Optics and Spectroscopy, 2022, Vol. 130, No. 6

20

Dependence of photoluminescence of carbon dots with different surface functionalization on hydrogen factor of water

© M.Yu. Khmeleva[1,2], K.A. Laptinskiy[1], P. S. Kasyanova[2], A.E. Tomskaya[3], T.A. Dolenko[2]

[1] Moscow State University, Skobeltsyn Institute of Nuclear Physics,
119991 Moscow, Russia
[2] Moscow State University, Department of Physics,
119991 Moscow, Russia
[3] Prokhorov Institute of General Physics, Russian Academy of Sciences,
119991 Moscow, Russia

e-mail: khmeliova.maria@gmail.com

Received December 20, 2021
Revised February 01, 2022
Accepted March 22, 2022

The pH dependences of the photoluminescence of carbon dots synthesized by the hydrothermal method with polyfunctional and monofunctional (carboxylated and hydroxylated) surfaces have been studied. As a result of the analysis of the obtained photoluminescence and absorption spectra of aqueous suspensions of all studied types of carbon dots at different pH values, a significant effect of the acidity of the environment of nanoparticles on their optical properties was found. It has been found that the greatest changes in the spectral characteristics of absorption and photoluminescence of carbon dots with COOH, OH, and NH_2 surface groups appear in the pH ranges of 2−5 and 8−12. The obtained results are explained are explained by the processes of protonation/deprotonation of the surface groups of carbon dots.

Keywords: carbon dots, surface functionalization, absorption spectroscopy, photoluminescence, hydrogen index, deprotonation.

DOI: 10.21883/EOS.2022.06.54706.36-22

Introduction

The active development and deepening of scientific knowledge in the field of biomedicine are conditioned upon the intensive development of known approaches and creation of new methods of research at the molecular level. Studying different intracellular biological processes dictates the need to develop new nano-scale sensors/markers. Nowadays, a promising nanomaterial are carbon dots (CD) possessing a unique combination of properties that provide for active application of these nanoparticles for different biomedical purposes [1–4]. Thus, CD have an intensive photoluminescence (PL) in the visible spectrum range: the luminescence quantum yield is about tens of percents [5,6]. PL spectrum characteristics of CD are sensitive to changes in parameters of the medium and its different components strength of hydrogen bonds in the suspension [7], presence of ions and biomolecules [8,9], pH factor [9–15], temperature [16], etc. This sensitivity suggests prospects of CD use as different nanosensors.

There are works [9–15] suggesting to use CD as nanosensors to determine pH value of the local environment. In most of the above-mentioned studies the effect of environment pH on the intensity of CD photoluminescence was shown, but the challenge to find out mechanisms of this sensitivity was not posed. In some works the studying of mechanisms of the PL change under changing environment pH was not possible due to the multifunctionality of nanoparticle surface. In [9], a nonlinear monotone increase in PL intensity of CD was shown for the transition from low values of pH of 3.5 to alkalinous pH of 8.5. The photoluminescence lifetime in this case was increasing linearly from 1.6 to 3.7 ns. Using the technique of fluorescence-lifetime imaging microscopy (FLIM), the authors differentiated CD located inside and outside of a lysosome (a cell organelle surrounded by the membrane with acidic environment maintained in its cavity) of the tumor cell *HeLa*. Due to the fact that authors used polyfunctional CD with carboxylic, hydroxylic, amide and other functional groups on their surface, in this study they did not succeed to determine specific mechanisms of pH effect on photoluminescence of CD. In [10], a non-monotone decreasing dependence of PL intensity of polyfunctional CD on the increase in pH from 2 to 13 was shown. The authors suggested a hypothesis that the obtained dependence can be explained by deprotonation of the functional groups with increase in pH, however the presence of a number of different functional groups on the CD surface impeded to confirm this hypothesis. It is evident that confirmation of the suggested hypothesis needs studying of the photoluminescence dependence on the environment pH for CD with their surface functionalized their surface functionalized only by one type of groups.

Unfortunately, there are very few works where the effect of pH on optical properties of monofunctional CD are investigated. Thus, in [15] CD-COOH, CD-OH and CD-NH_2 coated with carboxylic, hydroxylic and amide functional groups, respectively, were investigated. The authors have shown the difference between intensities of PL spectra of CD with above-mentioned functional groups on their surfaces at three values of hydrogen factor of the suspension. For this purpose CD suspensions were prepared with pH values of 1, 7 and 14, and their PL spectra were recorded under excitation by radiation with a wavelength of 338 nm. The obtained results indicated that in case of deprotonation of the carboxylic group a decrease in the PL intensity of CD-COOH is observed, while deprotonation of the hydroxylic group yields an increase in PL intensity of CD-OH. The PL intensity of CD-NH_2 decreased with pH changing from the initial neutral value towards both the acidic range and the alkalinous range, which authors had explained by the amphoteric behavior of the NH_2-group. The authors concluded that deprotonation of surface groups results in extinguishing of nanoparticle PL as compared with the protonated state of surface groups. However, no specific mechanisms were identified for this PL behavior of CD under protonation/deprotonation of surface groups.

To effectively use CD as a PL-sensor of pH of the local environment, it is necessary to find out the dependence of nanoparticle PL on pH in a wide measurement range, as well as to understand the mechanism of pH effect on the characteristics of PL spectra of CD. Currently available experimental dependencies of CD photoluminescence on pH are of contradictory character [11]. This is explained by the difference in methods of CD synthesis, variation of initial materials-precursors used to produce nanoparticles. In the vast majority of experimental works CD are used that have on their surface a set of different functional groups, which does not allow making firm conclusions from the observed dependencies of pH effect on the photoluminescence. There are very few publications devoted to investigation of CD with multifunctional surface (CD−COOH, CD−OH and CD−NH_2) and made it possible to suggest a hypothesis that the PL dependence on pH is caused by protonation and deprotonation of functional surface groups.

In this study we focused on the dependence of PL on pH of water for the CD synthesized by the hydrothermal method, with polyfunctional and monofunctional (carboxylated and hydroxylated) surfaces. The comparative analysis of obtained PL and absorbance spectra of water suspensions of all investigated CD types at different values of pH allowed us to confirm the hypothesis that the obtained dependencies are explained by the processes of protonation/deprotonation of surface groups of CD.

Materials and methods

Synthesis of CD and preparation of suspensions

CD were synthesized by hydrothermal method from citric acid and ethylendiamine. Detailed description of the synthesis of CD with polyfunctional surface (CD-poly) can be found in [16]. To obtain CD-poly, 550 mg of citric acid powder were diluted in 15 ml of deionized water, then 3.5 ml of ethylendiamine was added. Then the solution was held in an ultrasonic bath for 5−10 min to achieve homogeneous agitation of initial reagents. After that the mixture was transferred to a teflon autoclave container with a volume of 25 ml. The sealed autoclave was placed in a general-purpose drying cabinet and held for 2 h at a temperature of 190°C.

To functionalize CD with hydroxylic groups (CD-OH) CD (CD-OH) the dried residue of the suspension after the synthesis was mixed with 1.8 g of sodium nitride and 5.5 ml of hydrochloric acid to remove the amide groups. To obtain carboxylated surface of CD (CD-COOH), the dried residue was added with 12 ml of water and 5 ml of NaOH solution with a concentration of 0.5 M.

Water suspensions of CD were prepared using deionized water (*Millipore Simplicity UV* water purification system). Water suspensions of CD-OH and CD-COOH were prepared with a concentration of 0.1 mg/ml and water suspension of CD-poly with a concentration of 0.01 mg/ml. To change pH in the range from 2 to 12, either HCl acid or NaOH alkali were added to the suspensions. The choice of such a wide variation of pH is caused, first of all, by the fact that the hydrogen factor in the human body varies from 2 [17] to ~ 8.6 [18]. In addition, a large range of pH variation allows for better investigation of deprotonation of amine and hydroxylic groups, having their pK_a for many organic compounds in ranges of 9−10 and 9−12, respectively [19]. All measurements were carried out at a fixed temperature of 22°C.

The photoluminescence spectroscopy

PL spectra of CD water suspensions were recorded by a Shimadzu RF-6000 spectrofluorometer 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 slit width of 3 nm, low sensitivity of the instrument. The 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 [20].

pH measurements

Hydrogen factor of CD water suspensions was measured by an Akvilon I-500 ionometric transducer equipped with a pH-electrode of pH InLab Nano type (Mettler Toledo). Measured pH values of suspensions varied from 2 to 12 by adding aqueous solutions of HCl (Sigma Aldrich, with concentration of 1 M, pH=0) and NaOH (Dia-M, with a concentration of 1.8 M, pH=14).

The absorption spectroscopy

Optical density spectra of CD water suspensions with different surface functionalization were measured using a Shimadzu UV-1800 spectrophotometer. The spectra were recorded in a range of 200−400 nm with a step of 1 nm, at a medium scanning rate, with a spectral slit width of 1 nm.

The IR-absorption spectroscopy

To monitor the composition of CD surface groups after the synthesis and functionalization of surface, a Varian 640-IR FT-IR IR spectrometer was used equipped with

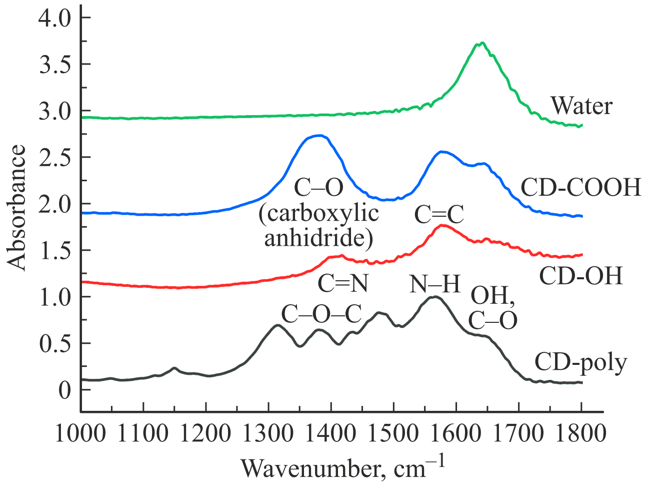

Figure 1. IR-absorption spectra of water and powders of synthesized CD.

a diamond crystal-based FTIR-ATR-add-on. The spectral resolution was 4 cm^{-1}.

Measurement of nanoparticle sizes

Sizes of nanoparticles in the suspension were determined using a Malvern ZetaSizer Nano ZS instrument.

Results and discussion

The CD characterization

According to results of the dynamic scattering of light, the CD synthesized in water suspensions have sizes of 13.0 ± 2.5, 8.1 ± 1.3 and 10.0 ± 1.6 nm for CD-poly, CD-OH and CD-COOH, respectively.

The composition of surface functional groups of the synthesized CD before and after functionalization was investigated using the IR-absorption spectroscopy. The analysis of IR spectra has shown that there are many different functional groups on the CD-poly surface, such as C–O–C, C=N, C=C, N–H, OH [21]. However, after the functionalization there are predominantly COOH and OH groups on the surfaces of CD-COOH and CD-OH, respectively (Fig. 1). It is worth to note that in the IR-absorption spectrum of CD-COOH a peak is found near 1375 cm^{-1}, that corresponds to the absorbance of carboxylic acid anhydrides [22]. The obtained IR-absorption spectra indicate the successful functionalization of CD surface groups.

The absorption spectroscopy

To study the effect of hydrogen factor on optical properties of CD with different functionalizations of their surfaces, CD water suspensions were prepared with different pH values and the optical absorbance spectra were recorded. Figure 2 shows optical absorbance spectra of CD with different functionalization of surface in a neutral medium.

As can be seen from the presented data, the absorbance spectra of CD water suspensions have some features. All the optical absorbance spectra of the water suspensions in question demonstrate an intensive absorption in the shortwave range, which right bandwidth part is extended up to ~ 250–300 nm. According to literature, the absorbance of CD in this spectral range is caused by $\pi-\pi^*$-transitions in aromatic sp^2-carbons [23]. In the absorbance spectra of CD with polyfunctional and carboxylic surfaces an absorption bandwidth is observed near 275 nm, which corresponds to $n-\pi^*$ transitions of C=O bonds and $\pi-\pi^*$ transitions of C=C bonds [24], as well as a bandwidth near 340 nm, which corresponds to $n-\pi^*$ transitions of –C=O, C–N or –C–OH bonds in sp^3-hybridized domains associated with carboxylic (–COOH) or amine (–NH$_2$) groups on the surface of CD [25]. There are no these absorption bandwidths in optical absorbance spectra of CD-OH.

To analyze the behavior of absorbance spectra of CD with change in hydrogen factor of the water, their second derivatives were calculated as shown in Fig. 3. The derivatives of optical density spectra of CD water suspensions were used to identify their features and differences between spectra at varied values of pH, in order to separate potentially overlapping bandwidths in the spectral analysis and to reduce the contribution of scattering.

As can be seen from the presented data, a change in hydrogen factor of the suspension results in various qualitative changes in optical absorbance spectra of CD specimens. Thus, considerable changes in the graphs of second derivative of optical density in the short-wave part of spectrum, near 200–250 nm, are observed for CD-poly at pH > 9. Graphs of second derivatives of absorbance spectra for CD-OH remain almost unchanged at low pH, however they start changing at pH greater than ~ 4.5. For CD-COOH changes in the graphs of second derivative of absorbance spectrum in ranges of pH < 3 and > 8.3 are observed. It is important to note that with an increase in hydrogen factor of suspension for all the CD under

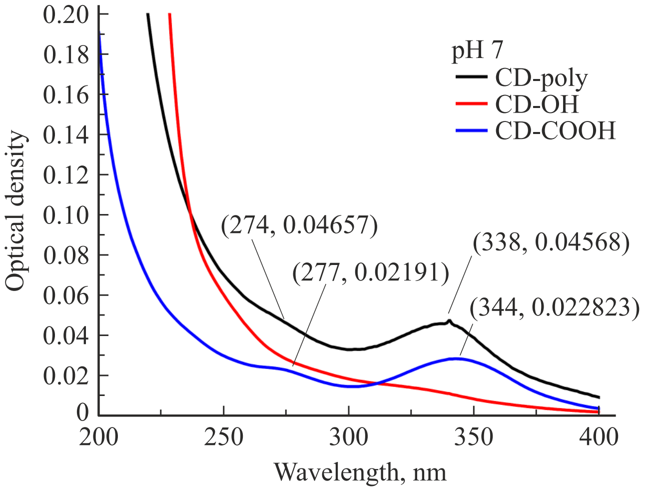

Figure 2. Optical absorbance spectra of water suspensions of CD under study in a neutral medium.

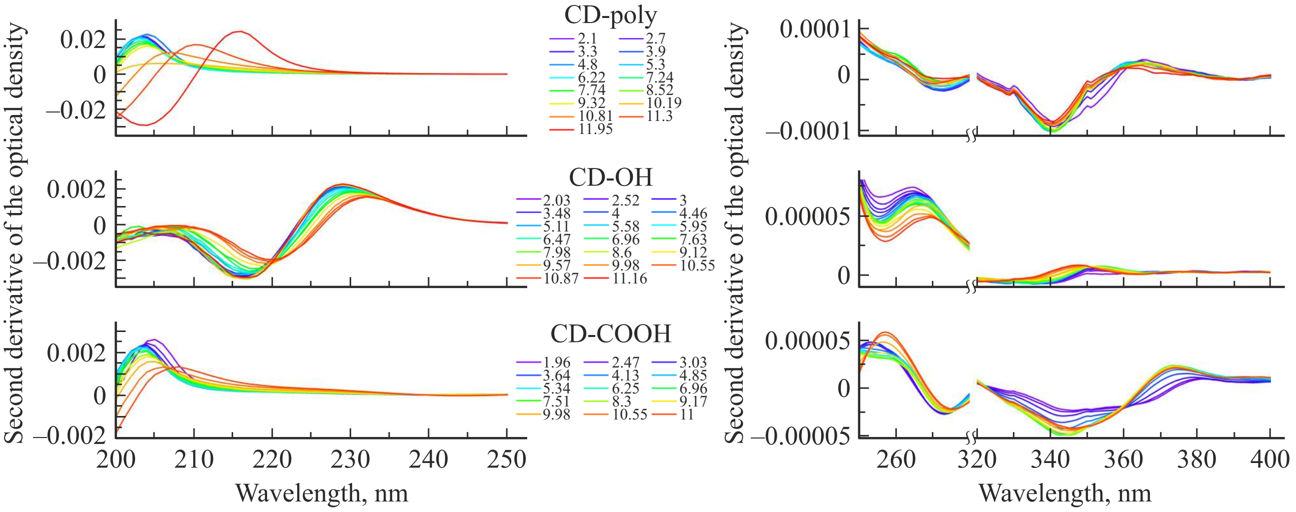

Figure 3. Graphs of second derivatives of absorbance spectra of CD water suspensions with investigated functionalizations of surfaces at different values of pH.

study a shift of peak was observed on the graphs of second derivatives of absorbance spectra towards longer wavelengths, which corresponds to decrease in the distance between electron levels of $\pi-\pi^*$ transitions in aromatic sp^2-carbons.

Changes in the graphs of second derivatives of absorbance spectra of CD water suspensions with different functionalizations of surfaces at varying values of pH were observed in the range of 250−400 nm as well. In the range of 250−320 nm, a sharp change in the graphs of second derivatives of absorbance spectra was found for water suspensions of CD-COOH at $\text{pH} < 3$ and > 9 with a clearly expressed shift of graph peak towards longer wavelengths with an increase in hydrogen factor of the suspension. In the range of 320−400 nm, a change in the graphs of second derivatives of water suspension absorbance spectra was found for all CD under study, but in different ranges of pH: for CD-poly — at $\text{pH} < 3$ and > 11, for CD-OH — at $\text{pH} > 8.6$, for CD-COOH — at $\text{pH} < 4.8$ and > 9. All these changes were characterized by a peak shift towards shorter wavelengths, which is an evidence of increase in the energy distance between the levels corresponding to $n-\pi^*$ transitions of −C=O, C−N or −C−OH bonds. The obtained results suggest a conclusion that the effect of pH on absorbance spectra has a holistic character: not only one bandwidth is changing, but a number of changes are taking place. It was found that the changes in characteristics of the graphs of second derivatives of CD water suspension absorbance spectra correspond to acidic ($<\sim 5$) and alkalinous ($>\sim 8$) pH, which confirms the hypothesis that the observed changes can be caused by protonation/deprotonation of different functional groups on the CD surface, in particular hydroxylic groups, amine groups and carboxylic groups. The observed shifts of bandwidths are an evidence of change in the structure of electron levels in the CD, which, in turn, provides the basis to assume that changes in PL spectra of CD are located in similar ranges of hydrogen factor variation.

To perform the comparative analysis of dependencies of absorbance and PL spectra of CD in water on values of pH, all the changes in graphs of second derivatives of CD water suspension absorbance spectra with pH variation are summarized in the table.

PL-spectroscopy

Figure 4 shows matrices of PL excitation and emission of water suspensions for three types of CD at a neutral pH value of 7 for the CD suspensions ($a-c$) and PL excitation and emission of CD in water, corresponding to the most intensive PL of each specimen ($d-f$). Preliminary experiments have shown that with the CD concentrations we used the inner filter effect is not manifested, therefore no any additional correction was performed for the recorded spectra.

It follows from the presented data that PL emission spectra of CD in water are wide structureless bandwidths with maxima at wavelengths of 445 nm for CD-poly, 405 nm for CD-OH and 432 nm for CD-COOH. Taking into account corrections for CD concentrations in water suspensions, the most intensive photoluminescence is demonstrated by polyfunctional CD, while the intensity of photoluminescence of CD-COOH is almost two times lower. The lowest PL is demonstrated by CD-OH: its intensity is almost 25 times lower than the intensity of the initial CD-poly. At the same time, half-height widths of PL emission spectra of CD-poly and CD-COOH coincide with each other, and the same width for CD-OH is about one-third greater, which indicates inhomogeneity of CD-OH fluorophores. Thus, from the analysis of obtained PL spectra of CD water suspensions at a neutral pH value of 7 a conclusion can be made that PL spectral characteristics of CD in water are significantly dependent on the surface functionalization.

Changes in absorbance and PL spectra of CD water suspensions with different functionalization of surface at different pH values of the suspension

	Spectrum type	Range of wavelengths/ peak location, nm	Spectrum change*	Range of pH
CD-poly	Absorbance	200–225	→ (12 nm)	> 9
	Absorbance	344–358	↑	< 3
CD-OH	Absorbance	210–225	→ (5 nm)	> 4.5
	Absorbance	220–240	→ (3 nm)	> 4.5
	Absorbance	330–370	← (9 nm)	> 8.6
CD-COOH	Absorbance	200–210	← (2 nm)	< 3
	Absorbance	200–210	→ (5 nm)	> 8.3
	Absorbance	250–320	→ (7 nm)	< 3
	Absorbance	250–320	← (4 nm)	> 9
	Absorbance	320–370	↓	< 4.8
	Absorbance	320–370	↑	9
	Absorbance	360–390	← (7 nm)	< 4
CD-poly	PL	382	↑	> 9
	PL	434	↑	< 5
CD-OH	PL	390	↑	> 8
CD-COOH	PL	380	↑	> 9
	PL	425	↑	< 4.8
	PL	425	↓	> 8

Note. * → — shift of the peak maximum to the red area, ↑ — increase in peak intensity, ← — shift of the peak maximum to the blue area, ↓ — decrease in peak intensity. Value in brackets is the shift of spectrum.

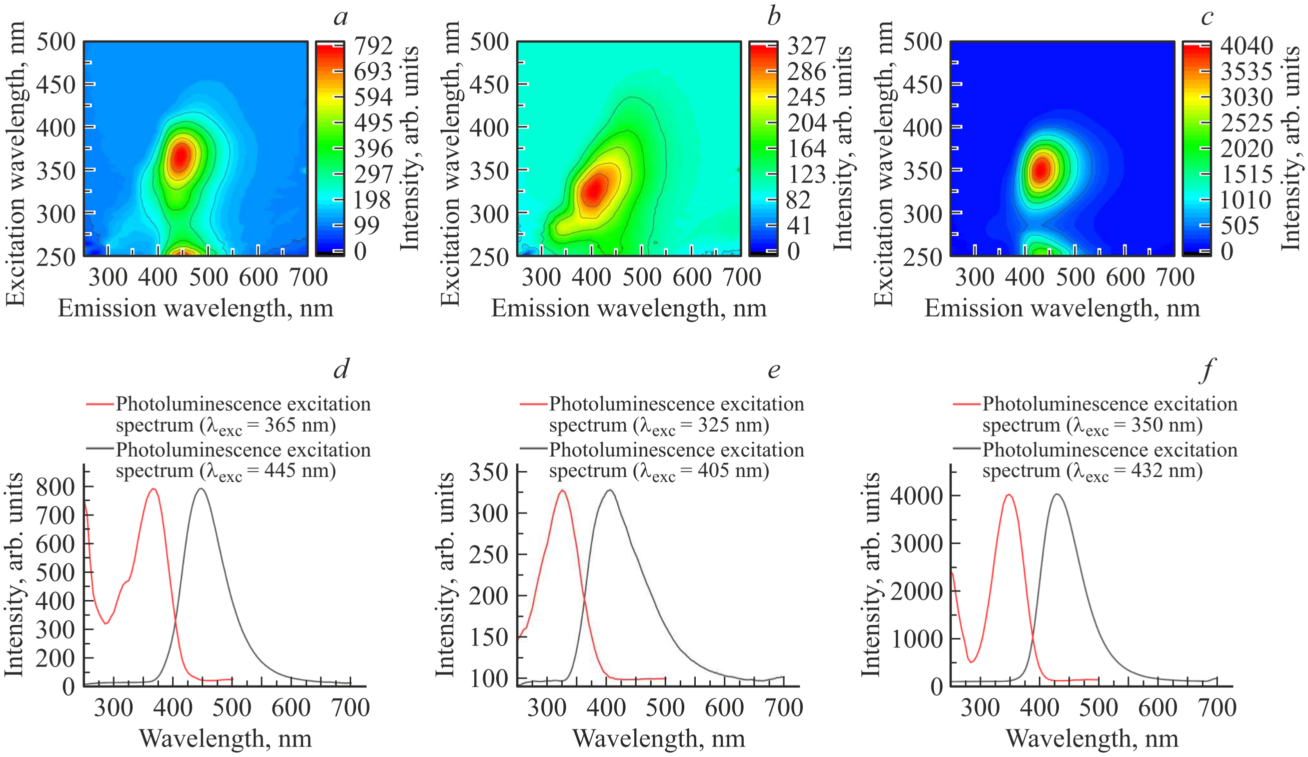

Figure 4. Matrices of excitation/emission of PL of water suspensions for three types of CD at pH 7: (*a*) CD-poly, (*b*) CD-OH, (*c*) CD-COOH. PL excitation and emission spectra (*d*) CD-poly, (*e*) CD-OH, (*f*) CD-COOH.

As mentioned above, to study the effect of hydrogen factor of water on PL properties of CD with different surface functionalization, pH of the suspension varied in the prepared water suspensions in the range from 2 to 12. It follows from the obtained PL excitation and emission matrices of CD suspensions (Fig. 4) that the highest PL

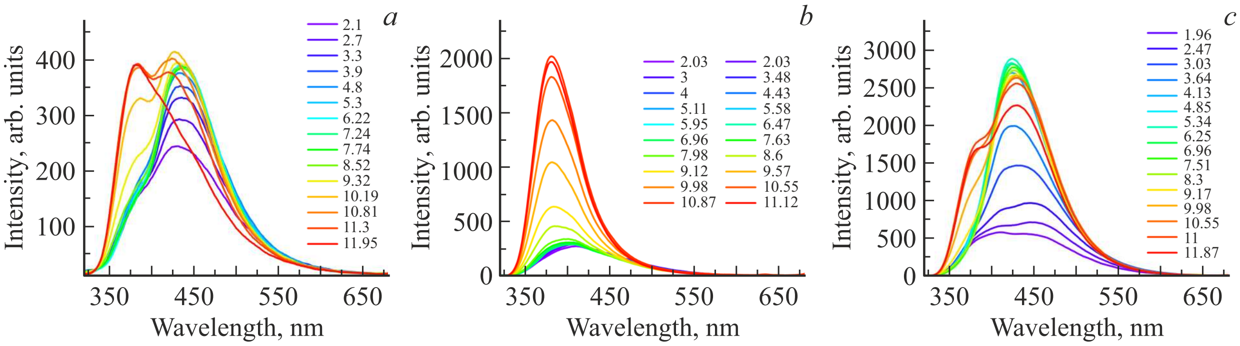

Figure 5. PL spectra of water suspensions of CD with different functionalizations of surfaces at pH variation: PL of (*a*) CD-poly, (*b*) CD-OH, (*c*) CD-COOH when excited at 320 nm.

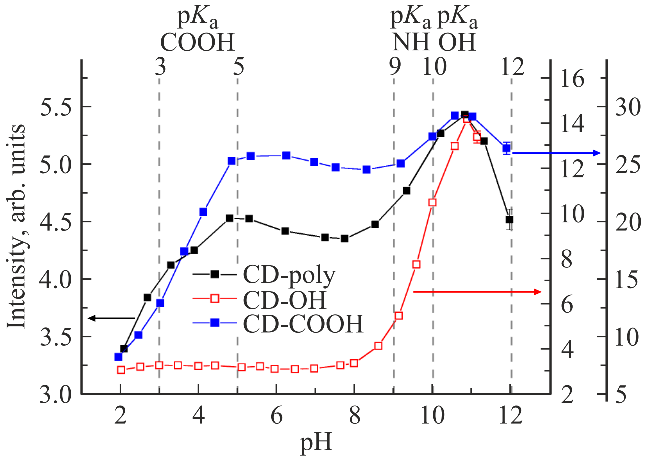

Figure 6. Dependencies of integral PL intensities of water suspensions of CD with different functionalizations of surfaces on pH. Vertical lines show pK_a ranges of carboxylic, amine and hydroxylic groups [19]. The excitation wavelength is 320 nm.

intensity of CD-OH is observed in case of excitation by radiation with a wavelength of 320 nm. Since Since CD-OH has the lowest PL properties CD-OH has the lowest PL properties as compared to other CD under study, for the better contrast of the changing of CD PL intensity as a function of pH, an excitation wavelength of 320 nm was selected for all CD for subsequent analysis of these dependencies. Figure 5 shows PL spectra of water suspensions of all CD types with pH variation in the range from 2 to 12.

As a result of analysis of the obtained PL spectra of water suspensions for all CD types with pH variation in the range from 2 to 12 a significant effect of suspension pH on PL of CD was found, and and this effect differs for various CD (Fig. 5). Changes of PL spectra and corresponding ranges of pH variation are shown in the table.

The dependencies of the integral PL intensity of CD water suspensions with different surface functional groups on the hydrogen factor of water were calculated and plotted. These dependencies are shown in Fig. 6.

It can be seen from the presented data (Fig. 6) that the dependencies of integral PL intensity of water suspensions of CD-poly and CD-COOH on pH have similar behavior: a monotone increase in the PL is observed with pH variation from 2 to 5 (for CD-COOH specimen this increase is approximately 2.5 times higher than for CD-poly). This increase is followed by a section of pH from 5 to ~ 8.5, where PL intensity decrease insignificantly. With further increase in pH from 8.5 to 11 a growth of PL intensity is observed, and in the pH range from 11 to 12 the PL intensity of both types of CD decreases. The dependence of integral PL intensity of CD-OH water suspensions on pH is fundamentally different: in the pH range from 2 to 8 the PL intensity remains nearly constant, however with further pH increase up to 11 a sharp increase in the PL intensity occurs (about 4 times as compared with the PL at pH equal to 2).

As can be seen from the table and Fig. 6, optical characteristics (absorbance and PL) of CD water suspensions with variation of the hydrogen factor of water are significantly dependent on functionalization of the CD surface. The most intensive changes in the spectral characteristics of CD-OH are observed in the range of $\text{pH} > 8$, and in the spectral characteristics of CD-poly, CD-COOH they are observed in the ranges of $\text{pH} < 5$ and > 8. These pH values fall into the ranges of pK_a of carboxylic, amide and hydroxylic functional groups (Fig. 6), which indicates the processes of deprotonation of carboxylic groups COOH taking place in the suspensions at $\text{pH} > 5$, deprotonation of hydroxylic groups OH and amine groups at $\text{pH} > 8$, that present in small quantities on the surfaces of CD-poly and CD-COOH [19]. As it was found from the IR spectroscopy of the specimen, there are numerous different functional groups on the surface of CD-poly, therefore in the optical spectra of CD-poly water suspensions significant changes are observed in both acidic range ($\text{pH} < 5$) and alkalinous range ($\text{pH} > 8$) of pH.

It follows from the obtained data that in case of deprotonation of COOH, OH and NH_2 surface groups a sharp increase in PL intensity of CD water suspensions is observed as compared with the case when these CD surface groups are protonated. A similar behavior — an increase in PL intensity under deprotonation of molecular groups — was detected in the case of fluoresceine dye-molecule [26,27]. According to the authors of [28], this phenomenon may be a consequence of the fact that the energy of triplet excitation (T_3) of the deprotonated form is located slightly below the energy of its singlet state (S_1), which makes the speed on interlevel transition from S_2 to T_3 higher in the protonated form than in the deprotonated form. Also, it should be noted that results obtained in this study for the effect of pH on the PL of several types of CD in water are fully compatible with results of similar studies for water suspensions of detonation-synthesized nanodiamonds having large amount of sp^2-hybridized carbon on their surfaces [29]. In the above-mentioned study confirmed by quantum-chemical methods the hypothesis that the obtained dependence of PL of the sp^2-hybridized carbon on the environment pH is caused by protonation/deprotonation processes.

Conclusion

In this study we focused on the CD synthesized by the hydrothermal method, with polyfunctional and monofunctional (carboxylated and hydroxylated) surfaces.

The comparative analysis of absorbance spectra and PL of water suspensions of three types of nanoparticles — CD with polyfunctional surface, with carboxylic and hydroxylic groups — has shown that optical properties of CD in a neutral environment (pH 7) are significantly dependent on functionalization of nanoparticle surface.

The study of the dependence of PL on the environment pH for water suspensions of CD with different functional groups on their surfaces revealed a significant effect of nanoparticle environment acidity on their optical properties. It is found that the biggest changes in spectral characteristics of all types of CD are manifested in the same ranges of pH variation: 2–5 and 8–12. The obtained results are explained by the processes of protonation/deprotonation of CD surface groups (COOH, OH and NH_2), which is a confirmation of the corresponding hypothesis suggested by a number of authors.

Acknowledgments

This study was supported financially by the Theoretical Physics and Mathematics Advancement Foundation „BASIS“ (project № 21-2-1-53-1), with support by the Interdisciplinary Scientific and Educational School of Moscow University „Photonic and Quantum Technologies. Digital Medicine“.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] W. Su et al. Materials Chemistry Frontiers, **4** (3), 821 (2020). DOI: 10.1039/c9qm00658c

[2] N. Azam, M. Najabat Ali, T. Javaid Khan. Frontiers in Materials, **8**, 700403 (2021). DOI: 10.3389/fmats.2021.700403

[3] O.E. Sarmanova et al. Nanomedicine: Nanotechnology, Biology and Medicine, **14** (4), 1371 (2018). DOI: 10.1016/j.na2018.03.009

[4] S.Sh. Rekhviashvili, D.S. Gayev, Ch. Margushev. Opt. i spektr., **129** (12), 1589 (2021) (in Russian). DOI: 10.21883/os.2021.12.51747.2560-21

[5] M.J. Molaei. RSC Advances, **9** (12), 6460 (2019). DOI: 10.1039/c8ra08088g

[6] K.A. Laptinskiy, S.A. Burikov, S.V. Patsaeva, I.I. Vlasov, O.A. Shenderova, T.A. Dolenko. Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy, **229**, 117879 (2020). DOI: 10.1016/j.saa.2019.117879

[7] T. Dolenko, S. Burikov, K. Laptinskiy, J. M. Rosenholm, O. Shenderova, I. Vlasov. Phys. Stat. Sol. (a), **212** (11), 2512 (2015). DOI: 10.1002/pssa.201532203

[8] K.A. Laptinskiy, S.A. Burikov, G.N. Chugreeva, O.E. Sarmanova, A.E. Tomskaya, T.A. Dolenko. Fullerenes, Nanotubes and Carbon Nanostructures, **29** (1), 67 (2020). DOI: 10.1080/1536383x.2020.1811236

[9] M. Huang et al. Nanomaterials, **10** (4), 604 (2020). DOI: 10.3390/nano10040604

[10] Y. Chen, X. Sun, W. Pan, G. Yu, J. Wang. Frontiers in Chemistry, **7**, 911 (2020). DOI: 10.3389/fchem.2019.00911

[11] C. Liu, F. Zhang, J. Hu, W. Gao, M. Zhang. Frontiers in Chem., **8**, 605028 (2021). DOI: 10.3389/fchem.2020.605028

[12] A. Pyne, S. Layek, A. Patra, N. Sarkar. J. Materials Chem. C, **7** (21), 6414 (2019). DOI: 10.1039/c9tc01629e

[13] W. Lv, X. Wang, J. Wu, H. Li, F. Li. Chinese Chem. Lett., **30** (9), 1635 (2019). DOI: 10.1016/j.cclet.2019.06.029

[14] S. Dutta Choudhury, J.M. Chethodil, P.M. Gharat, Praseetha P. K., H. Pal. J. Phys. Chem. Lett., **8** (7), 1389 (2017). DOI: 10.1021/acs.jpclett.7b00153

[15] J. Ren et al. Nanoscale, **11** (4), 2056 (2019). DOI: 10.1039/c8nr08595a

[16] O.E. Sarmanova et al. Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy, **258**, 119861 (2021). DOI: 10.1016/j.saa.2021.119861

[17] P.-J. Lu, World J. Gastroenterology, **16** (43), 5496 (2010). DOI: 10.3748/wjg.v16.i43.5496

[18] T. Takeshima, M. Adler, M. Nacchiero, J. Rudick, D.A. Dreiling. Am. J. Gastroenterol., **67** (1), 54 (1977).

[19] Bordwell pKa Table https://organicchemistrydata.org/hansreich/resources/pka/#pka_general [Accessed 10.10.2021].

[20] F. Menges. „Spectragryph — optical spectroscopy software“, Version 1.2.15, 2020, http://www.effemm2.de/spectragryph/

[21] I.Yu. Denisyuk, K.Yu. Logushkova, M.I. Fokina, M.V. Uspenskaya. Opt. i spektr., **126** (2), 177 (2019) (in Russian). DOI: 10.21883/os.2019.02.47200.300-18

[22] T. Petit, L. Puskar. Diamond and Related Materials, **89**, 52 (2018). DOI: 10.1016/j.diamond.2018.08.005

[23] K.J. Mintz et al. Colloids and Surfaces B: Biointerfaces, **176**, 488 (2019). DOI: 10.1016/j.colsurfb.2019.01.031

[24] B. De, N. Karak. RSC Advances, **3** (22), 8286 (2013). DOI: 10.1039/c3ra00088e

[25] A.N. Emam, S.A. Loutfy, A.A. Mostafa, H. Awad, M.B. Mohamed. RSC Advances, **7** (38), 23502 (2017). DOI: 10.1039/c7ra01423f

[26] E.A. Slyusareva, M.A. Gerasimov, A.G. Sizykh, L.M. Gornostaev. Russian Phys. J., **54** (4), 485 (2011). DOI: 10.1007/s11182-011-9643-y

[27] P. Zhou, Z. Tang, P. Li, J. Liu. J. Phys. Chem. Lett., **12** (28), 6478 (2021). DOI: 10.1021/acs.jpclett.1c01774

[28] S.A.K. Elroby, R.M. El-Shishtawy, M.S.I. Makki. Molecular Simulation, **37** (11), 940 (2011). DOI: 10.1080/08927022.2011.578137

[29] A.M. Vervald et al. J. Phys. Chem. C, **125** (33), 18247 (2021). DOI: 10.1021/acs.jpcc.1c03331