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The luminescence photostability of carbon nanodots synthesized by the plasma method from a glucose solution after UV radiation

© A.A. Tyutrin[1,2], A.L. Rakevich[1], E.F. Martynovich[1,2]

[1] Irkutsk Branch of Institute of Laser Physics, Siberian Branch, Russian Academy of Sciences, Irkutsk, Russia
[2] Irkutsk State University, Irkutsk, Russia
E-mail: tyutrin.aleks@gmail.com

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Carbon nanodots (CNDs) were synthesized by the microplasma method using a glucose solution as a precursor. The photoluminescence of CNDs before and after UV irradiation was studied. The spectral and kinetic properties of the synthesized CNDs were studied using a MicroTime 200 confocal scanning luminescence microscope. It was experimentally demonstrated that the short component (τ_1) of luminescence refers to C=O bonds on the CND surface. A significant decrease in the luminescence intensity of CNDs after UV irradiation due to a decrease in oxygen-containing groups on the surface of carbon dots was found.

Keywords: Luminescence, carbon nanodots, photostability, time-correlated photon counting.

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Carbon nanodots (CNDs) are being synthesized and studied since 2004 [1]. The key physical, chemical, and optical properties of CNDs have been examined since then, and various methods for their synthesis, which may be divided tentatively into two categories (top-down and bottom-up methods), have been proposed [2]. The influence of different precursors and chemical reagents on the properties of CNDs being synthesized has been examined [3–5]. Despite years of research, the interest in CNDs is still on the rise [6,7]. This is attributable mostly to their unique properties and the potential for application in various fields of research and engineering.

Photostability is one of the key parameters of CND luminescence in optical applications (biovisualization [8,9], sensors [10,11], optoelectronics [12], etc.). Therefore, one needs to examine the photostability of synthesized CNDs under optical irradiation prior to using them in practice.

The number of published studies into the photostability of CNDs is insufficient; a generally accepted explanation of the mechanism of photobleaching of CND luminescence centers has not been formulated. This is largely attributable to the fact that different research groups use different precursors, chemical reagents, and synthesis techniques, thus making it difficult to compare the results and analyze the presumed mechanisms of CND photoexcitation. For example, it has been demonstrated in [13] that the luminescence of CNDs synthesized by laser ablation shifts to longer waves after long-term UV irradiation (365 nm). The authors attributed this to an increase in the number of carboxyl groups. In [14], where CNDs were synthesized using the microwave technique and a phloroglucinol precursor, the luminescence spectrum became narrower after long-term UV irradiation (360 nm), and the luminescence intensity decreased. This was attributed, in contrast with [13], to deoxidation of the CND surface.

It may be concluded that the problem of CND luminescence photostability is a relevant and complex one and requires further study. In view of this, the purpose of the work is to study the luminescence photostability of the carbon nanodots synthesized microplasma method from a glucose solution after exposure to UV radiation. This precursor solution was chosen for its environmental compatibility, nontoxicity, and biocompatibility with live tissues.

Carbon nanodots were synthesized using the plasma technique. A more detailed description and explanation of this synthesis procedure was presented in [15]. Synthesized CNDs in solutions were subjected to UV irradiation by focused radiation of an LED assembly with a wavelength of 365 nm and an intensity of $\sim 20\,\mathrm{mW/cm^2}$. The aggregation of CNDs was monitored using the spectral–kinetic method. Luminescence spectra and the luminescence decay kinetics were measured right after synthesis and several days later. Having compared the obtained data, we did not find any changes. This confirms that the CND aggregation rate is low.

Solutions with synthesized CNDs before and after UV irradiation were studied using a MicroTime 200 (PicoQuant GmbH) time-resolved confocal scanning luminescence microscope equipped with an Ocean Optics QE65000 spectrometer.

The luminescence intensity decreases after long-term (5 h) UV irradiation of carbon nanodots (Fig. 1). It drops rapidly at first (within 15−30 min), but the process of intensity reduction does not stop at later times; instead, it proceeds further at a lower rate.

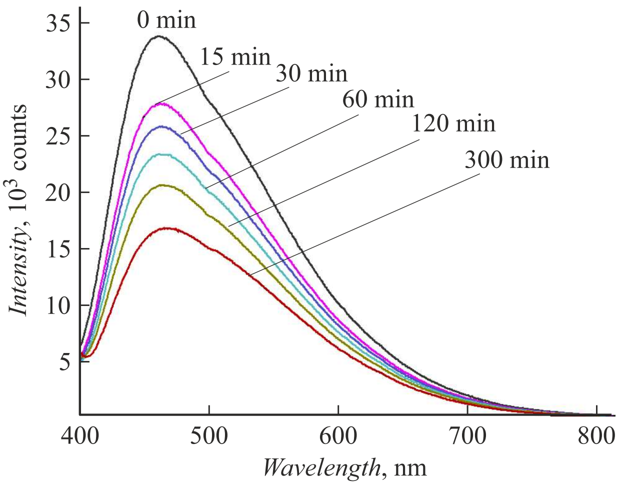

Figure 1. CNDs luminescence spectra depending on the UV irradiation time (365 nm).

Figure 2 shows the normalized spectra of CND luminescence before and after long-term UV irradiation at different excitation wavelengths. A small spectral shift was observed under excitation at 375 nm (Fig. 2, *a*). No marked changes (shift, narrowing, etc.) of luminescence spectra were found after UV irradiation.

The luminescence decay kinetics is another important parameter characterizing the optical properties of synthesized CNDs. Time-correlated counting of single photons is a useful tool for luminescence studies that allows one to identify and decompose luminescence into time components with the contributions of photons to each component taken into account. Table 1 lists the data on the percentage ratio of intensities and luminescence decay constants before and after UV irradiation. It can be seen that luminescence has three exponential time components. CNDs before and after UV irradiation have different features of luminescence kinetics. It is noteworthy that the fraction of centers with the short-term luminescence component (τ_1) decreases in all cases after long-term UV irradiation; conversely, the fraction of centers corresponding to the remaining two components (τ_2, τ_3) increases. This is indicative of transformation and/or destruction of the existing surface luminescence centers. It should be noted that UV irradiation induces

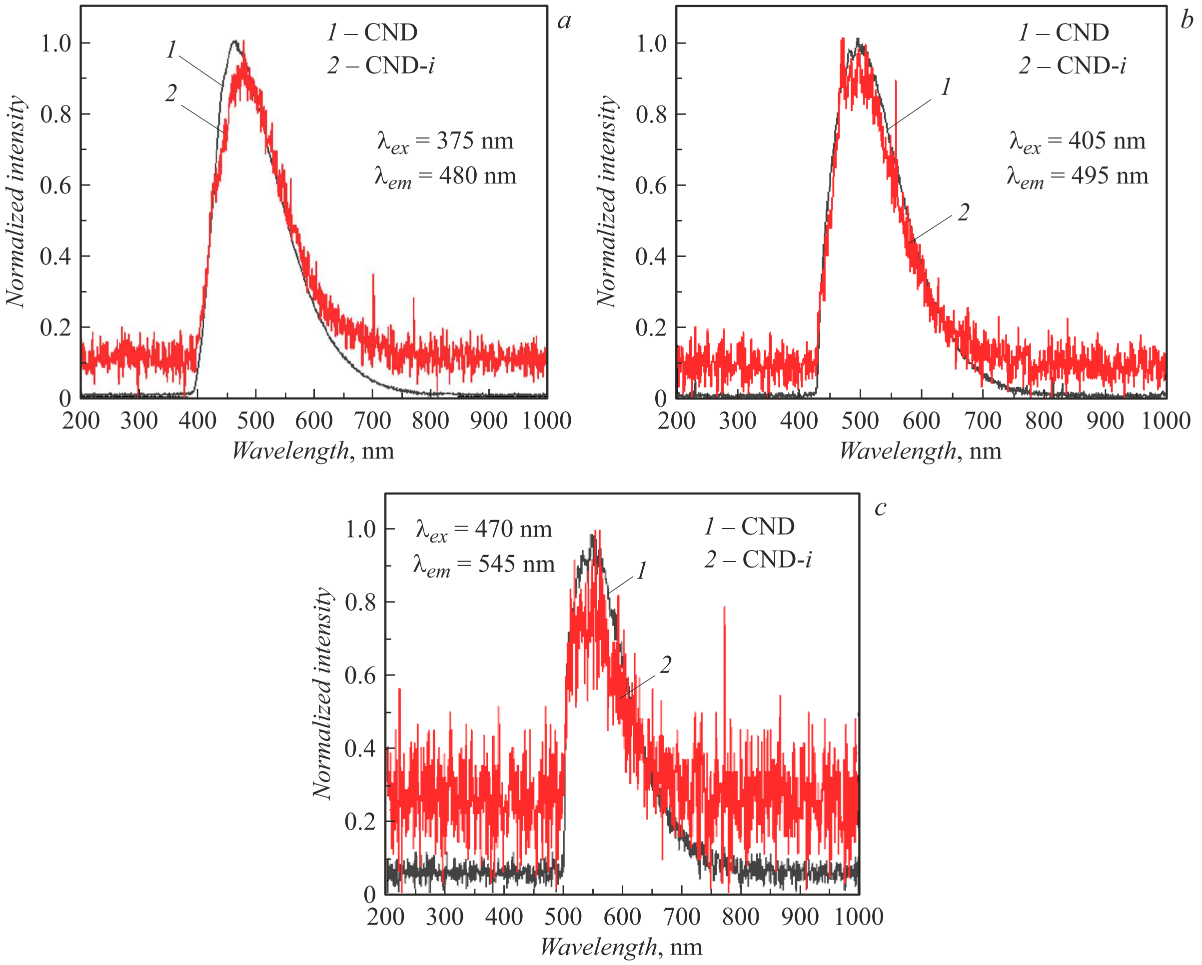

Figure 2. Normalized CND luminescence spectra before (CND, curves *1*) and after (CND-*i*, curves *2*) UV irradiation for 5 h measured under excitation by laser radiation with wavelengths of 375 (*a*), 405 (*b*), and 470 nm (*c*). λ_{ex} is the luminescence excitation wavelength, and λ_{em} is the emission wavelength corresponding to the maximum of the CND luminescence spectrum.

Table 1. Percentage ratio of time-integrated intensities of luminescence components (A) and their decay constants (τ) for CNDs before and after UV irradiation under laser excitation at various wavelengths

Parameter	λ_{ex}, nm							
	375		405		470		532	
	before	after	before	after	before	after	before	after
τ_1, ns	0.7	0.78	0.76	0.97	0.71	0.55	0.56	0.5
A_1,%	53	44	50	38	54	40	51	44
τ_2, ns	2.6	3.4	2.8	3.58	2.8	2.33	2.2	2.2
A_2,%	42	47	43	53	39	44	38	42
τ_3, ns	8.4	10	8.1	9.89	7.95	6.75	6.1	5.46
A_3,%	5	9	7	9	7	16	11	14

the destruction of surface CND luminescence centers for all three components (Table 2); i.e., the luminescence intensity reduction of CNDs after long-term UV irradiation is due to a decrease in the contributions of photons in each of the three luminescence components.

It is known that CNDs are functionalized in most cases by oxygen-containing (C=O, C−O, COOH, OH, etc.) groups [16], which play a big part in luminescence processes, essentially acting as surface luminescence centers. The results of software decomposition (SymPhoTime, TimeHarp 200) revealed that CND luminescence excited by laser radiation with wavelengths of 375, 405, 470, and 532 nm features three exponential time components, which may be indicative, e.g., of the presence of several types of luminescence centers. These luminescence centers may be formed by oxygen-containing groups on the CND surface.

The identification and matching of luminescence centers and time parameters of the CND luminescence decay is one of the important tasks in research into the properties and mechanisms of CND luminescence. This task is not a trivial one. Attempts to perform such a matching procedure have been made, e.g., in [17,18]. However, the results of these studies currently do not allow one to identify luminescence centers accurately based on the time parameter.

It was hypothesized in the course of analysis of measurement data on the CND luminescence kinetics that the short-term luminescence component (τ_1) is related to functional group C=O, since the percentage contribution (Table 1) of the short-term component to the overall intensity (A_1) always decreases after UV irradiation. The following experiment was performed in order to check whether the short-term component actually belongs to C=O groups on the CND surface. Sodium boron hydride ($NaBH_4$), which transforms selectively a carbonyl group into a hydroxyl one on the CND surface and leaves other functional groups (C=C, COOH) unaffected [19,20], was added to a CND solution. The results of measurements of the luminescence decay kinetics of CNDs with sodium boron hydride are listed in Table 2. It can be seen that the addition of sodium boron hydride to a CND solution leads to a selective suppression of the contribution of intensity A_1 of the first luminescence component (τ_1) and a slight increase in the contribution of intensity of the long-term luminescence component (τ_3). Therefore, the short-term luminescence component (τ_1) is associated with functional group C=O on the CND surface. It is also likely that the long-term component (τ_3) corresponds to a hydroxyl group (OH), but this assertion remains debatable at present.

Table 2. Ratio of integrated intensities (A) of individual time components of luminescence for nonirradiated (CND) and UV-irradiated (CND-UV) solutions and a nonirradiated solution with added sodium boron hydride (CND+$NaBH_4$) under laser excitation at 375 nm

Sample	A_1, rel. un.	A_2, rel. un.	A_3, rel. un.
CND	834 (47%)	811 (46%)	133 (7%)
CND-UV (> 5 h)	303 (44%)	312 (46%)	67 (10%)
CND+$NaBH_4$	458 (31%)	810 (55%)	204 (14%)

Thus, the photostability of CNDs synthesized by the microplasma method with a precursor glucose solution under long-term UV irradiation at a wavelength of 365 nm was studied. Spectra and the decay kinetics of luminescence before and after UV irradiation were examined. Time-correlated photon counting revealed that the observed luminescence features three time components. It was demonstrated experimentally that the short-term luminescence component (τ_1) corresponds to functional group C=O on the CND surface. Oxygen-containing groups on the CND surface decompose in the course of long-term UV irradiation, thus reducing the luminescence intensity.

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Conflict of interest

The authors declare that they have no conflict of interest.

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