

Investigation of the Optical Properties of Aminated Carbon Dots Based on Citric Acid and Ethylenediamine

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The most important parameter determining the efficiency of carbon dots as light absorbers in photocatalytic systems is the strength of their binding to the catalyst. It is rather difficult to estimate the contribution of this parameter of carbon dots to the overall efficiency of the photocatalytic system, since the post-synthetic modification of the surface of carbon dots is accompanied by a significant change in their optical and structural properties. In this work, we performed post-synthetic modification of the surface of carbon dots based on citric acid by amination with ethylenediamine molecules by activating the carboxyl groups of carbon dots with 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide and N-hydroxysuccinimide molecules. The use of this amination approach made it possible to change the charge of carbon dots without changing their main optical and structural properties, which can be further used to assess the contribution of the strength of their binding with Dubois-type molecular catalysts to the overall efficiency of the photocatalytic system.

Keywords: Carbon Dots, Photoluminescence, Luminescence Decay Kinetics, Atomic Force Microscopy, Infrared Absorption Spectroscopy.

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Introduction

Carbon dots (CDs) represent a class of relatively new carbon nanomaterials with a rather complex and intricate internal structure [1–5]. As suggested, CDs consist of a carbonized core and many optical centers of the molecular type [4,6,7]. This structure of the CDs causes PL from various competing centers, which leads to a dependence of PL on the excitation wavelength. The distinctive PL properties of CDs find many applications in sensors and optoelectronic devices [8–11]. The high biocompatibility and low cytotoxicity of CDs makes them attractive for the creation of biolabels, drug delivery devices, and also for use in bioimaging [12–14].

The ease of creating CDs capable of absorbing solar radiation in a wide spectral range of visible light allows them to be used as light absorbers in photocatalytic systems. Meanwhile, it seems extremely important to modify the surface of CDs for their effective binding to the catalyst. In traditional syntheses of CDs, the formation of their surface functional groups is determined by the initial precursors and synthesis conditions. Post-synthetic modification of the functional groups of CDs, due to the surface location of optical centers [15–18], is usually accompanied by a change in their optical and structural properties, which significantly impedes their effective use, as well as the study of the contribution of the surface structure of CDs to the resulting properties of photocatalytic systems. The best water-soluble

molecular catalysts for hydrogen generation of the Dubois type typically have negatively charged phosphonic groups in a neutral aqueous medium, whereas CDs currently used in photocatalytic systems have negatively charged carboxylate groups [19,20]. CDs coating with positively charged groups without changing their structural and optical properties can be achieved through mild amination of their surface. This method will not only improve the binding of components in a photocatalytic hydrogen generation system, but also study the contribution of the surface groups of CDs to the overall functionality of the photocatalytic system.

In this paper, the optical properties of aminated CDs were obtained and studied. First, CDs with carboxyl groups on the surface were obtained by pyrolysis of citric acid. Next, amination of the CDs surface was carried out by creating ethylenediamine (EDA) monoamide with surface carboxyls. To do this, we first prepared succinimidyl esters of CDs carboxylic acids using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and N-hydroxysuccinimide (NHS), then combined with excess EDA without isolation. Analysis of the obtained experimental data showed that the use of this approach allows to gently aminate the surface of CDs and preserve their basic optical and structural properties, which can be extremely useful when applying the obtained CDs as light absorbers in photovoltaic and photocatalytic systems.

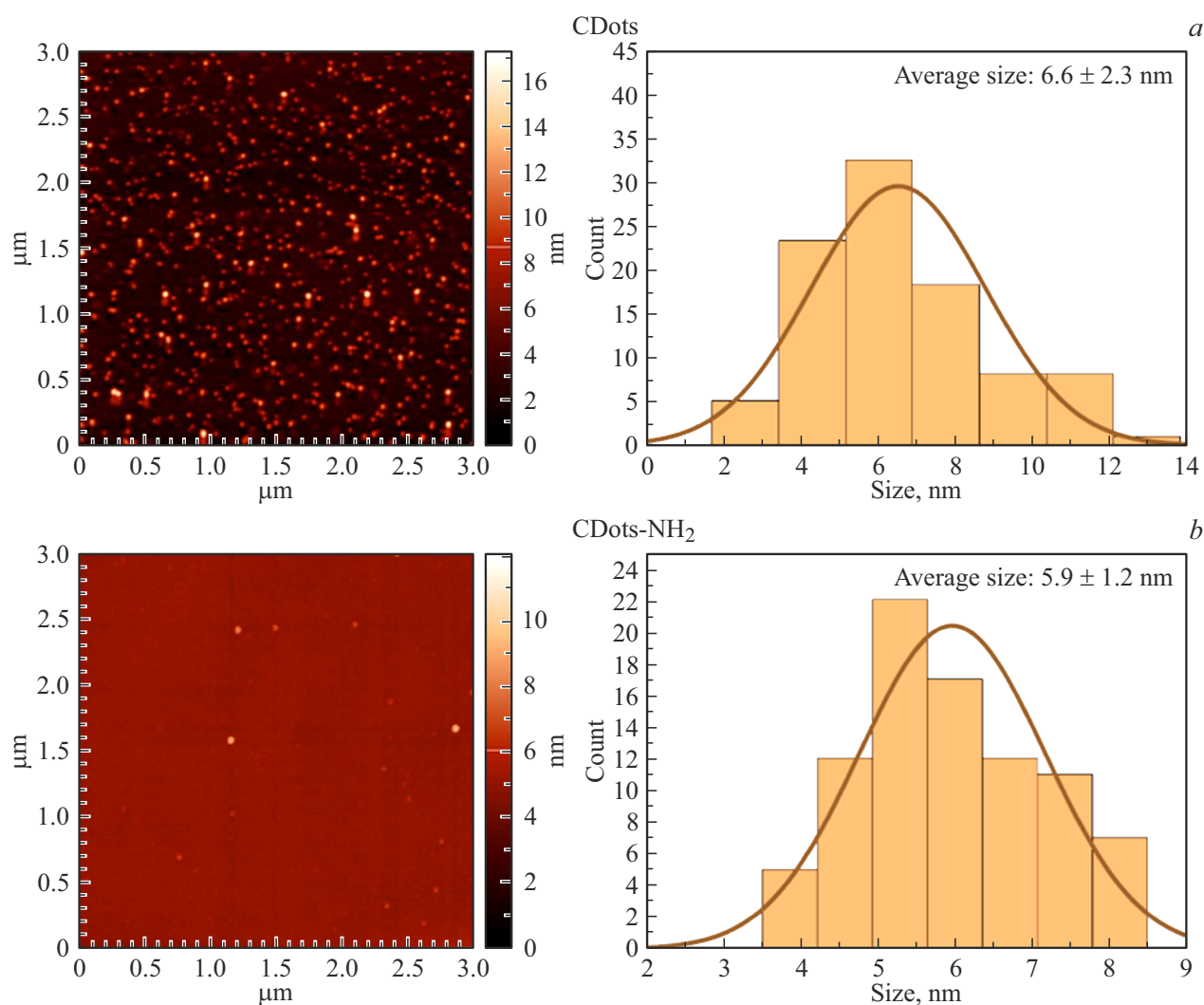


Figure 1. AFM images of CDs CDots and CDots-NH₂ and corresponding histograms of their size distributions.

Materials and research methods

The synthesis of water-soluble CDs coated with carboxyl groups (CDots) was carried out similarly to the procedure presented in the paper [19]. To do this, 2 g of citric acid (CA) were subjected to pyrolysis in an open pot in a muffle furnace at 180°C for 40 h with the formation of CDs in the form of a viscous dark brown liquid. The obtained solution was dissolved in 2.3 mL of water and neutralized to pH 7 by adding an aqueous solution of NaOH (5 M, 1.35 mL) to obtain CDs coated with sodium carboxylates. Subsequent application of the freeze-drying method allowed to isolate CDs CDots in the form of 0.9 g yellow-orange powder.

Aminated CDs (CDots-NH₂) were obtained from the original CDs CDots by additional surface treatment, which consisted of activation of carboxyl groups and subsequent covalent linking with EDA molecules. To do this, the carboxyl groups of CDs CDots were first activated by mixing 20.7 mg CDots, 48 mg EDC and 35.6 mg NHS in

0.75 mL water for 30 min. The resulting activated ester was added dropwise to a solution of EDA (0.2 mL) in water (3 mL) and stirred for 24 h to obtain CDs CDots-NH₂. Meanwhile, the use of an excess concentration of EDA relative to the concentration of carboxyl groups of CDs CDots allowed to preserve the second amino group of EDA in the form of a free base, i.e. to get CDs CDots-NH₂. Purification of the obtained CDs CDots-NH₂ from reaction products was carried out by dialysis using a 3.5 kDa membrane for 48 h.

The absorption spectra of CDs were recorded using a UV-3600 spectrophotometer (Shimadzu, Japan). Luminescence and luminescence excitation spectra of CDs were obtained using a Cary Eclipse spectrofluorimeter (Varian, Australia). Fourier-transform IR spectra of CDs were recorded using a Tensor II IR spectrophotometer (Bruker, USA) in the attenuated internal reflection mode.

The height (size) of the CDs was obtained using a Solver Pro-M atomic force microscope (AFM) (NT-MDT, Russia).

For this purpose, 70 μL CD solution was applied to the mica surface by centrifugation with the following parameters: 5 s at 500 min^{-1} and 25 s at 2000 min^{-1} . Next, the CDs deposited on talc were annealed for 15 min at 130 $^{\circ}\text{C}$ and after that they were used to measure the CD sizes.

CDs PL decay curves obtained using a MicroTime 100 scanning laser microscope (PicoQuant, Germany) were approximated by a biexponential function

$$I = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}. \quad (1)$$

The average decay time of the CDs PL was calculated using the formula

$$\tau_{av} = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i}, \quad (2)$$

where A_i and τ_i — amplitude and decay time of the i component, respectively.

The quantum efficiency (QE) of CDs PL was calculated relative to the PL QE of Rhodamine 6G using the formula

$$\varphi = \frac{(1 - 10^{-D_R}) I n^2}{(1 - 10^{-D}) I_{Rn} n_R^2} \varphi_R, \quad (3)$$

where D — absorbance, I — integral PL intensity and n — refractive index of water. The index „R“ denotes the reference solution of Rhodamine 6G in ethanol (QE PL — 0.95).

Results and discussion

Figure 1 shows AFM images for CDs CDots (*a*) and CDots-NH₂ (*b*) with corresponding histograms of their size distribution. It can be seen that the original CDs CDots have an average size of 6.6 ± 2.3 nm. The obtained size of CDs CDots, as well as its size distribution, is consistent with the previously established size of 6.8 ± 2.3 nm for CDs data using high-resolution transmission electron microscopy (TEM) [19]. According to TEM images, CDs CDots are characterized by a rather low crystallinity of their structure and a predominantly amorphous core. The histogram of the size distribution of aminated CDs (CDots-NH₂) in Fig. 1, *b* shows that their average size is 5.9 ± 1.2 nm. It should be noted that the preservation of the average size of CDs during their amination with EDA molecules indicates the participation of only one amino group (the second remains free) in covalent bonding with the carboxyl groups of the CDs surface, i.e. binding of CDs to EDA molecules occurs without the formation of aggregates. The free form of the second amino group of the EDA molecule may be due to the fact that the excess of free EDA molecules relative to the number of carboxyl groups on the CDs surface prevents the binding of CDs to an EDA molecule that is covalently linked to another CDs.

The surface structure of the original CDs CDots, as well as its modification in the CDs CDots-NH₂, were identified and monitored using IR absorption spectroscopy. Figure 2 shows the IR absorption spectra of CDs CDots, CDots-NH₂ and the CA precursor neutralized with NaOH for

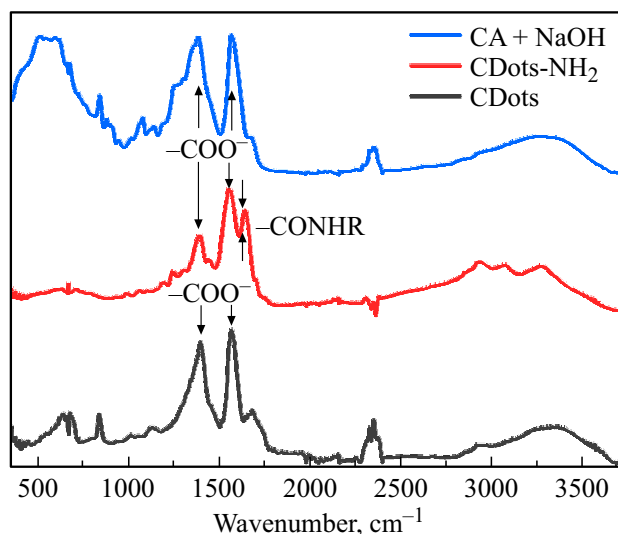


Figure 2. Fourier-transform IR spectra of CDs CDots, CDots-NH₂ and CA molecules neutralized with NaOH. Characteristic frequencies are marked with arrows.

comparison. The Fourier-transform IR spectra of CDs CDots is characterized by the presence of two characteristic bands at 1396 and 1566 cm^{-1} , corresponding to symmetric and asymmetric stretching vibrations of neutralized carboxyl groups on the CDs. The shift in the position of the CDs bands relative to the molecular precursor CA (1385 and 1569 cm^{-1}) is associated with their formation by the residues of the carboxyl groups of CA molecules on the surface of the CDs. The IR absorption spectrum of CDs CDots-NH₂ is characterized by, in addition to the bands at 1394 and 1552 cm^{-1} , corresponding to symmetric and asymmetric stretching vibrations of carboxyl groups, also the presence of another characteristic band at 1641 cm^{-1} , which corresponds to the stretching vibrations of the secondary amide (-CONHR). The presence of this secondary amide band is a consequence of the covalent binding of the carboxyl groups of CDs to the amino groups of EDA molecules. The presence of amino groups on the surface of CDs CDots-NH₂ is confirmed by the appearance of additional pronounced broad (due to hydrogen bonds) characteristic bands with maxima at 2934, 3078 and 3270 cm^{-1} , which are caused by stretching vibrations of the primary and secondary amine, as well as possibly their protonated forms. Accurate identification of these bands is further complicated by the presence of a broad band of OH stretching vibrations in this area.

Fig. 3 shows absorption and luminescence spectra of the CDs CDots and CDots-NH₂. The CDs CDots are characterized by absorption from the UV to the near visible region of the spectrum with a characteristic shoulder at 250 nm. The absorption spectrum of CDs CDots-NH₂ has a similar shape with a less pronounced shoulder. The features in the absorption spectra are in complete agreement with the data obtained previously for similar CDs [19,20].

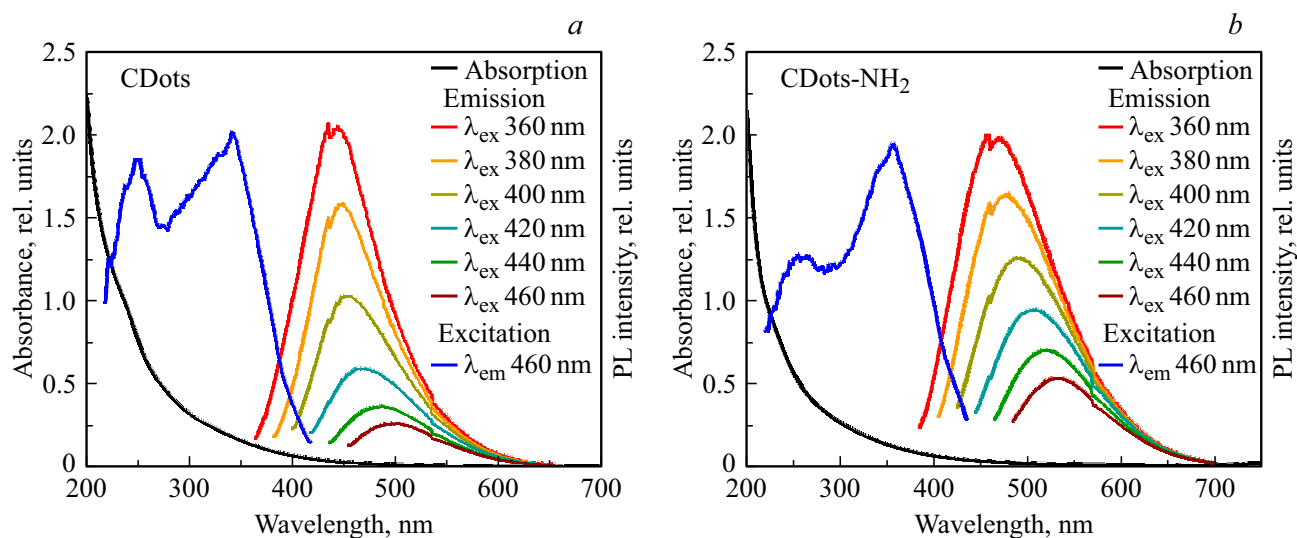


Figure 3. Absorption, PL and PL excitation spectra of CDs CDots (a) and CDots-NH₂ (b) at different excitation and emission wavelengths, as shown in the figure.

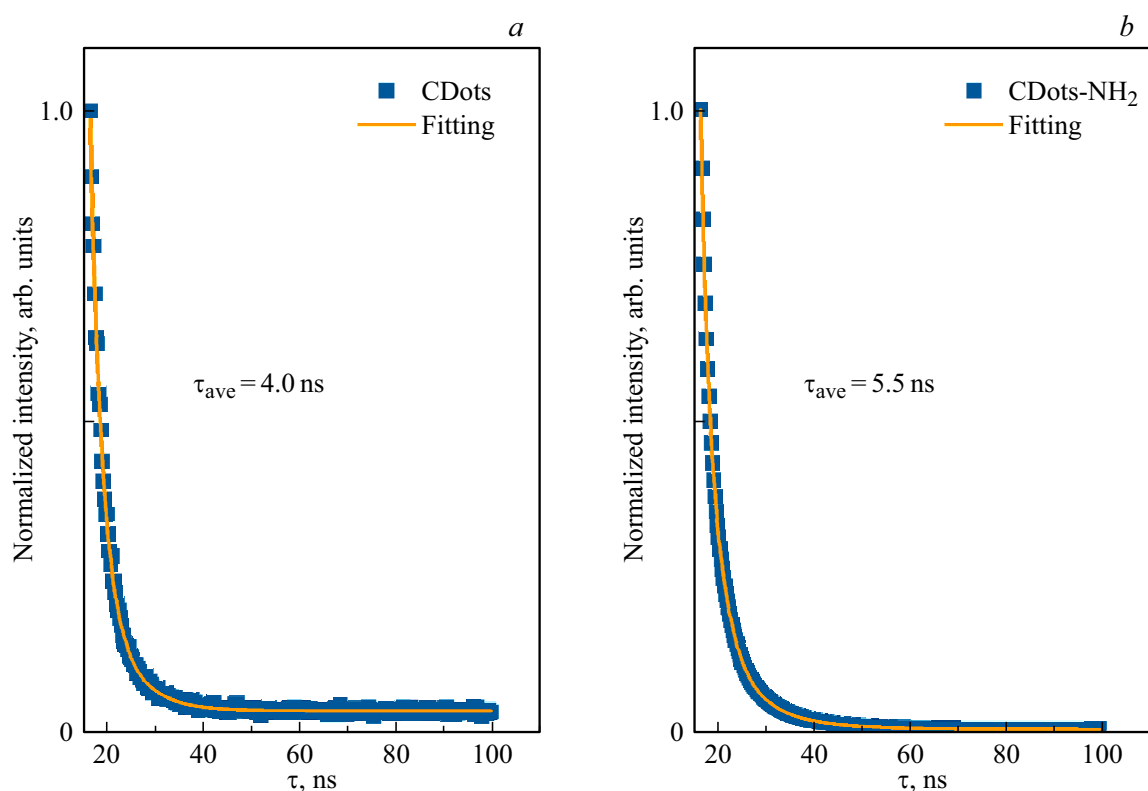


Figure 4. PL decay curves of CDs CDots (a) and CDots-NH₂ (b) when excited at 410 nm.

From Fig. 3, a it is clear that the position of the PL peak and its intensity for CDs CDots depends on the excitation wavelength; when the excitation wavelength shifts from $\lambda = 360$ to 460 nm, the emission maximum shifts from $\lambda = 459$ to 534 nm, and a significant drop in PL intensity occurs [3]. There is a similar dependence of the PL peak position for CDs CDots-NH₂ (Fig. 3, a). A shift in the

excitation wavelength for CDs CDots-NH₂ from $\lambda = 360$ to 460 nm leads to a shift in the position of their PL maximum from $\lambda = 459$ to 533 nm, and a smaller drop in PL intensity than that for the original CDs CDots. CDs CDots-NH₂ also exhibits wider luminescence bands. The most intense PL band with excitation at 360 nm has a width at half maximum that is 23 nm larger than that for the similar PL

band of the original CDs CDots (102 nm). The observed features in the PL spectra of CDs CDots-NH₂ in the form of wider PL peaks, as well as more intense long-wavelength PL, may indicate that when EDA is covalently bound to CDs, there is a slight change in the structure of some of the optical centers on the CDs surface, which is also confirmed by different luminescence excitation spectra of the original (CDots) and aminated CDs (CDots-NH₂) when recorded at 460 nm. It should be noted that the used method of amination of the CDs surface actually does not change their PL QE, measured upon excitation at 360 nm, which is 5.4 and 4.7% for CDs CDots and CDots-NH₂. The obtained PL QE values are in complete agreement with the data for similar CDs [19,20].

Figure 4 shows the PL decay kinetics of CDs CDots and CDots-NH₂ upon excitation at 410 nm. By approximating the PL decay curves with a biexponential function (1), average values of decay times of 4.0 and 5.5 ns were obtained for CDs CDots and CDots-NH₂, calculated according to expression (2). The data obtained are consistent with typical PL decay times for CDs [19,20]. Similar values of the decay times for CDs CDots and CDots-NH₂ indicate that amination of the surface of the CDs has no effect on the ratio of the rates of radiative and nonradiative relaxation of photoexcitations in the CDs.

Conclusion

In this paper, the structural and optical properties of aminated CDs were obtained and studied as well. First, CDs with carboxyl groups on the surface were obtained by pyrolysis of citric acid. Amination of the CDs surface was carried out by creating the monoamide EDA with activated carboxyls of the CDs surface. Activation of the carboxyl groups of CDs was carried out using EDC and NHS molecules. The covalent binding of EDA molecules to the CDs surface was monitored using IR absorption spectra. Data from atomic-force microscope images showed that amination of the surface of carbon dots occurred without the formation of aggregates, i.e. upon binding to the CDs surface, one of the two amino groups of EDA remained in free form. The use of this amination approach allowed to preserve the main optical and structural properties of CDs, which can be useful for studying the influence of their surface on the efficiency of photovoltaic and photocatalytic systems.

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Conflict of interest

The authors declare that they have no conflict of interest.

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