Effect of Temperature on Photoluminescence of Nanodiamonds and Carbon Dots in Aqueous Suspensions

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Abstract. Carbon nanoparticles – carbon dots and nanodiamonds – possess characteristic broadband photoluminescence, which depends on their functional surface groups. Such photoluminescence also depends on the properties of the environment of nanoparticles – the polarity of the solvent, the pH value, and the possible adsorption of ions and macromolecules. However, the nature of the surface photoluminescence of nanodiamonds and of the photoluminescence of carbon dots, as well as the mechanisms of the surrounding molecules' influence on it are currently not fully known. This work is devoted to the study of the effect of temperature on the surface photoluminescence of carboxylated carbon nanoparticles in aqueous suspensions. A similarity between the temperature dependences of the photoluminescence of nanodiamonds and carbon dots was found, and an explanation was proposed for the observed changes in photoluminescence.

Keywords: nanoparticles, carbon dots, nanodiamonds, photoluminescence, suspensions.

Introduction

Zero-dimensional carbon nanoparticles (CNPs) – carbon dots (CDs) and nanodiamonds (NDs) – are of great interest for applications in biomedicine. These nanoparticles with a nearly spherical shape have a carbon core (diamond for NDs and graphite/amorphous for CDs) and a multifunctional surface consisting of various functional groups on carbon of various hybridization, often different from that of the core [1]. Their high biocompatibility, stable photoluminescence (PL), ease of synthesis, and the possibility of targeted modification of their surface provide them with a wide range of applications as drug carriers, adsorbents, markers, and nanosensors [1,2]. An important role in these applications is played by CNPs' photoluminescence. For NDs and CDs, photoluminescence of the core is possible: of defects in the diamond lattice of NDs [3], of conjugated π-domains for graphite CDs, or of local core-states of more amorphous CDs [4]. Both NDs [5] and CDs [6] are also characterized by the surface photoluminescence related to their surface groups. Such photoluminescence significantly depends not only on the type and number of

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CNPs' surface groups [7–9], but also on the properties of their environment: polarity [7, 10] and pH [5, 11] of the solvent, adsorption of macromolecules and ions [12–15]. A wide variety of NDs' and CDs' structures and the composition of their surfaces often causes different dependences of their photoluminescence on these parameters. Like that, PL of CDs with different structures and groups reacts differently to changes in the pH of the medium [11,16]. This variability was shown even more clearly by the authors of this publication for NDs: deprotonation of the same surface groups in the same pH ranges of various oxidized NDs led to an increase, decrease, or unchanged intensity of NDs' photoluminescence [5].

The mechanisms of the photoluminescence depending on the surface cover of CDs and NDs is not fully known yet. The difficulty is caused by the local inhomogeneity of the surfaces of such CNPs, which cannot be fully controlled. In the case of nanodiamonds, even the source of this surface PL did not immediately become clear, although now the authors of an increasing number of papers indicate that such a source is the functionalized non-diamond carbon on NDs' surfaces [5, 17, 18], structural analogue of some types of carbon dots.

One way to study the mechanisms of surface PL of NDs and CDs is to study the dependence of their photoluminescence on temperature. According to the results of studies of the PL of various CDs in powders and liquids as a function of temperature, systematized in review [19], in most cases, an increase in temperature led to quenching of their PL, accompanied by a spectral shift. Such quenching was most often explained by the increasing probability of non-radiative transitions from an excited state that increases with temperature. However, in some cases, with an increase in temperature, an increase in the intensity of certain CDs' PL bands is also possible. Such an effect was observed for two-band photoluminescence of dCDs: with increasing temperature, the intensity of the blue PL band decreased, while that of the infrared band increased [20]. The effect of temperature on the surface PL of NDs was studied only for NDs powders [21]: for them, temperature quenching of PL similar to CDs was observed.

The purpose of this work was to answer the questions: is the effect of temperature on the surface photoluminescence of NDs and CDs in aqueous suspensions the same, and if the temperature can affect this PL indirectly through a change in the properties of the solvent.

Materials and methods

The objects of study were DNDs — detonation nanodiamonds, well purified from non-diamond carbon by treatment in air at 400 °C for one hour (Adámas Nanotechnologies, USA), and CDs — carbon dots of hydrothermal synthesis (M. K. Ammosov North-Eastern Federal University, Yakutsk, Russia). The surface of all samples was carboxylated: COOH groups ensure high colloidal stability and biocompatibility of CNPs [22]. In the case of DNDs, the carboxylated surface was the result of annealing of NDs in air [23], while the carboxyl groups of CDs were a direct consequence of their synthesis method described in [16].

Suspensions of DNDs and CDs nanoparticles were prepared in deionized bidistilled water (Millipore Milli-Q), ethanol 95 vol.% (classification reactive grade, Sigma-Aldrich, USA) and acetone (classification chemically pure/analytical grade) with concentrations of 0.5 and 0.02 g/L, respectively. Using a Malvern ZetaSizer Nano ZS zeta-sizer, it was determined that in aqueous suspensions, the average hydrodynamic sizes of the used DNDs and CDs are 22.3 and 10.0 nm, and their average values of ζ-potentials are –40.6 and –29.1 mV, respectively.

The PL spectra of these suspensions were obtained by excitation with an unfocused diode laser (wavelength 405 nm, power 150 mW, beam width 2 mm) in a 90-degree registration scheme using

an Acton 2500i monochromator (focal length 500 mm, grating 900 lines/mm) and Hamamatsu PMT H8259-01. The samples were placed in a thermostated cuvette, the temperature was controlled with an accuracy of 0.1 °C and varied in the range from 11 to 90 °C.

Results and discussion

Examples of the spectra of aqueous suspensions of the studied CNPs are shown in Fig. 1a. The obtained spectra consist of a Raman scattering (RS) band of stretching vibrations of OH groups with a maximum in the region of 470 nm and a broad weakly structured PL band, which is different for different nanoparticles and varies with the temperature of the suspension. For a quantitative analysis of the PL intensity, the parameter F_0 [7, 24] was used, which is equal to the ratio of the integral intensity of CNPs' photoluminescence S_{PL} to the integral intensity of the Raman band of stretching vibrations of the solvent S_{RS}, brought to the value of water RS signal (the case for aqueous suspensions is shown in the inset in Fig. 1a):

$$F_0 = \frac{S_{PL}}{S_{RS}^{CNPs+solvent}} \Big/ \frac{S_{RS}^{Water}}{S_{RS}^{Solvent}}.$$

The obtained values of F_0 divided by the concentration of nanoparticles for CNPs' suspensions at a temperature of 20 °C are presented in Tab. 1. The change in the PL intensity with a change in temperature is shown in Fig. 1b by displaying the obtained dependences of the F_0 parameter, normalized to the F_0 value of suspensions at 20 °C. It can be seen that with an increase in the temperature of aqueous CNPs suspensions from 11 to 50 °C, a gradual decrease, and in the range from 50 to 90 °C, a gradual increase in the PL intensity is observed. The maximum change in PL intensity relative to the 20 °C point for CDs is about 70 %, while for NDs it is only 5 %. However, the changes in the PL intensity for NDs and CDs themselves are of the same character, which is clearly seen if the scale of changes in F_0 of NDs' suspensions is stretched by 8 times (dashed line in Fig. 1b).
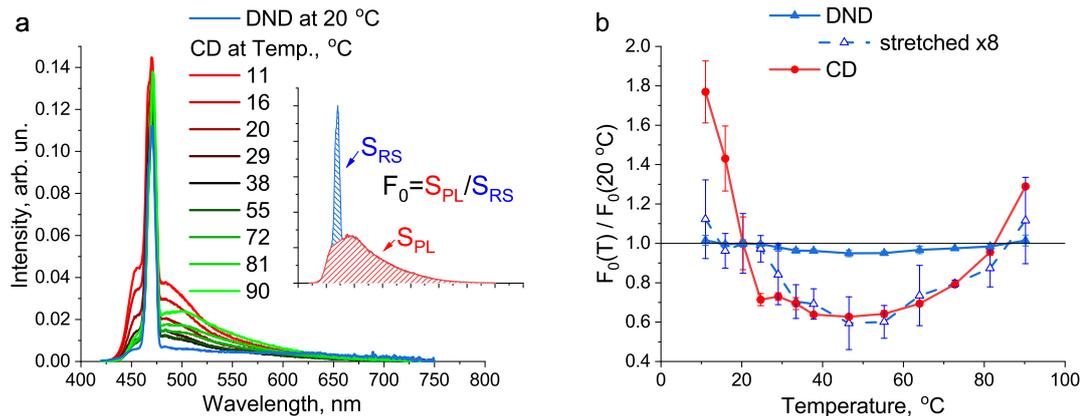

Fig. 1. a) PL and Raman spectra of aqueous suspensions of DNDs at 20 °C and of CDs at different temperatures. The spectra are normalized to the area of the valence band of water. The inset shows an illustration of the calculation of the parameter F_0. b) Dependence of the CNPs' F_0 parameter on temperature normalized to a value at 20 °C

Table 1. Value of parameter F_0/conc. f the studied CNPs' suspensions at a temperature of $20\,°C$

	F_0/conc., L/g		
	In water	In ethanol 95 col.%	In acetone
DND	2.2 ± 0.1	4.1 ± 0.1	13.2 ± 0.4
CD	136 ± 12	99 ± 20	495 ± 56

The quenching of PL with increasing temperature in the range of 11–50 °C occurs without a significant change in the shape of the PL spectrum, the maximum of which overlaps with the valence band of water and is located in the region of 460–470 nm (see for CDs in Fig. 1a). Such quenching is an expected effect, and it can be explained by the temperature activation of non-radiative excitation decay channels [18, 20].

An increase in the CNPs' PL intensity with an increase in temperature in the range of 50–90 °C is a much more unexpected effect. For CDs, it is accompanied by a change in the shape of the PL spectrum (Fig. 1a): the intensity of a band with a longer wavelength maximum near 500 nm appears and grows. For DNDs, a similar increase in the intensity of the longer-wavelength part of the spectrum is observed, however, due to the small scale of these changes, it is difficult to speak of the appearance of a separate PL band.

The observed increase in the CNPs' PL intensity as the temperature changes from 50 to 90 °C we explain by the change in PL quenching by water molecules. It is known that water, a protic solvent with high polarity, is one of the strongest quenchers of photoluminescence of various substances [25, 26]. The temperature weakening of hydrogen bonds and the increased formation of cavitation bubbles around nanoparticles under the action of laser radiation and high suspension temperature [27, 28] causes a decrease in the interactions of CNPs' surface groups with water molecules and, thereby, a decrease of its quenching effect.

To confirm that it is the reduction of the quenching effect of water with an increase in the temperature of the suspensions that is the reason for the increase in the intensity of the CNPs' PL in the temperature range of 50–90 °C, we obtained the PL spectra of all samples under the other method of reducing the influence of the solvent: water with high polarity and proton content was replaced by protic ethanol 95 vol.% with lower polarity and by polar, but not protic, acetone. For example, Fig. 2 shows the CDs spectra in these three solvents. From the given values of the parameter F_0 divided by the concentration of CNPs (Tab. 1), it can be seen that the PL intensity of CNPs in water and ethanol 95 vol.% is of the same order of magnitude, and the PL intensity of CNPs in acetone is several times greater than the PL intensity of protic solvents. Moreover, from Fig. 2 it can be seen that the intense PL of CDs in acetone has a clear maximum in the region of 500 nm, the same maximum that manifested itself upon significant heating of aqueous suspensions of these CNPs. These data speak in favor of our hypothesis, that it is the reduction of water quenching that is the cause of the observed increase in the CNPs PL intensity when suspensions are heated from 50 to 90 °C. In addition, the data obtained indicate that protic polar solvents quench the PL of CNPs much more strongly than aprotic ones.

Conclusions

In result of studying the dependence of CNPs' PL on temperature in the range from 11 to 90 °C, it was found that the photoluminescence spectra of aqueous suspensions of nanodiamonds
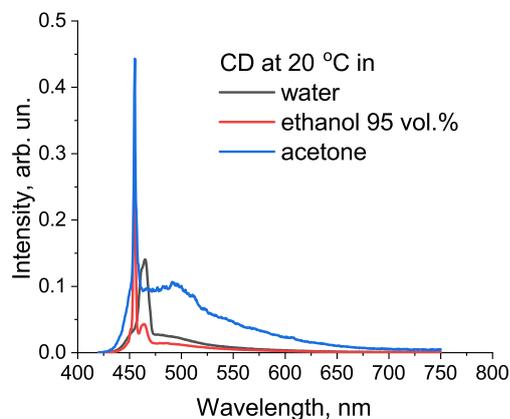
Fig. 2. PL spectra of CDs' suspensions at 20 °C in different solvents. The spectra are normalized to the area of the solvent valence band normalized to water

and carbon dots upon laser excitation at a wavelength of 405 nm depend on the temperature of the suspensions in a complex way: in different temperature ranges both a decrease and an increase in the PL intensity with increasing temperature are observed. The scale of changes in the PL of NDs is an order of magnitude smaller than that of CDs, but the course of these dependences for NDs and CDs is the same. This result points to the similarity of the mechanisms of formation of photoluminescence of CDs of hydrothermal synthesis and undoped NDs.

The observed decrease in the CNPs' PL intensity as the temperature changes from 11 to 50 °C is explained by the expected temperature activation of nonradiative transitions from the excited state. An increase in the CNPs' PL intensity in the range from 50 to 90 °C is a much more unexpected effect and is explained by the gradual reduction of the quenching effect of water. This hypothesis is confirmed by the results of studying the CNPs' PL in solvents with different polarity and number of protons. It was found that polar protic solvents quench CNPs' photoluminescence more strongly than polar aprotic solvents.

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Влияние температуры на фотолюминесценцию наноалмазов и углеродных точек в водных суспензиях

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Аннотация. Углеродные наночастицы — углеродные точки и наноалмазы — обладают характерной широкополосной фотолюминесценцией, зависящей от их функциональных поверхностных групп. Такая фотолюминесценция существенно зависит от свойств окружения наночастиц — полярности растворителя, величины pH, возможной адсорбции ионов и макромолекул. Однако природа поверхностной фотолюминесценции наноалмазов и фотолюминесценции углеродных точек и механизмы влияния на нее окружающих молекул на данный момент известны не полностью. Данная работа посвящена исследованию влияния температуры на поверхностную фотолюминесценцию карбоксилированных углеродных наночастиц в водных суспензиях. Обнаружено сходство температурных зависимостей фотолюминесценции наноалмазов и углеродных точек, предложено объяснение наблюдаемым изменениям фотолюминесценции.

Ключевые слова: наночастицы, углеродные точки, наноалмазы, фотолюминесценция, суспензии.