Investigation of the properties of carbon quantum dots synthesized by the hydrothermal method

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Abstract. Carbon quantum dots have a number of advantages and can be widely used as a material for photodetectors, chemical element detectors, biosensors, and for various optoelectronic applications. The optimal conditions for the hydrothermal synthesis of carbon quantum dots from glucose are considered. Carbon quantum dots, having an amorphous-crystalline structure with functional surface groups, were obtained. Luminescence spectra of these dots showed the presence of bright luminescence in the green region. The dependences of the luminescence spectra as a function of the excitation length were measured. Experiments on the functionalization of the carbon quantum dots with chromophores were carried out in order to study their effect on the luminescence intensity.

1. Introduction
In the recent years, quantum dots have gained increasing attention. They are of great interest in the field of bioimaging and biomedicine due to their high quantum yield and unique optical properties. However, their wider use is limited due to some of their drawbacks such as high toxicity, low biocompatibility, high cost, and low chemical inertness. Moreover, they show poor solubility in aqueous solutions [1]. Considering this, carbon-based quantum dots look increasingly advantageous. Carbon quantum dots (CQDs) belong a class of zero-dimensional carbon nanomaterials that contain sp² carbon structures and functional groups. They are superior to the conventional semiconductor quantum dots in terms of low toxicity, high biocompatibility, good chemical inertness and solubility. [2,3] Can also work as effective drug carriers due to their small size and biocompatibility [4, 5]. In addition, their excellent photo- and electro-catalytic characteristics also allow their use in the field of energy saving and environmental protection [6, 7].

CQDs exhibit unique photoluminescent properties that depend on several factors – first, on the particle size and the uniformity of the particle size distribution, second, on the surface passivating compounds which affect not only spectra of luminescence, but also its intensity, and third, on the functionalization of the surface with organic molecules, which can be used to control luminescence spectra. The possibility of controlling the photoluminescence of CQDs (spectra and intensity of luminescence, quantum yield, band gap, and the other parameters) with simple changes in the synthesis conditions makes them a promising material in various areas [8].

The aim of this work was to synthesize CQDs by the hydrothermal method and to study the effect of chromophore functionalization on their luminescence properties.
2. Experimental

For CQD synthesis, 1 g of glucose (C₆H₁₂O₆, “Ruskhim”, Russia) was dissolved in 15 mL of deionized water. 6 ml of an aqueous solution of ammonia (NH₃, 25.6%, “Vostokreaktiv”, Russia) were added and mixed. The solution was transferred to a polytetrafluoroethylene autoclave (“TOPTION Laboratory Store”, China). The autoclave was placed into a universal drying oven (ShSP-0.25-60-C, Russia) for 10 min, 30 min, 1 h, 4 h, 8 h, 10 h, and 18.5 h at a temperature of 180 °C. The resulting brown suspension was filtered through a 100-nm track membrane, then dialyzed in a dialysis bag (“Aksioma-Bio”, Russia) with a pore size of 3.5 kDa for 12 h. For further characterization, a solution from the dialysis bag was used. CQD particles were size-separated by electrophoresis. The electrophoresis equipment was self-made from a 10 mL syringe body (vertical positioning of a syringe), with gold contacts. The CQD suspension from a dialysis bag was poured into the syringe body and a constant voltage of 30 V from a voltage source was applied (APS-7151, “AKTAKOM”, Russia) for 20 min. During this time, the solution was separated by size and charge: in the lower part of the syringe (positive contact), the dark part of the suspension (larger particles) was collected, whereas in the upper part (negative contact), the lighter part (smaller particles) was remained.

Chromophore is a covalently saturated group causing electron absorption (for instance, C=C, C=O and NO₂). For synthesizing them, 1 g of glucose was dissolved in 10 mL of deionized water and subjected to pyrolysis on a hot plate until evaporation and browning. The resulting black precipitate was dispersed with deionized water. Then, the solution was filtered through a 100-nm track membrane and dialyzed (3.5 kDa) for 12 h. This solution contained glucose chromophores. Similarly, chromophores of citric acid were obtained.

For functionalization of the CQD with chromophores, 3 mL of the chromophores from the glucose or citric acid were added to 7 mL of the CQD solution. As a result, two CQD mixtures with chromophores were obtained. Then, the mixtures were transferred to the polytetrafluoroethylene autoclave and heated for 1 h in a drying oven at 90 °C.

The luminescent properties were determined using a Perkin Elmer LS 50B spectrometer (USA). The absorption properties were measured using a UNICO UV-VIS 2804 spectrophotometer (Russia). Structural studies were performed on a Varian 7000 FT-IR Fourier transform infrared (IR) spectrometer (USA).

3. Results and discussion

The resulting carbon dot solutions had brown color under room lighting, exhibited green luminescence upon excitation with a laser (λ = 420 nm) and had greenish blue glow under UV light (λ = 325 nm) (figure 1).

![Figure 1. The CQD solution from the glucose exposed to daylight (a), under the laser irradiation (λ = 420 nm) (b), and under UV light (λ = 325 nm) (c).](image-url)
Figures 2(a) and 2(b) show the photoluminescence spectra of the CQD aqueous suspensions from the glucose after 4 and 8 h of hydrothermal treatment at different excitation wavelengths (300, 350, and 400 nm), whereas figure 2(c) demonstrates the IR spectra of the glucose+ammonia solution at different duration of hydrothermal treatment. From the luminescence spectra, it can be observed that the positions of the maxima of the photoluminescence peaks is shifted from 400 to 473 nm, when the excitation wavelength changes from 300 to 400 nm. The position of the fluorescence emission peak depends on the excitation wavelength. This is due to the inhomogeneous size distribution of the CQDs, chemical composition of the surface, presence of various emission traps, or characteristics of the fluorescence mechanism which is currently not explained [9].

![Luminescence spectra of the CQD solutions from the glucose after hydrothermal treatment for: 4 h (a) and 8 h (b) at different excitation wavelengths. IR spectra of the glucose+ammonia mixture after hydrothermal treatment for: 10 m (1), 18.5 h (2), 4 h (3), and 1 h (4) (c).](image)

The IR spectra show that most of the obtained CQDs consists of both sp²-carbon structures and oxygen-containing functional groups, including carboxyl, carbonyl, hydroxyl and epoxy groups.

During the hydrothermal treatment, the glucose is dehydrated to form a C=C bond, which is the elementary unit of the obtained CQDs. The absorption peak at 1641 cm⁻¹ is related to the C=C stretching, a broad peak at 3392 cm⁻¹ is assigned to the O-H groups, the absorption at 1027, 2927 and 1380 cm⁻¹ refers to the C-OH and C-H stretching vibrations and the N-H bond, respectively (figure 2(c)). In addition to the C-OH, COC, and C-H vibrations, the C=O stretching vibrations (~1610 cm⁻¹) were also detected, in combination with asymmetric and symmetric stretching vibrations of C-O-C.
(-1300 and ~1200 cm\(^{-1}\)) in the carboxyl group. This may be due to the oxidation of the C–OH bonds by residual or decomposed oxygen atoms under hydrothermal conditions [10,11].

The IR spectra of the CQD solution from the glucose after 10 min of hydrothermal treatment indicates the presence of wide absorption bands in the areas of 2450-3100 and 3200-3600 cm\(^{-1}\) related to the vibrations of the bonds of aliphatic C-H and O-H groups, respectively. A sharp and intense peak with a center in the region of 1100 cm\(^{-1}\)corresponds to the C-OH vibrations [12]. The detected functional groups located on the CQD surface act as a passivating layer that facilitates the solubility of the CQDs in water, and improve their photoluminescence properties [13].

The presence of a large number of residual hydroxyl groups increases the hydrophilicity and stability of the CQDs in polar solvents [9,12]. These hydrophilic groups not only provide luminescence, but also contribute to the safety of the product, allowing them to be used in biochemical studies. As the synthesis time increases, the intensity of the absorption bands decreases, which can be explained by the decrease in the number of functional groups on the CQD surface as a result of intramolecular changes in the composition of the functional groups during the hydrothermal processing.

Investigation of UV-VIS spectra showed (figure 3a) that both glucose and the glucose+ammonia mixture have no absorption above 350 nm without hydrothermal treatment. However, after the hydrothermal treatment, significant absorption appears in the wavelength region above 300 nm (figure 3(b)), which is consistent with the presence of visible luminescence. The positions of the absorption maxima shift in different ways with the time of the hydrothermal treatment. The reason for this may be a change in the composition of the surface functional groups during the hydrothermal treatment.

![Figure 3](image-url)  
**Figure 3.** UV-VIS absorption spectra of the initial solutions of the glucose (1) and the glucose+ammonia mixture (2) (a), and the CQD solutions from the glucose obtained after hydrothermal treatment at different duration (b).

For the separation of particles by size, the method of electrophoresis was used. Further, to adjust the luminescence spectra of the CQDs, the chromophores from the glucose or the citric acid were added to the solution obtained after the electrophoresis. After the hydrothermal treatment, the samples were characterized.

Figure 4 shows the luminescence spectra of the CQDs from the glucose after the electrophoresis and chromophore functionalization. After analyzing the luminescence spectra, it was found that the chromophores shift the spectra to the long-wavelength region and increase the luminescence intensity of the CQD solution. The shift in the position of the maxima of the luminescence peaks may be due to the different composition of the chromophore functional groups (figure 5).
Figure 4. Photoluminescence spectra recorded for: the CQD suspension from glucose (λ = 350 nm): after electrophoresis (a); the CQD solutions after the introduction of the chromophores from the citric acid (1) and the glucose (2) before autoclaving (b); the CQD solutions with the chromophores from the citric acid (1) and the glucose (2) after autoclaving (c); and normalized spectra of the CQD solutions with the chromophores from the citric acid (1) and the glucose (2) (d).

Figure 5(a) shows the IR spectra of the chromophores from the citric acid and the glucose and the CQD solutions from the glucose after the functionalization by the chromophores and heating in an autoclave. It can be seen that after the hydrothermal treatment, the intensity of the OH and C–O–C functional groups decreases. Besides, from the spectra, it can be concluded that the composition of the functional groups for the CQDs from the citric acid (figure 5(a) - (1)) and the glucose (figure 5(a) - (2)) is different.
Figure 5. IR spectra of the chromophores from citric acid (1) and from glucose (2), the CQD solutions functionalized with the chromophores from the glucose (3) and the citric acid (4) (a); and UV-VIS spectra of the CQD solutions from the glucose after functionalization with the chromophores from the citric acid (1) and the glucose (2) (b).

Figure 5(b) presents the UV-VIS spectra of the CQD solutions from the glucose after additional functionalization with the chromophores from the citric acid and the glucose. It can be concluded that the functionalization with different chromophores can be used to control the luminescence spectra of the CQDs. Absorption peaks can be observed in the regions of 215 and 268 nm. For the samples with the citric acid chromophores, an absorption peak is observed in the region of 230 nm, and a weak absorption shoulder at 270 nm caused by the π – π* and n – π* transitions associated with the C=C and carbonyl/hydroxyl groups [14].

Figure 6. SEM image (a) and Raman spectra (b) of the CQDs from the glucose.

Figure 6 shows the SEM image of the CQDs from the glucose and its Raman spectra. The average size of the CQDs was found to be 23 nm.
4. Conclusion
Hydrothermal methods were used to synthesize CQDs, which have bright luminescence in the green spectral region. It was shown that the luminescence spectra are shifted to the long-wavelength region, depending on the excitation wavelength. It was suggested that this phenomenon is caused by energy states associated with surface defects of the CQDs. It was found that the functionalization of CQDs with chromophores changes the luminescence spectra and their intensity. The presence of the chromophores on the CQD surface gives a bright, stable luminescence and provides good solubility and stability in water. Luminescent CQDs synthesized from glucose are environmentally friendly, biocompatible and have great prospects for applications in the field of biology and medicine.

Acknowledgments
The work was supported by the Russian Foundation for Basic Research, grant No.18-02-00449, and by the Ministry of Science and Higher Education of Russia, State Assignment No.FSRG-2017-0017.

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