Investigation of luminescence quantum yields of carbon dots synthesized from ethylene glycol, citric acid and berries

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Abstract
The paper describes the investigation of luminescence quantum yields of carbon dots (CDs) synthesized from different carbon precursors. In the synthesis, were used precursors such as ethylene glycol (EG), citric acid (CA) and juice of berries grown in the Far North. Synthesis was carried out by two methods of hydrothermal synthesis using microwave and a polytetrafluoroethylene autoclave. The photoluminescence quantum yields of these CDs were determined to be from 0.008 to 0.46. The obtained CDs can be used to develop detectors for chemical elements and various optoelectronic applications, as well as in biomedicine and bioimage production.

Introduction
Synthesis of organic luminophores with a high quantum yield in the visible region, low-toxic, sensitive to heavy metals ions is an urgent task of applications in biomedicine and ecology. One of the most promising materials used as luminophores are carbon dots.

Carbon dots (CDs) are biocompatible and easily functionalized nanoparticles attracting considerable interest of researchers around the world as replacement of semiconductor quantum dots. This interest is related to their nanoscale, low toxicity and unique physical and chemical properties. CDs can potentially be used in such areas as bioimaging, photocatalysis, optoelectronic devices, delivery of drugs and genes, chemical sensors and biosensors. [1-3]

Carbon dots can be synthesized from a variety of environmentally friendly and inexpensive materials without the use of expensive equipment in various ways. The possibility of adjusting the photoluminescence (PL) of CDs with simple changes in the conditions of synthesis makes them promising materials in various applications, depending on the necessary photoluminescence conditions (radiation wavelength, radiation intensity, quantum yield, width of the forbidden band, etc.).

Experimental
Synthesis of carbon dots from ethylene glycol (EG-CDs) and citric acid (CA-CDs)
The synthesis of EG-CDs and CA-CDs was carried out by means of microwave synthesis. Microwave heating provides simultaneous, homogeneous and rapid heating, which leads to a uniform distribution of quantum dots dimension. [4] The technology of obtaining CDs used by us generally corresponds to that of described in [5], except that the microwave heating method is applied instead of heating on a tile.

A solution of citric acid (CA solution) was prepared by mixing 2 g of CA, 0.5 mL of a solution of PANI-graphene, 2 ml of 26% aqueous ammonia solution and 15 ml deionized (DI) water. A solution of ethylene glycol (EG solution) was prepared by mixing 10 ml of EG with 2 ml of aqueous ammonia and 2 ml of DI water. The solutions were then heated in a microwave oven for about 5 minutes at a power of 900 W. After the solutions changed color, 20 ml of DI water was added and suspensions of green CDs (G-CDs) and yellow CDs (Y-CDs) were obtained. To prepare brown CDs
(B-CDs) the CA solution was mixed with 2 ml of H$_3$PO$_4$, then heated in microwave oven for 5 minutes (CA solution + H$_3$PO$_4$). To prepare red CDs (R-CDs) EG solution was mixed with 4 ml of H$_3$PO$_4$, then heated as well as above for 5 minutes (EG solution + H$_3$PO$_4$). To prepare orange CDs (O-CDs) 10 ml of EG were mixed with 3 ml of H$_3$PO$_4$ and heated in microwave oven for 5 minutes (EG + H$_3$PO$_4$). The obtained solutions were purified by the addition of ethyl alcohol, by centrifugation and subsequent removal of the alcohol.

**Synthesis of CDs from Berry Juice**

CDs were synthesized from the juice of red bilberry, bog blueberry and red currant. Juices were made by pressing berries and subsequent centrifugation. 2 ml of the obtained juice of each berry was mixed with 6 ml of 26% aqueous ammonia solution and 15 ml of DI water. The solutions was transferred to a poly (tetrafluoroethylene) autoclave and heated for 1 hour at 180 °C. The resulting mixture was then purified with a dialysis bag (MWCO 3.5 kDa) for 12 hours for further characterization.

**Measurement of the quantum yield**

The simplest way to determine the PL quantum yield (QY) of is the comparison method, which involves the use of a sample with a known quantum yield as a reference. Rhodamine 6G with a quantum yield of ethanol of 96% was chosen as the reference. Thus, the PL quantum yield of the test substance can be determined as follows:

$$\phi = \phi_R \frac{I \cdot D_R \cdot n^2}{I_R \cdot D \cdot n^2_R}$$

where I is the integral luminescence intensity; D is the optical density at the excitation wavelength of the luminescence; n is the refractive index of the solvent (to take into account the effect of the solvent on the optical properties of the phosphor). The index R refers to the parameters of the reference sample (standard) [13].

**Results and discussion**

In several series of experiments with EG-CDs and CA-CDs, we obtained the PL spectra shown in Fig. 1.

For sample №1, the shift of luminescence spectra maxima from the change in the excitation wavelength (300, 350, 400, 450 nm) is observed. The shift of spectra maxima is from 487 nm to 534 nm. In sample №2, the dependence of the luminescence spectra maxima shift on the excitation wavelength is also observed. The maxima shift is from 425 nm to 498 nm. Sample №3 exhibits the same properties as the previous samples. The luminescence spectra maxima in this sample shift from 431 nm to 507 nm. The most interesting result is for sample №4 that is a mixture of CA solution + H$_3$PO$_4$. In this sample, the luminescence spectra maxima do not depend on the change in the excitation wavelength. This agrees with the data given in [5].
Fig. 1 (a, b, c, d) Normalized PL spectra of CDs: (a) №1 (CA+NH$_3$ + PANI-graphene+H$_2$O); (b) №2 (EG+H$_3$PO$_4$); (c) №3 (EG solution+H$_3$PO$_4$); (d) №4 (CA solution+H$_3$PO$_4$).

Figure 2 shows the absorption spectra of EG-CDs and CA-CDs. In sample №1, one peak at 206 nm is observed, which can be attributed to the p-p* transition of C = O [14] bonds. The shoulder at 336 nm refers to the n-π* -transition of C = O-bonds [15].

In sample №2, peaks at 195 nm and 220 nm are observed related to the π-π* C=C transition and the p-p* C=O transition, respectively. The shoulder in the region of 352 nm refers to the n-π* -transition of C=O-bonds [15].

Sample №3 has two shoulders about 211 and 310 nm, one peak at 270 nm in the absorption spectrum and extends to 600 nm without noticeable structures. According to [16, 17], the shoulder at 211 nm is attributed to the π-π* transition of C=C aromatic bonds, whereas the 320 nm shoulder refers to the π-π* -transition of C=O-bonds. The peak at 270 nm refers to the π-π* transition of C=C aromatic bonds, [15].

Sample №4 has a peak at 202 nm related to the n-p* transition C=O bonds [14] and one shoulder at 328 nm, referring to the n- π* -transition of C=O-bonds [15].
Fig. 2 Absorption spectra of CDs: 1 - №1 (CA+NH$_3$ + PANI-graphene+H$_2$O); 2 - №2 (EG+H$_3$PO$_4$); 3 - №3 (EG solution+H$_3$PO$_4$); 4 - №4 (CA solution+H$_3$PO$_4$).

Table 1 shows the results of measuring the PL QY of carbon dots. Rhodamine 6G was used as a standard. For the sample the CDs №1 (CA + NH$_3$ + PANI-graphene+H$_2$O) QY was 0.12, for the CDs №2 (EG + H$_3$PO$_4$) - 0.15, for the CDs №3 (EG solution + H$_3$PO$_4$) - 0.46, for CDs №4 (CA solution + H$_3$PO$_4$) - 0.10. As can be seen from the results, the largest quantum yield is observed for sample №3 (EG solution + H$_3$PO$_4$).

The photoluminescence QY of CDs from the red bilberry juice was 0.021, of bog blueberry - 0.017, of red currant - 0.008. Low OYs for CDs from berries may be due to the small number of functional groups on the surface of CDs under these conditions.

| Sample                       | Integrated emission intensity (I) | The optical density at the excitation wavelength 300 nm (D) | Refractive index of solvent (n) | Quantum yield (φ) |
|------------------------------|----------------------------------|-----------------------------------------------------------|---------------------------------|------------------|
| Rhodamine 6G (ethanol)       | 72.58                            | 0.104                                                     | 1.36                            | 0.96             |
| CDs №1                       | 11.25                            | 0.122                                                     | 1.33                            | 0.12             |
| CDs №2                       | 30.83                            | 0.272                                                     | 1.33                            | 0.15             |
| CDs №3                       | 113.5                            | 0.323                                                     | 1.33                            | 0.46             |
| CDs №4                       | 6.944                            | 0.094                                                     | 1.33                            | 0.10             |
| CDs from red bilberry        | 1.907                            | 0.118                                                     | 1.33                            | 0.021            |
| CDs from bog blueberry       | 2.031                            | 0.150                                                     | 1.33                            | 0.017            |
| CDs from red current         | 0.967                            | 0.150                                                     | 1.33                            | 0.008            |
Fig. 3 shows the PL spectra of CDs from berries when excited at different wavelengths. They look identical, which indicates a similar composition of functional groups on the CDs surface. As can be seen from the figure, all CDs samples have the property of the luminescence spectra maxima shift dependence on the excitation wavelength. For CDs from red bilberry, the luminescence spectra maxima shift was observed from 419-508 nm, for CDs from bog blueberry - from 407-511 nm, for CDs from red currant - from 396-503 nm.

Fig. 3 (a, b, c) PL spectra of CDs from: (a) red bilberries; (b) bog blueberries: (c) red currants.

Fig. 4 shows the absorption spectra of CDs from berries. The spectra look the same and have one peak at 269 nm. This absorption band was attributed to the $\pi-\pi^*$ transition of C = C aromatic bonds [15]. The results obtained are consistent with the results shown in Fig. 3, which speak of the functional groups composition similarity on the CDs surface.

Fig. 4 Absorption spectra of UV-VIS CDs from berries.

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