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THE EFFECT OF LASER ENERGY DENSITY ON THE PROPERTIES OF GRAPHENE DOTS

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The structural and optical properties of dots based on graphene oxide (GO) obtained by laser ablation method with various energy densities of radiation were studied. It was shown that after laser ablation, the average lateral size of GO sheets was decreased from 1280–1900 nm to 230±95 nm and 110±42 nm for samples prepared at a laser radiation with energy density of E~15 and 21 mJ/cm^2, respectively. Raman spectroscopy data showed that after ablation, the I_D/I_G ratio decreased from 1.04 to 0.97, indicating an increase in the number of sp^2-hybridized domains in GO after ablation. A change in the energy density has practically no effect on a change in its functionalization, as well as the ordering of sp^2 domains inside a GO sheet. The optical density of GO dispersions and the intensity of their fluorescence depend on the ablation conditions. For non-ablated dispersions along with the luminescence band at 450 nm, additional band appears in the spectrum with a maximum at about 600 nm. After ablation the distribution of particles becomes more uniform, as evidenced by both the change in the shape of the GO luminescence band and the constancy of the fluorescence lifetime upon registration at different wavelength.

Keywords: graphene oxide, graphene dots, laser ablation, structure, optical properties.

Introduction

Laser ablation in a liquid is a reliable and simple method for the preparation of nanosized objects and nanoparticles [1–3], carbon and graphene dots [4]. It is known that, under the influence of laser radiation, a laser-induced breakdown occurs on the surface of the sample in a liquid. As a result, shock waves are formed, and the resulting plasma expands and cools. Then the cavitation bubble expands and collapses, releasing a large amount of energy and breaking the substance into smaller fragments [5]. The properties of the resulting nanomaterials depend on the parameters of laser radiation (wavelength, energy and pulse duration, exposure time) and the properties of the ablated dispersion [6].

Currently, this method is a good alternative for the preparation of graphene luminescent dots. By changing the radiation characteristics during laser ablation, it is possible to obtain graphene dots of various shapes and sizes, which exhibit unusual photoluminescence associated with a circular polygonal shape and corresponding edge effects [7]. In particular, the laser ablation method was used in Ref. [8] to obtain graphene oxide (GO) nanostructures. It was shown that during the ablation process, nanostructures of various shapes are formed: ribbons, flakes, and quantum dots with simultaneous photoreduction of graphene oxide. Graphene oxide dots exhibit blue photoluminescence. By changing the ablation time, it is possible to achieve different fluorescence quantum yields of graphene dots [9, 10]. It is known that the power of laser radiation directly affects the mechanism of material ablation. For example, it was shown in Refs. [11–14] that at high laser radiation energy densities (>10 J/cm^2), the ablation mechanism changes from melting to explosive boiling or fragmentation, which do not lead to the formation of nanoparticles.

The aim of the present work is studying of the effect of laser pulse energy density on the properties of GO in aqueous dispersions. This will open up possibilities for controlling the optical and luminescent properties of graphene dots by changing the conditions for their synthesis. Graphene and carbon dots [15] can be used in various fields, such as energy storage [16], photovoltaics [17], photoelectrochemical [18] and photocatalytic [19–22] generation of hydrogen/hydrocarbon fuels, and photocatalysis of organic pollution [23]. In addition, their high photostability and biocompatibility make them a good alternative to conventional semiconductor quantum dots.

1. Experimental part

To prepare and study dispersions of graphene oxide the method and equipment described in Refs. [9, 10] were used. Briefly, single layer graphene oxide (GO, Cheaptubes) [24] was dispersed in deionized water (AquaMax) by sonication for 30 min. The solution was then centrifuged at 6000 rpm for 1 hour. The height of the ablated liquid was equal to 0.8 cm. During laser ablation, the dispersion was continuously stirred. The Nd:YAG laser with λ_{gen}=532 nm, τ=10 nm and pulse energy density equal to E~15 and 21 mJ/cm^2 was chosen as the radiation source. Previous studies have shown that after 20 min of ablation, GO is reduced and graphitized, which leads to an increase in the average crystallite size of sp^2 carbon domains and a decrease in the number of GO layers in the obtained particles [9]. Based on this, the ablation time was chosen equal to 30 minutes.

According to data obtained with a Zetasizer Nano S90 analyzer (Malvern), the particle size of GO was estimated. To study the particle morphology, the dispersion was spreaded onto the surface of silicon wafers. The images were registered with a scanning electron microscope Mira-3 LMU (Tescan). The Raman spectra of the prepared samples were recorded using a Confotec MR520 (3D Scanning Raman Confocal Microscope, Sol Instruments) with laser excitation at a wavelength of 532 nm. Absorption spectra were measured on a Cary-300 spectrometer (Agilent). Fluorescence was recorded using an Eclipse (Agilent) spectrofluorimeter. Fluorescence decay kinetics of graphene dots were measured by using TCSPC (time-correlated single photon counting) system (Becker&Hickl) at excitation wavelength λ_{exc}= 375 nm. All measurements were carried out at room temperature in 1 cm quartz cells.

2. Results and discussion

Measurements of the particle size of graphene oxide by dynamic light scattering showed that, before ablation in solution, about half of the particles are larger than 1 μm (1280–1900 nm). After ablation at 15 mJ/cm^2, the average particle size was noticeably decreased from 1575 nm to 230±95 nm. An increase in the ablation power leads to a further decrease in the particle size of graphene oxide to 110±42 nm (Fig. 1).

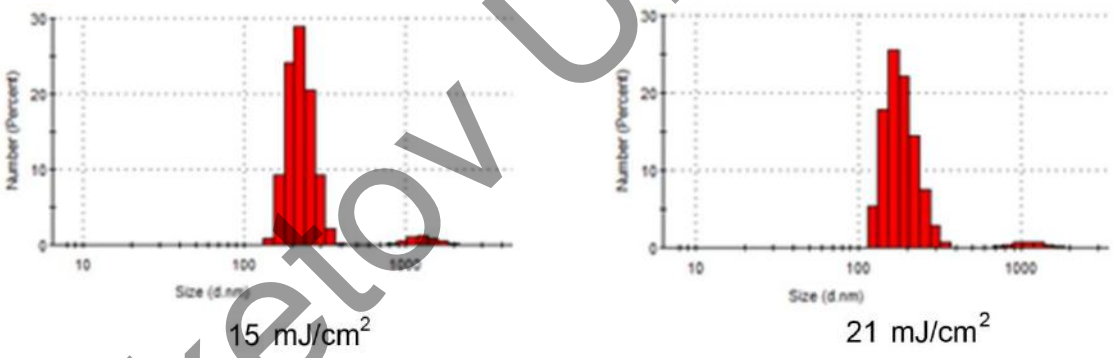

Fig. 1. Size distribution of GO after ablation at various laser radiation energy densities

SEM studies have shown (Fig. 2) that on the substrates GO dispersion forms a film consisting of both single-layer and multi-layer GO sheets. In multilayer particles, graphene oxide is prone to the formation of folds and wrinkles.

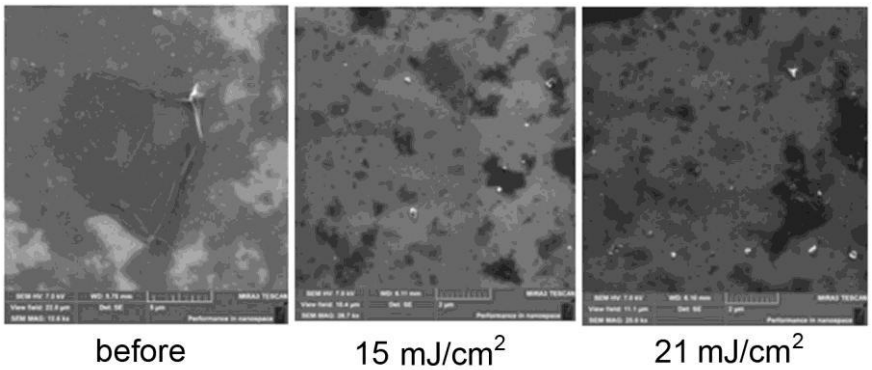

Fig. 2. SEM images of GO before and after ablation at various laser radiation energy densities

After laser processing, smaller particles are visualized on SEM images. At an energy density of 21 J/cm^2 the size of particles is smaller and they are uniformly distributed over the surface. The SEM data correlate well with the results obtained by dynamic light scattering, showing that the size distribution of graphene dots decreases with changing in the E from 15 to 21 mJ/cm^2.

It can be seen from the Raman spectroscopy data (table 1) that the maximum of the G-band of GO is shifted to higher frequencies compared to the band for graphene, which indicates the presence of C=O bonds in the structure of the GO sheet [25]. At the same time, the I_D/I_G ratio decreased markedly from 1.04 to 0.97 after ablation of the GO dispersion. A change in the radiation energy density has almost no effect on the change in its functionalization, as well as the ordering of the sp^2 domains inside the GO sheet.

Table 1. Position and intensity Raman bands of GO in dispersion after ablation at different laser radiation energy densities

	E, mJ/cm^2	D, cm^{-1}	I, r.u.	G, cm^{-1}	I, r.u.	I_D/I_G	2D, cm^{-1}	I, r.u.	I_{2D}/I_G
Before ablation	–	1360	18895	1602	18109	1.04	2734	11249	0.62
After ablation	15	1360	42482	1602	43738	0.97	2740	24413	0.56
	21	1368	26100	1602	27140	0.96	2740	15906	0.59

Studies of the optical properties of graphene dots showed (Fig. 3) that an increase in the energy density of laser radiation leads to a slight increase in the optical density (D) of GO at the maximum of the absorption band (~228 nm, Fig. 3a). It should be noted that, compared with the optical density of solutions before ablation, the value of D increased by almost 80%, which indicates an increase in the number of absorbing particles.

However, such an increase leads to the effect of self-quenching of the GO luminescence [26], which is clearly seen in Fig. 3b. Along with the luminescence band at 450 nm, additional band appears in the spectrum in the form of a shoulder with a maximum at about 600 nm. After laser treatment of the GO dispersion, the shape of the fluorescence spectrum changes and exhibits only one maximum at 490 nm. As it was shown by the recorded excitation spectra, the deformation of the GO luminescence band in dispersions before ablation is associated with the presence of several luminescence centers, because the curve shows maxima at 340 and 370 nm.

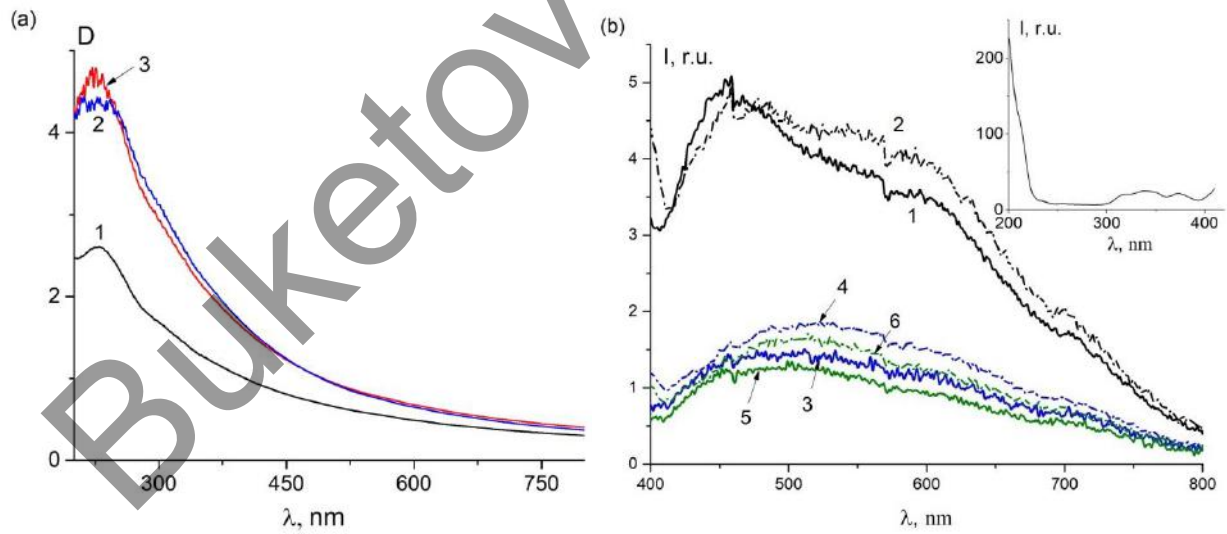

Fig. 3. Absorption (a) and fluorescence (b) spectra of GO before and after ablation at different laser energy densities E, mJ/cm^2: 1 – 0; 2 – 15; 3 – 2. Fluorescence spectra were recorded at λ_{exc}=320 nm – 1, 3, 5; λ_{exc}=350 nm – 2, 4, 6. On the inset: excitation spectra of GO before ablation at λ_{reg}=480 nm.

Figure 3b shows that as the excitation wavelength increases, the GO fluorescence spectra shift bathochromically and have different intensities. This may be due to the luminescence of various centers or the localization of electron-hole pairs in isolated sp^2 clusters in the sp^3 matrix. After ablation, the particles become more uniform both in size and composition. In this case the shape of the band does not change upon

the changing in the power density of laser irradiation, and the intensity of the fluorescence GO is only on 10% higher for dots, prepared at 21 mJ/cm^2 compared to 15 J/cm^2.

The lifetimes estimated from the fluorescence decay kinetics are presented in table 2. The decay kinetics can be described with using a biexponential equation with different contributions from the first and second components.

However, as can be seen from the data, the presence of a long-lived component has almost no effect on <τ> the average GO fluorescence lifetime. At the same time, the fluorescence lifetimes of GO particles after ablation slightly decreased, however, they are the same when λ_{reg} was changed.

Table 1. Fluorescence lifetimes of GO ablated at different laser energy densities

λ_{reg}, nm	<τ>, ns	τ_1, ns	σ_1, %	τ_2, ns	σ_2, %
Before ablation					
450	0.36	0.26	92	1.55	8
511	0.34	0.30	96	1.40	4
21 mJ/cm^2					
450	0.34	0.26	94	1.57	6
511	0.31	0.28	97	1.18	3
15 mJ/cm^2					
450	0.32	0.28	92	1.13	8
511	0.32	0.28	97	1.57	3

Conclusion

The studies performed have shown that an increase in the energy density of laser radiation leads to a decrease in the size of graphene oxide particles after ablation. At the same time, no noticeable changes in the morphology and structure of the particles were registered.

A slight increase in both the optical density and fluorescence intensity was registered for graphene oxide dots obtained at 21 mJ/cm^2, relative to these parameters recorded for dots that were synthesized at 15 mJ/cm^2. In this case, the distribution of particles becomes more uniform, as evidenced by both the change in the shape of the GO luminescence band and the constancy of the fluorescence lifetime upon registration at different λ_{reg}.

The results obtained can be used to create organic luminescent materials, in optical nanotechnologies, as well as in photovoltaics, biophysics, and bioimaging.

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