

OBSERVATION OF THE "RED EDGE" EFFECT IN THE LUMINESCENCE OF WATER SUSPENSIONS OF DETONATION NANODIAMONDS

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UDC 535.37:620.3

The variations in the luminescence spectra of detonation nanodiamond (DND) with probe light wavelength are studied and these dependences are compared for water suspensions of DND and graphene oxide (GO). It is found that changing the laser excitation wavelength from 405 to 532 nm shifts the broad-band luminescence peaks of DND and GO from 530 to 615 nm and from 490 to 580 nm. The observed dependences are explained by the luminescence "red edge" effect, which shows up when the electrostatic interaction (solvation) times of a luminophore with a polar solvent are comparable to the luminescence lifetime. These data confirm the common origin of luminescence in nanodiamonds and oxidized graphene nanoclusters.

Keywords: luminescence, diamond, graphene oxide, solvation, polar solvent.

The luminescence of diamonds associated with color centers has almost unlimited temporal photostability and a high quantum yield at room temperatures, so that luminescent diamond is a promising material for use in information technology and biomedicine. Isolated color centers, such as nitrogen vacancies or silicon vacancies, are used to create active single-photon sources [1–3], and, conversely, to produce a high concentration of luminescence centers in small-volume diamond particles for use as a biological marker [4]. In both cases, it is preferable to select diamonds with the smallest possible dimensions. Nanodiamond crystallites with single color centers can be used to form bulk sources of isolated photons with any specified architecture. When a diamond marker is small, it is more easily captured by a living cell. Reducing the size of diamond crystallites, however, increases the relative surface to volume ratio of the material, so that the intensity of luminosity associated with surface defects will be higher.

The luminescence of diamond surfaces is emitted over a broad spectral band with a maximum usually in the 500–600 nm range. As opposed to the luminescence of color centers, it is unstable in time and depends strongly on the functional state of the surface. "Surface" luminescence is observed in all currently known types of nanodiamonds: detonation, meteoritic, and made from microdiamonds by mechanical grinding [5–7]. Surface luminescence must be suppressed if the aim is to produce highly efficient luminescence sources in nanodiamonds. It can also be used as the principal source of luminescence, e.g., in nanodiamond markers, if ways can be found to stabilize and enhance it.

In recent years it has been found that a nondiamond (graphite) phase formed on the surface of nanodiamonds, e.g., during explosive synthesis or mechanical crushing, can be a source of "surface" luminescence. The structure of this phase and its interaction with a diamond surface are still unclear. A correlation has been found [8] between a high level of "surface" luminescence and small spherical graphite clusters (carbon dots) with dimensions of 1–2 nm and consisting of one or two graphene layers produced on detonation diamond surfaces during acid cleaning. We assume that the structure of carbon dots on nanodiamond surfaces is analogous to the structure of luminescing oxidized graphene, which contains covalently bonded oxygen on its surface that can presumably interact with surrounding oxygen atoms to create localized quasimolecular electronic structures in the oxidized graphene [9]. Thus, it is assumed that the luminescence in acid-cleaned nanodiamonds is similar to that in oxidized graphene.

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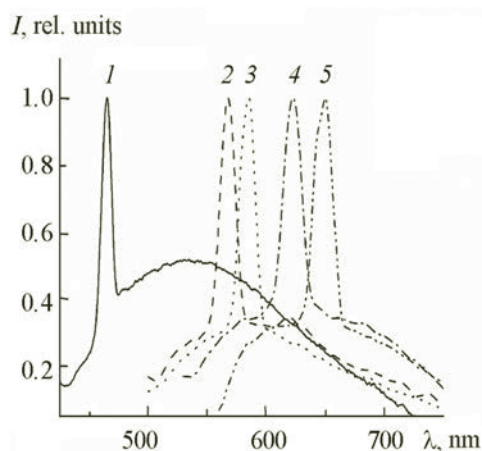


Fig. 1. Fluorescence spectra of a water suspension of DND (concentration 2 g/L) (normalized to unity with respect to the intensity of the coherent scattering band of the valence oscillations of water), $\lambda_{\text{exc}} = 405$ (1), 476 (2), 488 (3), 514.5 (4), and 532 nm (5).

In order to test the hypothesis of a common origin for the luminescence in nanodiamonds and oxidized graphene nanoclusters, it is necessary to find as many signs as possible of similarity in the luminescence of these two materials. Thus, the maximum luminosity of organic dyes and inorganic quantum dots is independent of excitation wavelength. On the other hand, for oxidized graphene in polar solvents, in particular in water, the luminescence peak has a strong dependence on excitation wavelength. The luminescence shifts to the red with increasing excitation wavelength. This effect is known as the "red edge" in luminescence and shows up when the electrostatic (solvation) interaction times of a luminophore with a polar solvent are comparable to the luminescence lifetime [10–12].

In this paper we show results from a study of the dependence of the luminescence spectra of detonation nanodiamonds (DND) in water suspensions on excitation wavelength and compare these dependences for water suspensions of DND and oxidized graphene.

The objects of study were detonation nanodiamonds synthesized by the detonation explosive method from a mixture of trinitrotoluene (TNT) and 1,3,5-trinitrotoluene-1,3,5-triazine (RDX) in a medium with water cooling (from the firm "Novye tekhnologii," Russia) and then cleaned and modified with carboxyl groups at the International Technological Center (Rayleigh, USA) [13]. Dynamic light scattering showed that the average particle size of the DND–COOH particles in water suspension was 10 nm. Water suspensions of DND–COOH with a concentration of 2 g/L were prepared, as well as water suspensions of oxidized graphene with a concentration of 0.1 g/L. The synthesis and properties of the oxidized graphene nanoparticles that were used have been described in detail elsewhere [8, 14].

Excitation wavelengths of 405, 476, 488, 514, and 532 nm were used to produce luminescence of the water suspensions of DND and oxidized graphene. The excitation source for $\lambda_{\text{exc}} = 405$ nm was a diode laser with a radiative power of ~50 mW incident on the cell, except for the sample of oxidized graphene, for which the power was reduced to 25 mW. The excitation source for $\lambda_{\text{exc}} = 476, 488,$ and 514 nm was an argon laser with an incident power of ~200 mW (reduced to 50 mW for the suspension of oxidized graphene). The excitation source for $\lambda_{\text{exc}} = 532$ nm was the second harmonic of a YAG laser with an incident power of ~230 mW (reduced to 50 mW for the suspension of oxidized graphene).

The spectra were recorded in a 90° configuration with a photomultiplier after passage of the signal through a monochromator (Acton, 1800 lines/mm, focal distance 500 mm, slit 500 μm , spectral resolution 0.5 nm, readout time 250–500 ms). The spectra were corrected for the laser power and the photomultiplier sensitivity. The intensities of the spectra were normalized to the area of the coherent scattering band of the valence oscillations of water (after subtraction of the pedestal).

Figure 1 shows the luminescence spectra of DND in water suspensions obtained for different laser excitation lines. It can be seen that the luminescence peak shifts to the red as λ_{exc} is increased. Similar behavior of the luminescence peak is observed for oxidized graphene in water for excitation at the same wavelengths. The dependences for DND and oxidized graphene are shown as histograms in Fig. 2.

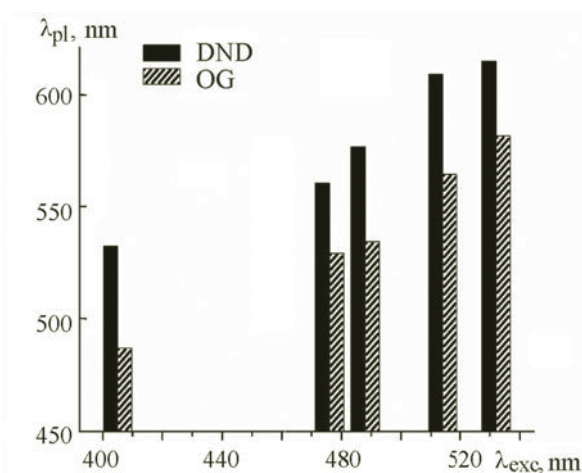


Fig. 2. The position of the fluorescence maximum as a function of excitation wavelength for water suspensions of DND (2 g/L) and oxidized graphene (OG, 0.1 g/L).

The dependences of the fluorescence peak on excitation wavelength can be explained by solvation of the luminophore molecules in the ground and electronically excited states of polar solvent molecules owing to their dipole–dipole interactions [10–12]. When the luminophore absorbs light in the liquid, the dipoles of the luminophore and solvent are in a nonequilibrium state. The solvent dipoles begin to reorient themselves and become aligned parallel to the luminophore dipole, thereby reducing the energy of the interaction and the energy of the excited luminophore. The relaxation (or reorientation) time for ordinary polar solvents (1–10 ps) is considerably shorter than the characteristic excitation relaxation time for organic luminophores (1–10 ns). Thus the process of reorienting the solvent dipoles is completed before the onset of luminescence. The rapid reorientation of the solvent dipoles usually leads to a red shift of the luminescence band relative to the absorption band. If the time for reorientation of the solvent dipoles becomes comparable to the luminescence lifetime, then the luminophore begins to emit simultaneously with a reduction in the energy of the excited state, and this leads to a time dependent energy of the emitted photons, as well as to a dependence of the luminescence peak on the excitation wavelength. This phenomenon is referred to as the "red edge" effect in the spectroscopy of luminophores. It is known that the characteristic time for reorientation of water molecules is ~ 1 ps, while the luminescence damping time for oxidized graphene and DND is ~ 1 ns. In order for the "red edge" effect to show up, the reorientation time of the water dipoles must also be ~ 1 ns. This is possible for a strong interaction of the water molecules with oxidized graphene nanoparticles or nanodiamonds. This kind of interaction has been discovered for oxidized graphene [15] and for DND [16]. It was manifested through a significant weakening of the hydrogen bonds of water during dispersion of DND or oxidized graphene, as indicated by the shift in the bands of the valence oscillations of OH-groups in the coherent scattering spectrum of water. The interaction of the DND with water was stronger than that of oxidized graphene. This explains the larger red shift in the luminescence peak for nanodiamond than for oxidized graphene with the same excitation wavelengths (Fig. 2).

In sum, it has been found that when the laser excitation wavelength is changed from 405 to 532 nm, the position of the maximum of the broad-band luminescence of detonation nanodiamonds suspended in water shifts from 530 to 620 nm. We have shown that an analogous excitation wavelength dependence of the luminescence peak is observed for water suspensions of oxidized graphene. The dependences found for both materials can be explained by interactions of the dipoles of excited luminophore nanoparticles with water dipoles under conditions such that the time for reorientation of the water dipoles and the luminescence damping time for the nanoparticles are similar. These results confirm the hypothesis of a common origin for luminescence in nanodiamonds and in oxidized graphene nanoclusters.

This work was supported by a grant from the Russian Science Foundation (project No. 14-12-01329).

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