merit for an optical limiter is a non-monotonous function of the ND concentration. Our analysis reveals that the concentration that corresponds to the optimum OL performance essentially depends on the incident intensity.

1. Introduction

The phenomenon of optical limiting (OL), which manifests itself as a suppression of transmittance for intense light beams, is of interest for eye and sensor protection [1]. Materials capable of attenuating potentially dangerous laser radiation and promptly transmitting low-intensity ambient light are used in nonlinear optical devices usually referred to as optical limiters [2]. Among such materials, the attention of the optical community has recently been attracted to suspensions of various nanocarbon species (e.g. carbon nanotubes, nanoonions, graphene flakes, etc. [3]) that show strong broadband nonlinear absorption [4].

In order to be employed in optical limiters, nanocarbon suspension should be stable and maintain the colloidal stability both during and after the exposure of laser radiation. It has been demonstrated [5] that aqueous suspension of detonation nanodiamonds (NDs) with modified surfaces comply with the above requirements. In particular they are capable to maintain OL properties for a long time at intensities up to 1 GW/cm^2 [6].

In this paper we report the OL performance of aqueous ND suspensions as a function of the ND concentration. The obtained results show that these suspensions can be employed in the optical limiters with different initial transmittance coefficients. We also find out the optimum concentration of nanodiamond particles that gives the maximum reduction of the transmittance coefficient.

2. Materials and methods

In our experiments, we studied detonation ND clusters with an average particles size of 49.6 nm (for preparation details, as well as the X-ray diffraction pattern and the TEM image see previous publication [7]). The optical density and Raman spectra of the ND clusters are presented in Fig. 1(a) and (b), respectively.

The inset to Fig. 1(a) shows the size distribution of ND clusters at a temperature of 25 °C that was estimated by the dynamic light scattering technique using a Malvern Zetasizer Nano-ZS particle size analyzer. The Raman spectra with two excitation wavelengths of 473 and 633 nm (see Fig. 1(b)) clearly show the peak at 1325 cm^{-1} which is the ND signature [9–12]. However, at both excitation wavelength, the Raman spectrum has a broadband background due to luminescence [8,13,14] of numerous defects and vacancies in detonation ND particles [15].

The main distinctive feature of these suspensions is that the ND clusters did not change their properties upon drying, i.e. they can be re-used to make a stable suspension again if necessary [16]. Such a property promises that high power laser action does not lead to the formation and precipitation of ND aggregates. Aqueous suspensions of detonation ND are stable up to concentrations of as high as 10–12% (hereafter, wt.%) [16], however in our experiments, we used suspensions with the maximum ND concentration of $C = 3\%$. At this concentration, the linear transmittance coefficient of the cell with a thickness of 1.01 mm is $T_0 = 61\%$ at a wavelength of 1064 nm. The same cell containing ND suspensions with concentrations of 1%, 0.1% and 0.01%, which were obtained from 3%

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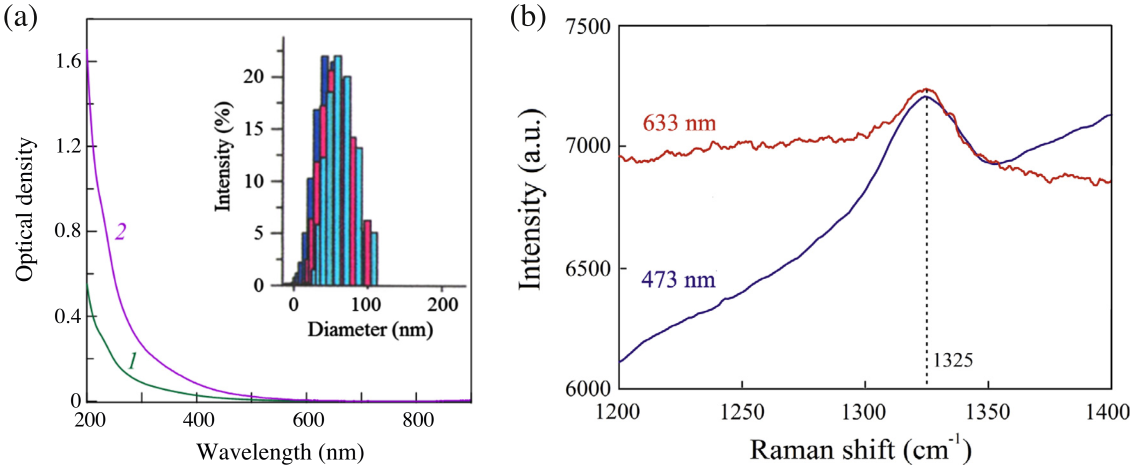

Fig. 1. (a) Optical density of 1 mm thick samples of 0.03 (1) and 0.1 wt.% (2) aqueous ND suspension as a function of wavelength. The inset shows the ND particle size distribution estimated by the dynamic light scattering technique. The average particle size is 49.6 nm. (b) Raman spectra of ND clusters at excitation wavelengths of 473 and 633 nm. The ND clusters were prepared by evaporation of a liquid phase of the ND suspension at a temperature of 25 °C [8].

suspension by adding distilled water, has linear transmittance coefficients of 78%, 89% and 90%, respectively.

3. Experimental technique

In the OL measurements, we employed TEM_{00} mode ($M^2 = 1$) of a single-frequency Nd^{3+}:YAG laser with passive Q-switching with 17 ns pulse duration operating at the repetition rate of 1 Hz. The diameter of the beam waist was 100 ± 5 μm at the $1/e^2$ intensity level. The vertically polarized laser beam at a wavelength of 1064 nm was focused into the edge of the sample by a lens with a focal length of 100 mm. The OL was studied by the extended open-aperture Z-scan technique (see [17]) that allows one to measure simultaneously the energy and the temporal profile of the incident, transmitted and scattered light pulses as the functions of cell position with respect to the focal point [18]. For the vertically polarized incident beam the maxima scattering is observed in the plane that is perpendicular to the electric field plane, i.e. in horizontally plane as one may expect for the Mie–Rayleigh scattering [19]. Therefore, the measurements of the energy and the temporal profile of scattered horizontally light pulses at an angle of 90° with respect to the incident beam were carried out. As the light detector and the cell containing suspension are mounted on the positioning stage [18], therefore for the chosen angle of registration (90°) the active area of the sensor is always opposite to the lateral side of the cell. This significantly simplifies registering of the scattered photons in the course of Z-scan measurements. Such an approach allowed us to reveal the effect of the nonlinear scattering on the optical limiting at different concentrations of ND clusters.

4. Results and discussion

Fig. 2 shows the transmittance T and the energy of the 90° scattered pulses E_s as functions of the sample position z. $z = 0$ corresponds to the position of the focal point at the center of the sample, i.e. to the maximum incident intensity. Measurements were performed at the incident pulse energy of 1.1 mJ for samples with ND concentrations of $C = 3\%$ (a), $C = 1\%$ (b), $C = 0.1\%$ (c) and $C = 0.01\%$ (d). One can see from Fig. 2 that when z approaches to zero (i.e. when the intensity increases), the transmittance (squares) sharply decreases while the energy of the scattered pulses (circles) increases. This means that the higher the energy of the scattered pulses, the lower the transmittance. At low input intensity ($|z| > 15$ mm), the energy of the scattered pulse does not depend on z being more than 20 times smaller than that at $z = 0$. This value originates from the linear scattering that depends on the size and concentration of ND clusters. It is clear from Fig. 2 that in ND suspensions, the nonlinear scattering contributes to the OL in a wide range of concentrations, however the lower the concentration, the weaker the nonlinear scattering. Specifically, the reduction of the concentration from 3% to 0.01% leads to an increase in the transmittance minimum from 12% to 82% and to ten times lower energy of the scattered pulse.

One may expect that similarly to carbon nanotubes [20] and carbon black [21] suspensions, the light absorption in the ND suspensions results in heating of the clusters and formation of the vapor microbubbles surrounding them. The size and hence scattering cross section of these microbubbles increases with laser fluence giving rise to the thermal mechanism of the nonlinear light scattering. However when the fluence increases further, the multiphoton ionization may result in the formation and expansion of microplasma as it was observed by Blau et al. for nanotubes [22] and Mansour et al. for carbon black [21]. One may also expect that under high fluence the microplasma can be formed due to the photoionization [23] of some defects in the detonation ND. The formation of microplasma results in lower ray stability of suspensions. However, in our experimental conditions, the optical properties of the suspensions did not change because the ND possess higher ray stability in comparison with CNT and carbon black. Nevertheless, it is worth noting that earlier we have observed a slight transmittance change after exposure of suspension of ND clusters with a diameter of 50 nm with more than 8000 pulses of energy of 0.14 mJ [7].

Fig. 3 shows the E_s at $z = 0$ as a function of ND clusters concentration. One can observe that a 300 times increase of the ND concentration gives a 15 times increase in the energy of the 90° scattered pulse.

It is of interest to find out the optimal ND concentration that corresponds to the maximum of the OL performance. For this purpose, in Fig. 4 we plot the transmittance at $|z| = 25$ mm (i.e. out of the beam waist) and $z = 0$ (in the beam waist) as functions of the ND concentration using data presented in Fig. 2. One can observe from Fig. 4 that at $|z| = 25$ mm (squares), $\ln(T_{|z|=25\mathrm{mm}})$ is a linear function of C in agreement with the Bouguer–Lambert law [24]. When $|z|$ decreases, i.e. light intensity increases, the $\ln T$ becomes nonlinear function of C (see plotted $\ln T$ for $z = \pm 5$, $z = \pm 2.5$, $z = \pm 1.5$ (circles) and $z = 0$ mm (triangles) in Fig. 4). The obtained the experiment dependence of the transmittance on the ND