

The influence of PH on the properties of carbon dots with different surface functionalization: sizes and photoluminescence quantum yield

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In this work carbon dots synthesized by the hydrothermal method and subsequent functionalization of the surface with carboxyl and hydroxyl groups were explored. As a result of studying the optical and colloidal properties of monofunctionalized carbon dots, a significant effect of the acidity of the nanoparticle environment on them was found. It has been found that for the photoluminescence quantum yield of carbon dots the greatest changes occur in the pH range from 2 to 5 for carbon dots with carboxyl surface groups and from 8 to 12 for carbon dots with hydroxyl groups. The mechanisms of the influence of surface functional groups on the photoluminescence of carbon dots with a change in the pH of the suspension are proposed.

Keywords: carbon dots, photoluminescence spectroscopy, nanosensors, pH, surface functionalization, aggregation.

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Introduction

Currently, the research of carbon nanoparticles is being actively developed due to their wide application prospects in biomedicine, optoelectronics, etc. One of the representatives of such nanomaterials are carbon dots (CD), that feature intense and stable photoluminescence (PL), non-toxicity, biocompatibility, and chemical stability [1–3]. Also, it is worth to note low cost and environmental friendliness of their synthesis [1–3]. Thanks to the combination of above-listed properties, CD can be used in such biomedical fields as cancer bioimaging, nanosensors, targeted drug delivery, etc. [4–7]. It is clear that when using CD as theranostic nanoagents, it is necessary to study how they interact with the molecules of the environment and how these interactions and the properties of the medium affect the properties of the nanoparticles themselves. At the same time, account should be taken of the dependence of interactions at the „CD surface-environment“ interface on the composition of surface groups, i.e. on the functionalization of CD surface.

Previously CD with multiple functional groups on their surfaces have been mainly considered in literature. Investigations over the past few years have shown that photoluminescent and colloidal properties of CD with polyfunctional surface depend to a significant extent on the composition and type of surface functional groups [8–12]. Thus, in [8,9] it was found that -OH, -COOH and -NH₂ surface groups determine the position of CD PL spectra: the presence of predominantly carboxyl groups and aminogroups is responsible for green or red radiation, and prevailing presence of hydroxyl groups is responsible for blue radiation. Authors of [10] varied the thermopyrolysis

temperature and the ratio of precursors (citric acid and urea) to increase the degree of CD surface coverage by carboxyl groups, thereby gradually shifted the PL spectrum peak from the blue spectral range to the red spectral range. In [11], results of experimental and theoretical study are presented for CD synthesized by the microwave method and having different composition and functionalization of surface. PL spectra the obtained CD had the form of bands with multiple peaks: all spectra had predominant PL with an emission maximum at 445 nm presumably attributable to the presence of surface aminogroups; also, PL peaks with maxima at 305, 355, 410, 500 nm were observed. Calculations of energy levels of the carbon backbone and surface states using the density functional theory have shown that the HOMO-LUMO gap in the backbone model of the CD under study is less than the HOMO-LUMO gap for surface states. This result allowed the authors to suggest that it is the PL mechanism due to surface states that is of decisive importance in the formation of the photoluminescent properties of CD. The authors of [12] investigated photoluminescent properties of CD synthesized by ultrasonic and hydrothermal methods from sodium sulfate and *o*-phenylenediamine with further treatment with sulphuric acid to produce protonated aminogroups on the CD surface. It has been found that the position of CD PL spectrum peak depends on pH of suspensions: in the pH range from 5 to 14 the PL maximum has been observed in the region of 550 nm, and in an acidic environment (with pH from 1 to 3) the PL peak has been shifted toward long wavelengths of up to ~ 620 nm. As a result of studies using IR absorption spectroscopy, nuclear magnetic resonance and measurement of the zeta-potential, the authors of [12] have shown that with a decrease in

the pH of the suspension, the CD-NH₂ surface functional aminogroups are actively protonated and converted to NH₃⁺. The analysis of structure of internal energy levels of CD using UV photoelectron spectroscopy has shown that the protonation of aminogroups decreases the band gap between HOMO and LUMO of the carbon backbone and the surface state. Thus, authors of this study have shown that the position of PL spectrum peak of CD with surface aminogroups depends on protonated/deprotonated state of the aminogroups on the CD surface.

Numerous studies have shown that PL of nanoparticles depends to a significant extent on their aggregation in suspensions [13–16]. Thus, authors of [15] have shown that in the case of aggregation, as the concentration of CD synthesized from citric acid and thiourea by pyrolysis increases in the suspension, the peak of intensity of their PL shifts toward longer wavelengths, and quantum efficiency of the PL decreases. At the same time, the aggregation of CD results in a gradual decrease in the band gap, from 2.18 to 1.56 eV. For CD synthesized by the same method with the addition of zirconium chloride (Zr-CD) in a similar experiment, no dependence of the PL of Zr-CD on the concentration of nanoparticles (i.e., on the aggregation) is observed. Measurements of the zeta-potential of Zr-CD have shown that these CD are in a highly dispersed state regardless of the concentration of nanoparticles: zirconium complexes on the surface of Zr-CD prevent the aggregation of nanoparticles with an increase in the concentration of nanoparticles; as a result, the band gap of Zr-CD does not change (it is equal to ~2.21 eV) and PL remains unchanged.

A comprehensive study of CD PL was conducted in [16]. Carbon dots synthesized by the hydrothermal method and doped with nitrogen were investigated. Samples had different compositions of functional surface groups: CD produced from *n*-phenylenediamine and urea (N-CDR) mainly contained amide and carboxyl groups on their surfaces; CD produced from citric acid and ammonium hydroxide (N-CDB) as precursors contained carboxyl and hydroxyl groups. Studies of the CD PL dependence on pH of the environment have shown that the protonation of CD surface groups in an acidic environment (~pH 2 and ~pH 4) causes CD PL peaks to shift toward longer wavelengths. Measurements of the zeta-potential and hydrodynamic diameter of CD at different pH values have shown an increase in the size of both CD types at pH from pH 3 to pH 8 for N-CDR and at pH < pH 6 for N-CDB, which was correlated with the decrease in zeta-potential modulus of these CD. Thus, authors of [16] have demonstrated the dependence of PL of polyfunctional CD on the protonation of their surface groups and the aggregation in acid suspensions.

Unfortunately, the authors of this study have succeeded to find only a few works covering CD with monofunctional surface (having predominantly one type of functional groups). It is clear that based on the results of studying nanoparticles with a polyfunctional surface, it is impossible

to draw unambiguous conclusions about the interactions of specific surface groups with surrounding molecules. The study of CD with surface functional groups of the same type makes it possible not only to learn how to control the optical properties of CD but also provides a subsequent qualitative modification of their surface with various polymers or drugs. This will allow more efficient use of CD in biomedical applications. Thus, authors of [17] have investigated PL of three CD types with monofunctional surfaces: with carboxyl (CD-COOH), hydroxyl (CD-OH), and amide (CD-NH₂) functional groups. It was found that with the excitation by radiation with a wavelength of 388 nm the highest PL intensity is exhibited by the water suspension of CD-NH₂, and the lowest intensity is demonstrated by CD-COOH suspensions. The same study has been investigated the CD PL at different pH values of the water suspension: pH 1, pH 7, and pH 14. The obtained PL spectra indicated that with an increase in the pH value of the suspension, a decrease in the PL intensity of CD-COOH and an increase in the PL intensity of CD-OH are observed. The PL intensity of CD-NH₂ decreased as the pH changed from the initial neutral level toward both the acidic and alkaline regions, which is due to the manifestation of amphotericity of the NH₂-group. The authors concluded that deprotonation of appropriate surface groups results in extinguishing of nanoparticle PL as compared to the protonated state of surface groups.

This study continues the studies reported in [8]. Previously the authors studied the effect of water suspension pH on the PL intensity of CD with different surface functionality. This publication presents results of the investigation of the dependence of quantum efficiency of the PL of CD-COOH and CD-OH monofunctional nanoparticles and their sizes on pH. It is found that quantum efficiency of the CD PL depends to a significant extent on the environment acidity, moreover, these dependencies are different for the CD with different monofunctionalizations of surface. It was found that in the same ranges of pH a manifold increase in CD sizes takes place with decrease in pH of the suspension. The observed changes in photoluminescent properties of CD with changes in water suspension pH are explained by the processes of de-/protonation of surface functional groups and aggregations of nanoparticles.

Materials and methods

Synthesis of CD and preparation of samples

The subject of study were carbon dots synthesized by hydrothermal method from citric acid and ethylenediamine. The CD synthesis is described in detail in [8]. The IR-absorption spectroscopy was used to investigate the composition of surface functional groups of synthesized CD before and after the functionalization of their surface (Fig. 1). The obtained spectral data has shown that after the functionalization -COOH and -OH groups significantly

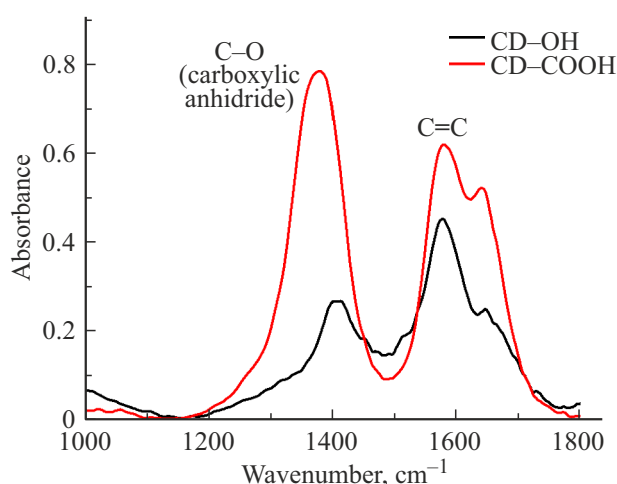


Figure 1. IR absorption spectra of powders of synthesized monofunctional CD.

prevail on CD-COOH and CD-OH surfaces, respectively (Fig. 1).

To study the dependence of optical properties and suspendability of CD on pH, a wide measurement range of pH has been chosen, from 2 to 12, that has been caused first of all by the pH value variation in human body from pH 2 [18] to \sim pH 8.6 [19]. It is worth noting that such a large measurement range of pH, among other things, will allow for a better study of the deprotonation of aminogroups and hydroxyl groups, because their pK_a values are in the range of 9–10 and 9–12, respectively [20]. All measurements were carried out at a fixed temperature of 22°C.

The photoluminescence spectroscopy

The PL of water suspensions of CD were studied using a Shimadzu RF-6000 spectrofluorometer. PL spectra of CD water suspensions were recorded in a range of excitation wavelengths from 250 to 500 nm with a step of 5 nm and in a range of PL emission wavelengths from 250 to 700 nm with a step of 1 nm, with a spectral slot width of 3 nm and a low sensitivity of the instrument. The obtained PL spectra were processed by means of subtracting the PL excitation lines and smoothing over 10 points by a Savitzky-Golay filter using the Spectragryph software [21].

pH measurements

pH values of CD water suspensions were measured by an Akvilon I-500 ionometric converter equipped with a pH InLab Nano pH-electrode (Mettler Toledo). pH values of suspensions varied in the measurement range from 2 to 12 by adding aqueous solutions of HCl (Sigma Aldrich, with a concentration of 1 M, pH 0) and NaOH (Dia-M, with a concentration of 1.8 M, pH 14).

Measurements of sizes and zeta-potentials of nanoparticles

Zeta-potentials and sizes of nanoparticle in water suspensions were measured by the method of dynamic light scattering using a Malvern Zetasizer NanoZS instrument.

Results and discussion

To study the dependence of photoluminescent properties and suspendability of functionalized CD on pH of the environment, water suspensions of CD-COOH and CD-OH with a concentration of 0.1 mg/ml were prepared. pH values of suspensions were varied in the range from pH 2 to pH 12.

The effect of suspension pH on photoluminescent properties of CD-COOH and CD-OH

Fig. 2 shows matrices of excitation and emission of CD PL and the diagram of intensities in PL spectra peaks for CD-COOH and CD-OH at pH 7. It can be seen from the obtained data that PL emission/excitation spectra of CD are wide structureless bands with peaks at emission/excitation wavelengths of 405/320 nm for CD-OH and 432/350 nm for CD-COOH. As it follows from Fig. 2, *c*, the photoluminescence intensity of CD-COOH is 16 times higher than that of CD-OH, which suggests that characteristics of CD PL depend on the surface functionalization.

The dependencies of PL spectral characteristics of CD-COOH and CD-OH water suspensions on pH of the environment in the range from pH 2 to pH 12 have been investigated in detail by the authors earlier in [8]. A significant effect of the environment acidity of nanoparticles on their optical properties was found. It is found that the biggest changes in PL spectral characteristics of all types of CD are manifested in the same ranges of pH variation: pH 2–pH 5 and pH 8–pH 12. The observed features have been explained by the processes of protonation/deprotonation of surface groups of -COOH and -OH CD. This study is focused on the investigation of the pH-dependence of the CD PL quantum efficiency in water suspensions.

Quantum efficiency of PL (PL QE) is defined as a ratio between the number of emitted photons and the quantity of absorbed photons. The PL QE of CD in water suspensions was determined by the method of reference dye [22,23] by the following formula

$$Q = Q_r \frac{OD_r}{OD} \frac{I}{I_r} \left(\frac{n}{n_r} \right)^2,$$

where Q is PL QE of the sample, OD is optical density at a certain excitation wavelength λ_{ex} , I is integral intensity of the PL, n is refraction index of the medium. The r subscript indicates the use of known parameters of the reference dye. Quinine sulfate in aqueous solution of sulphuric acid with a concentration of 0.05 mol/l was used as a reference dye. The choice of quinine sulfate as a reference dye is due to the fact

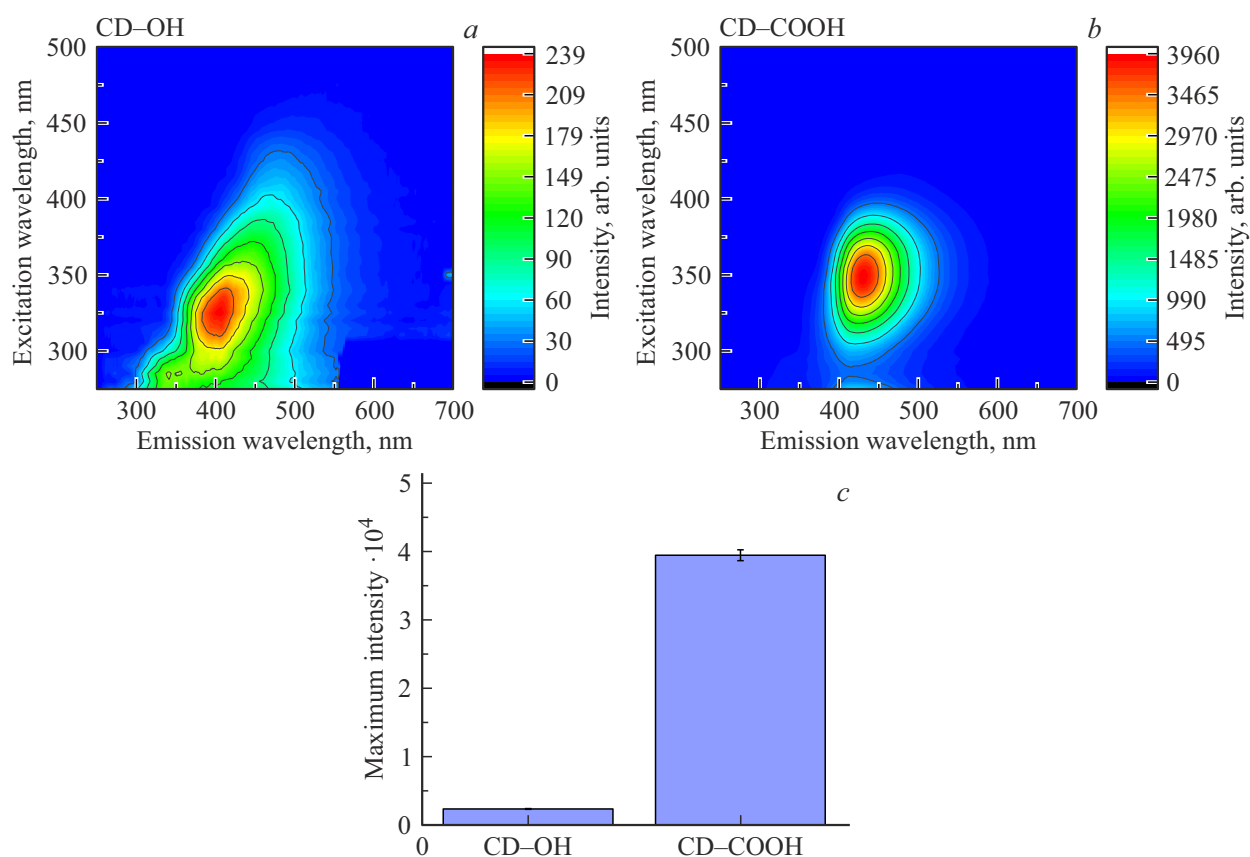


Figure 2. Matrices of excitation/emission of PL of water suspensions for CD-OH (a) and CD-COOH (b) at pH 7. Diagram of intensities in PL spectra peaks of studied CD at pH 7 (c).

that, first, its PL emission band in terms of shape, width and peak position is close to the same spectral characteristics of the CD under study. Second, the QE of quinine sulfate in aqueous solution of sulphuric acid has been measured by many researchers, it is known with a high accuracy and recommended for the use as a reference. Known values of PL QE of quinine sulfate were used: at an excitation wavelength of 310 nm $Q_r = 0.546$ [24], at an excitation of 350 nm $Q_r = 0.58$ [22]. Due to the fact that QE of quinine sulfate PL is known in literature for wavelengths of 310 and 350 nm, these excitation wavelengths were chosen to determine the QE of CD PL by the method of reference dye.

QE values of PL for initial water suspensions of CD (\sim pH 11) were 16.9% for CD-COOH with excitation at 350 nm, 63.8% for CD-OH with excitation at 310 nm. The resulted dependencies of PL QE of water suspensions for CD-COOH and CD-OH on the pH value of water are shown in Fig. 3. It is worth noting that the PL QE values for CD suspensions were calculated without subtraction of the contribution of light scattering in nanoparticle suspensions from the optical density spectra because there is no contribution to the CD optical density from this scattering at the excitation wavelengths of 310 nm used for CD-OH and 350 nm used for CD-COOH.

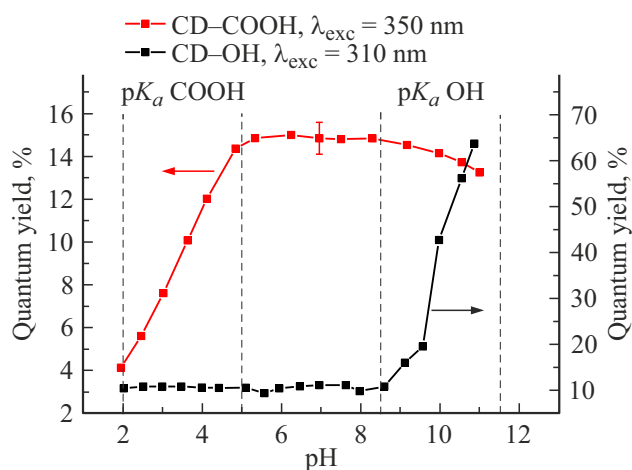


Figure 3. Dependencies of PL QE of CD on the suspension pH. Vertical lines show pK_a ranges of carboxylic and hydroxylic groups [24].

Expectedly [8], the water suspension pH has a significant effect on the PL QE of CD with different types of surface. The PL QE of the CD-COOH increases sharply in the range from pH 2 to pH 5 (approximately by 4 times) and remains nearly unchanged as the suspension increases up

to pH 8, and at pH from pH 8 to pH 12 it decreases insignificantly. The PL QE of the CD-OH remains unchanged at $\text{pH} < \text{pH} 8$, then it increases sharply in the range from pH 8 to pH 11 (approximately by 6.5 times).

Thus, the most significant changes in photoluminescent characteristics of CD-OH are observed in the region of $\text{pH} > \text{pH} 8$, and in the case of CD-COOH they are observed in the region of $\text{pH} < \text{pH} 5$. These pH values are within the ranges of pK_a for carboxyl and hydroxyl functional groups (Fig. 3), which suggests the processes of deprotonation taking place in suspensions in -COOH carboxyl groups at pH from 2 to 5 and in hydroxyl groups at $\text{pH} > \text{pH} 8$ [8,25]. It follows from the obtained data that in case of deprotonation of -COOH and -OH surface groups a sharp increase in the PL QE of CD water suspensions is observed as compared with the case when these CD surface groups are protonated. It is worth noting that the significant difference of CD PL intensities at a neutral suspension pH in Fig. 2, c can be explained by the increase in the QE of CD with deprotonated state of surface (as compared to the protonated state). With a neutral pH (pH 7) of suspension the hydroxyl groups of CD-OH are in protonated state and hydroxyl groups of CD-COOH are deprotonated. That is why with this suspension pH the photoluminescence of CD-COOH is considerably more intensive than that of CD-OH. It is worth noting that in the under-study dependencies of PL QE on pH a range of pH values can be distinguished where an unambiguous solution to the inverse spectroscopic problem, i.e. the problem of determining the parameter (pH) from optical spectra, is possible. Thus, it is possible to implement a CD-COOH-based nanosensor of pH operating in the acidic range of pH — from pH 2 to pH 5 (for example, to visualize diseases (in particular, cancer) in the gastrointestinal system). Despite the fact that the PL QE of CD-OH achieves a level of a bit less than 70% at basic pH values, its application as a pH sensor is restricted by the fact that the most informative section of PL intensity dependence on pH is within the range of $\text{pH} > \text{pH} 8$, while most of biologic fluids and tissues have $\text{pH} < \text{pH} 8$. Nonetheless, properties of CD-OH allow their use for the diagnostics of pancreatic fluid, which pH is normally varied in the range of pH 8.0–pH 8.3.

Dependence of CD-COOH and CD-OH sizes in water on pH

To study the relationship between the PL of CD and the possible aggregation of nanoparticles, the dependencies of sizes of CD with different surface functionalization on suspension pH were investigated. Water suspensions of CD-COOH and CD-OH with a nanoparticle concentration of 0.1 mg/ml at pH 12 were prepared. According to the obtained data, sizes of CD under study in the prepared suspensions were 105 ± 12 , 176 ± 23 nm for CD-COOH, CD-OH, respectively. In addition, zeta-potentials of CD in initial suspensions were measured. These potentials were -29.1 ± 4.5 , -17.2 ± 1.3 mV for CD-COOH, CD-OH,

respectively. The measured zeta-potentials are indicative of the colloid stability of water suspensions of all CD.

To detect possible CD aggregation, their sizes with decrease in pH of water suspensions from pH 12 down to pH 2 were measured by the method of dynamic light scattering (Fig. 4). It can be seen from the presented data that sizes of CD-COOH and CD-OH change significantly as the suspension pH decreases from pH 12 down to pH 2. Sizes of CD-COOH mainly fluctuate insignificantly around 100–300 nm, however, in the pH range from pH 2 to pH 4 a sharp increase in nanoparticle sizes up to 1–2 μm is observed. So, a nanoparticle aggregation in an acidic environment takes place in the case of CD-COOH. In the case of CD-OH, an increase in nanoparticle sizes by 2 times was observed at $\text{pH} < \text{pH} 8$ as compared with sizes at $\text{pH} > \text{pH} 8$. Thus, it may be concluded that as the suspension pH changes, an aggregation of the particles under study takes place, that can affect their photoluminescent properties.

Mechanisms of the effect of deprotonation/protonation of surface functional groups on the photoluminescence of CD

Fig. 5 shows PL QE, positions of PL peak (for the corresponding excitation wavelength [8]), full widths at half-maximum (FWHM) of spectra and CD sizes as the suspension pH changes in the range from pH 2 to pH 12 for CD with two monofunctional surfaces. Based on the obtained dependencies, the following mechanisms of the effect of surface functional groups on the CD PL with changes in suspension pH can be suggested. As it was already noted above, the PL QE of CD-COOH increases in the range from pH 2 to pH 5 with simultaneous deprotonation of the carboxyl functional group, which becomes negatively charged as a result of this process. No significant changes in the QE are observed with further increase in pH. In the case of CD-OH the QE of PL increases only in the pH range corresponding to the pK_a

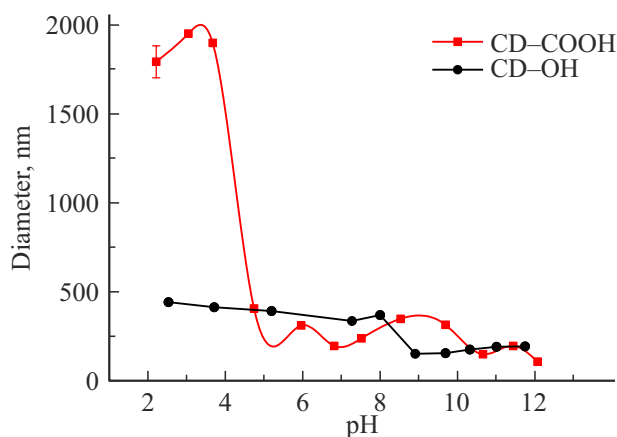


Figure 4. Dependence of sizes of CD with different surface functionalization on suspension pH.

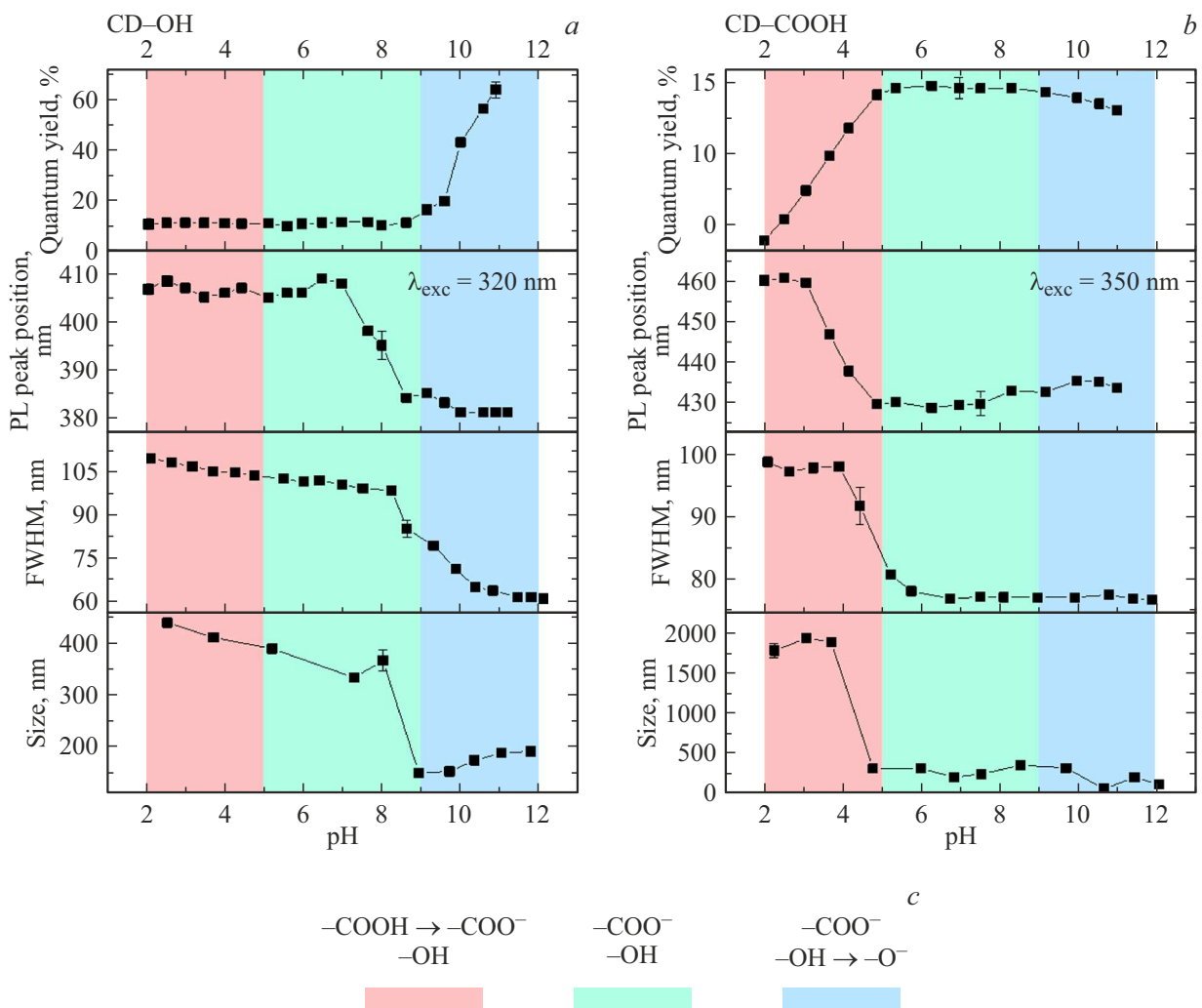


Figure 5. Dependencies of PL QE, position of PL peak, peak width at half height and size of CD-OH (a) and CD-COOH (b) on suspension pH. Under the graphs — color notation of functional group sets corresponding to a certain range of pH (c).

range of hydroxyl groups. In this range, -OH hydroxyl groups are transformed to $-O^-$ (Fig. 5, c), the number of charged groups on the CD surface increases and, as can be seen from Fig. 5, b, the quantum efficiency of PL of CD-OH increases. In other pH ranges no changes of the above-specified parameters occur. Thus, on the basis of the experimental data it may be concluded that in the case of CD with deprotonated forms of surface functional groups an increase in the intensity of CD PL QE is observed as compared with the CD that contain protonated forms of prevailing surface functional groups.

Similar PL dependencies on deprotonated/protonated states of functional oxygen-containing groups have been observed for detonation-synthesized nanodiamonds in [14]. Measurements of nanoparticle zeta-potentials in suspensions in the studied pH range and quantum-chemical modeling of nanodiamond surface with different groups carried out by the authors of [14] have shown that all main changes in the PL of studied nanodiamonds with pH variation are due to de-/protonation of oxygen-containing groups: carboxyl

groups in the region of pH 2–pH 5 and hydroxyl groups located on carbon in the sp^2 -hybridization in the region of pH 9–pH 12.

However, it is worth noting that in the case of CD under consideration, a nanoparticle aggregation is manifested with variation in suspension pH values. In the case of CD-COOH, a nanoparticle aggregation is observed with increase in sizes by 6–6.5 times at $pH < pH 5$. In this pH range carboxyl groups become protonated and electrically neutral, which results in decrease in the surface charge of CD, and nanoparticle aggregation becomes more probable due to the decrease in Coulomb repulsion between them. Also, in the case of CD-OH, a nanoparticle aggregation is manifested at $pH < pH 8$. When pH decreases from pH 11 down to pH 8, hydroxyl groups of CD-OH are protonated, thanks to which the repulsion between nanoparticles decreases and the CD-OH aggregation becomes more probable. Thus, the change in PL QE of under-study CD with monofunctional surfaces within the above-specified ranges of pH may be caused by not only the change in surface charge under protonation

of CD groups but also the nanoparticle aggregation caused by the same protonation. This conclusion is confirmed by the fact that typical changes in the dependence of size and position of the CD PL peak on pH (Fig. 5, *a*) take place in the same regions: in the case of CD-COOH the position of PL peak, the peak width at half-height, the size remain unchanged with a decrease of suspension pH from pH 12 down to pH 5. Then a stepwise increase in the above-specified parameters takes place at pH 4 and with further decrease in suspension pH the position of PL peak, the width at half-height and the size of CD-COOH remain nearly unchanged. A similar behavior of dependencies of PL peak position and size on pH is also observed for the CD-OH (Fig. 5, *b*), however, the corresponding stepwise change in parameters takes place at pH 8.

Conclusion

The effect of water suspension pH on PL of monofunctional CD synthesized by the hydrothermal method from citric acid and ethylenediamine with further functionalization of the surface of carboxyl and hydroxyl groups is studied. A significant dependence of CD PL QE on acidity of the nanoparticle environment was found. It is found that in spectral characteristics of PL of the CD under study small changes are manifested in the ranges from pH 2 to pH 5 for CD-COOH and from pH 8 to pH 12 for CD-OH. The obtained results can be explained by the processes of de-/protonation of -COOH and -OH groups on the CD surface with pH variation.

As a follow-up to the obtained results [8] it has been shown that in the case of CD under study a nanoparticle aggregation is manifested with variation of suspension pH. In the case of CD-COOH, a nanoparticle aggregation is observed with increase in sizes by 6–6.5 times at pH < pH 5. In the case of CD-OH, a nanoparticle aggregation is observed at pH < pH 8. Thus, the change in PL QE of under-study CD with monofunctional surfaces within the above-specified ranges of pH may be caused by not only the change in surface charge under de-/protonation of CD groups but also the nanoparticle aggregation caused by the same de-/protonation.

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Conflict of interest

The authors declare that they have no conflict of interest.

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