

G. Amanzholova^{1*}, E. Seliverstova¹, N. Ibrayev¹, E.I. Terukov²¹*Institute of Molecular Nanophotonics, Karaganda University of the name of academician E.A. Buketov, Kazakhstan;*²*Toffe Institute, R&D Center of Thin Film Technologies in Energetics, St. Petersburg, Russian Federation*

(*E-mail: gelnur_as@inbox.ru)

Structural and optical properties of carbon nanodots based on citric acid doped with nitrogen atoms

A study of the luminescent properties of carbon nanodots obtained by microwave and hydrothermal methods of synthesis from citric acid and urea was performed. The resulting nanoparticles were characterized using transmission electron microscopy, dynamic light scattering, and Fourier transform infrared spectroscopy. The sizes of the obtained carbon nanodots after dialysis was varied from 2 to 8 nm. FTIR spectra confirm the presence of oxygen-containing –OH, –CN and –NH groups in the resulting solutions. For all studied carbon nanodots, the maximum fluorescence intensity is observed upon excitation at a wavelength of 350 nm. The fluorescence spectrum does not change its position on the wavelength scale for the samples under study due to changes in the molar ratio of precursors and the method of synthesis. The highest fluorescence quantum yield was obtained for carbon nanodots with a ratio of citric acid and urea 1:4 obtained by the microwave synthesis method. The fluorescence lifetime of carbon nanodots doped with nitrogen atoms is ~7.4 ns. It is shown that a change in the ratio of precursors does not significantly affect the size and morphology of carbon nanodots.

Keywords: carbon nanodots; microwave synthesis; hydrothermal synthesis; optical properties; citric acid; urea.

Introduction

Carbon nanodots appeared not so long ago and they are showing great interest as a new class of carbon nanomaterials. Carbon nanodots (CNDs) can become as promising alternative to semiconductor quantum dots and dyes due to their good biocompatibility, low cytotoxicity, high photostability, variety of surface functional groups, ease of preparation and unique photophysical properties [1-3].

The most interesting from the point of view of fluorescent properties are carbon nanodots obtained by pyrolysis of citric acid [4-6]. These materials have a number of advantages, such as biocompatibility, simple synthesis, and excitation-dependent luminescence spectra, but they have a relatively low quantum yield of <10 % [4, 5]. For the solution of this problem, many researchers used various amine-based agents for surface passivation and doping of CNDs with various functional groups [7-10]. Doping of citric acid-based organic dots with nitrogen greatly improves their luminescent properties. A large number of studies were devoted to the synthesis of carbon nanodots based on citric acid using urea as a nitrogen source [7, 8, 11-13].

In the present work, the effect of the precursor composition and synthesis conditions on the structural and optical properties of carbon nanodots was studied. Microwave and hydrothermal synthesis methods were used to obtain CNDs. These methods of CNDs obtaining are simple, safe and cheap. In addition, when synthesizing CNDs by the microwave method, it is possible to control the main parameters of the reaction (pressure, temperature, time, power).

Experimental

CNDs were obtained using hydrothermal and microwave synthesis. Citric acid was used as a carbon source, and urea was used for doping with nitrogen atoms. The starting materials were taken in molar ratios of 1:1, 1:4, 1:5, and 1:6. Figure 1 shows the structural formulas of the starting materials.

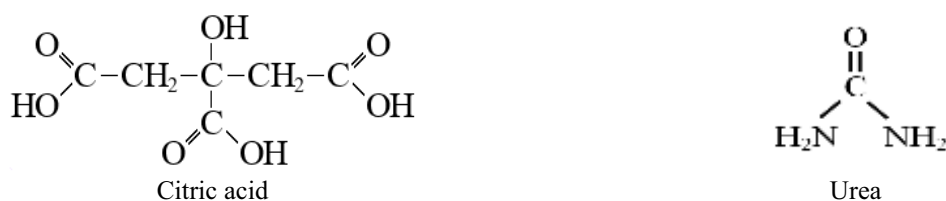


Figure 1. Structural formulas of starting substances

Microwave synthesis. The necessary amount of citric acid and urea was dissolved during ultrasound treatment in 5 mL of deionized water in a borosilicate glass tube. The synthesis was carried out in a Monowave 200 microwave reactor (Anton Paar) at a temperature of 160 °C for 1 hour with continuous mixing. Then the solution was cooled to 70 °C in a microwave reactor and further, to room temperature in natural conditions. The resulting product was centrifuged at a speed of 10000 rpm for 30 minutes, and then dialyzed. The carbon dots obtained by the microwave method at different ratios of citric acid and urea are further designated as CNDs(m) 1:1 and CNDs(m) 1:4.

Hydrothermal synthesis. The necessary amount of citric acid and urea was dissolved in 5 mL of deionized water during ultrasound treatment. The resulting transparent colorless solution was placed in an autoclave with a teflon vessel and heated in an oven at 160 °C for 6 hours. After this time, the autoclave was cooled in an open oven. As a result of the synthesis, a greenish-brown solution was obtained. To separate large particles, the solution was centrifuged at 10000 rpm for 30 minutes, and then purified by dialysis. The carbon points obtained by the microwave method at different ratios of citric acid and urea are further designated as CNDs(g) 1:1 and CNDs(g) 1:4.

Results and Discussion

The structure and dimensions of the obtained CNDs were studied using a transmission electron microscope (Jeol JEM-1400plus) and the method of dynamic light scattering on a ZetasizerNano ZS (Malvern) submicron particle size analyzer.

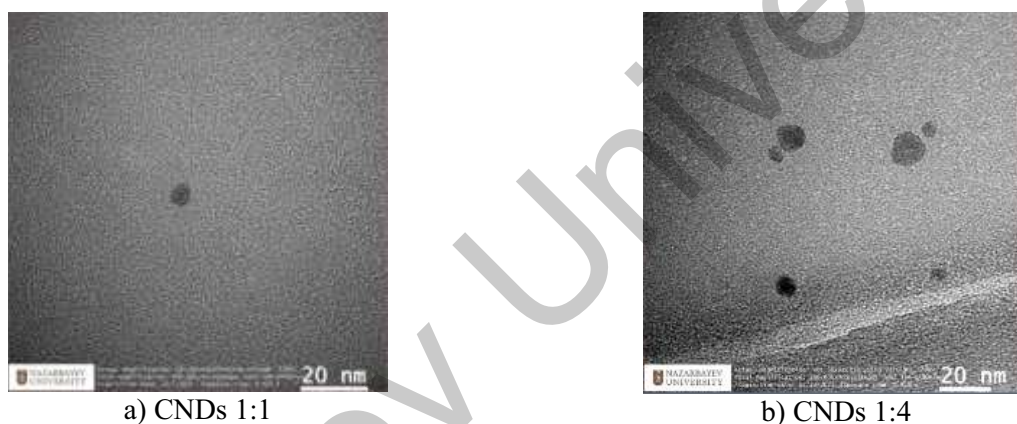


Figure 2. TEM images of CNDs synthesized by the microwave method

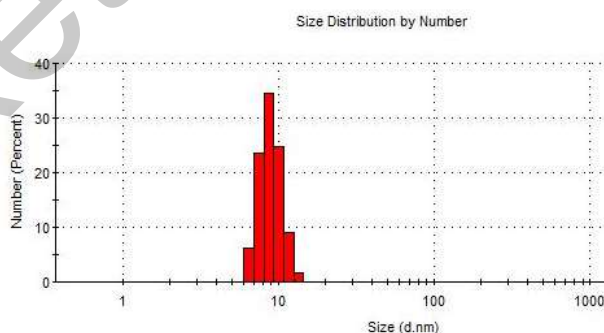


Figure 3. CNDs(m) (1:4) size distribution obtained by dynamic light scattering

As can be seen from the obtained TEM images (Fig. 2), the prepared CNDs are of spherical shape, their sizes vary from 5 to 16 nm. Similar data were obtained by the method of dynamic light scattering (Fig. 3). The different ratio of precursors did not affect the size of the CNDs. The average size was 9 nm.

The structure of the synthesized CNDs was studied on the basis of FTIR spectra, which were registered on an FSM 1201 IR Fourier spectrometer (Infraspec) in the transmission mode. The obtained FTIR spectrum exhibits maxima at 3417 and 3216 cm^{-1} , which belong to the stretching vibrations of –OH and –NH bonds (Fig. 4). Peaks at 1717, 1409 and 1452 cm^{-1} are caused by stretching vibrations of –C=O, –CN bonds

and vibrations of the benzene core, respectively. Thus, the recorded FTIR spectra confirm the doping of the synthesized CNDs with groups containing oxygen and nitrogen. The FTIR spectra of CNDs synthesized at different molar ratios of precursors are practically the same.

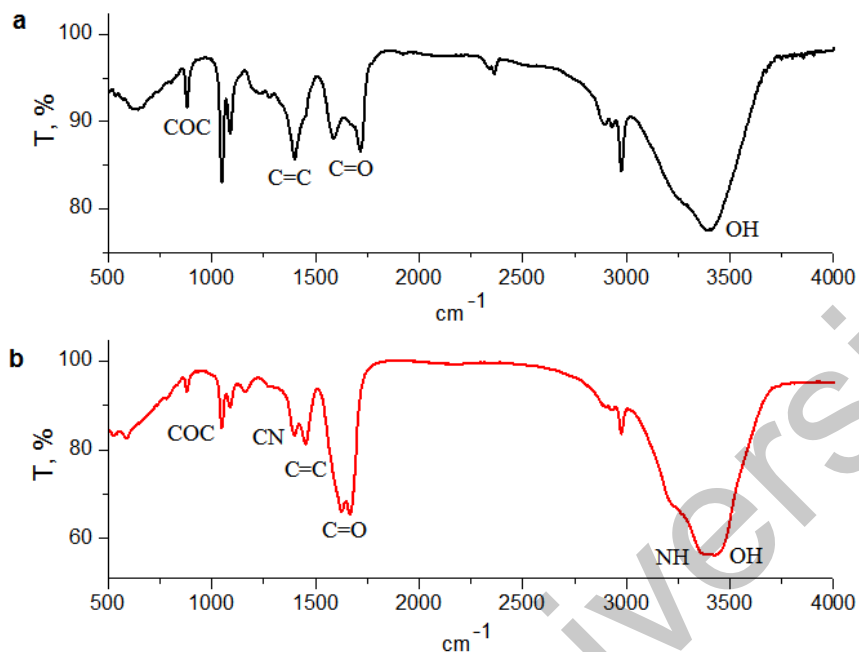


Figure 4. FTIR spectrum a) CNDs (m) 1:1; b) CNDs (m) 1:4.

The absorption and fluorescence spectrum of the obtained CNDs were measured on Carry 300 and Eclipse (Agilent) spectrometers, respectively. The studied solutions were prepared so that their optical densities were almost the same.

The absorption spectra of CNDs (Fig. 5) have a maxima in the region of 234 nm and 330–340 nm. The absorption band at 200–250 nm is caused by π - π^* transition in conjugated carbon bonds of carbon dots, the long-wavelength absorption band is the result of n - π^* transitions in C=O bonds of CNDs. Absorption on the long-wavelength wing ($\lambda > 400$ nm) is the result of the presence of surface groups, which include -CN, -NH bonds.

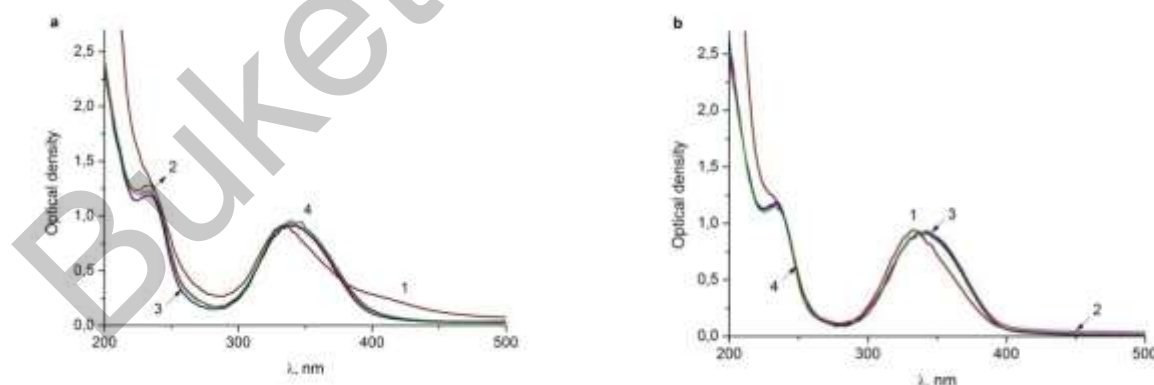


Figure 5. Absorption spectra of CNDs obtained by hydrothermal (a) and microwave (b) methods of synthesis with different molar ratios of precursors: 1 — CNDs 1:1, 2 — CNDs 1:4, 3 — CNDs 1:5, 4 — CNDs 1:6

It can be noted that the short-wavelength absorption band, regardless of the method of synthesis and the ratio of precursors, practically coincides for all samples, and the long-wavelength band of carbon dots obtained by the microwave method is slightly redshifted. At the same time, in both series, the long-

wavelength absorption maxima of CNDs with a ratio of 1:1 exhibits in the shorter-wavelength region, compared with the spectra of other CNDs (Table 1).

Table 1

Absorption maxima and full width at half maximum of absorption spectra of the studied CNDs

Solution	$\lambda_{\max 1}, \text{ nm}$	$\lambda_{\max 2}, \text{ nm}$	FWHM ₂ , nm
CNDs (h) 1:1	234	334	66
CNDs (h) 1:4	234	340	64
CNDs (h) 1:5	233	340	64
CNDs (h) 1:6	233	340	64
CNDs (m) 1:1	234	332	54
CNDs (m) 1:4	234	342	60
CNDs (m) 1:5	234	342	60
CNDs (m) 1:6	234	340	60

Since CNDs often exhibit excitation wavelength dependent luminescence [14-16], the fluorescence spectra of the obtained carbon dots were measured over a wide excitation range from 230 to 450 nm (Fig. 6). With an increase in the excitation wavelength from 230 to 350 nm, an increase in the emission intensity is observed; above 350 nm, a decrease in the fluorescence intensity is observed. At the same time, in the excitation range of 230–370 nm, the position of the emission maximum remains practically unchanged. Upon excitation at a wavelength of 390 nm and above, a shift of the emission band to the long wavelength region of the spectrum was observed.

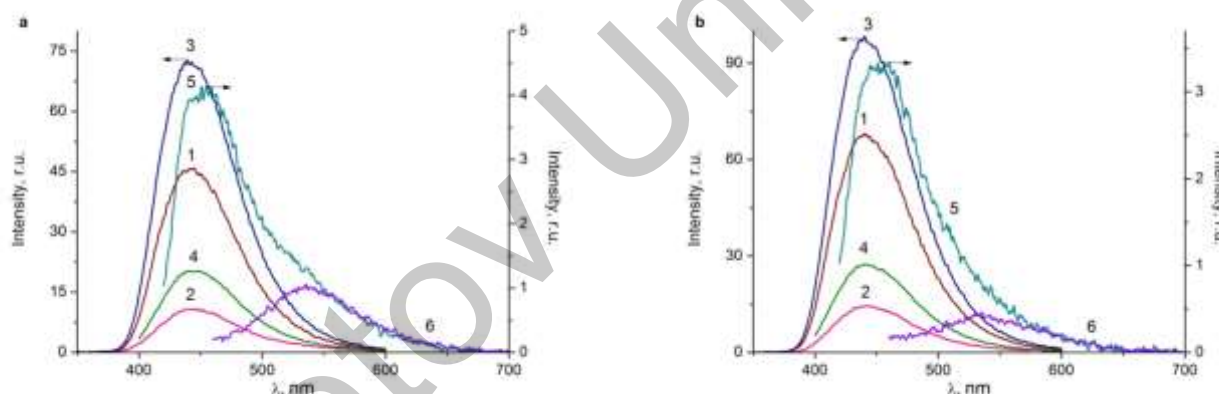


Figure 6. Fluorescence spectra of CNDs (1:4) obtained by hydrothermal (a) and microwave (b) methods upon excitation at different wavelengths, nm: 1 — 230; 2 — 330; 3 — 350; 4 — 390; 5 — 410; 6 — 450.

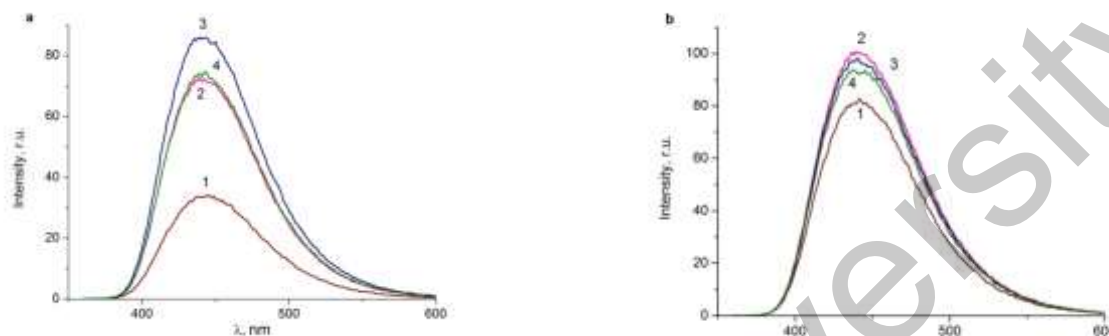
As the obtained emission spectra show, the maximum fluorescence intensity is observed upon excitation at 350 nm and does not depend on the method of synthesis of UT and the ratio of precursors. For both series of CNDs, the emission maximum falls at 443 nm.

Figure 7 shows the fluorescence spectra of the obtained CNDs depending on the composition of the precursors. The highest radiation intensity is observed for CND(g) 1:5 and CND (m) 1:4. Fluorescence quantum yields were measured for CND by the relative method [17]. As a standard, a 0.5 M solution of quinine sulfate in sulfuric acid was used, the quantum yield (QY) of which is 0.54 at an excitation wavelength of 345 nm. Table 2 shows the calculated fluorescence quantum yields. The data obtained show that the highest values of fluorescence quantum yield was demonstrated by carbon dots obtained by microwave synthesis at a ratio of citric acid and urea equal to 1:4.

Table 2

Fluorescence quantum yields of synthesized CNDs.

Sample	Quantum yield	Sample	Quantum yield
CNDs (h)1:1	0.1	CNDs (m)1:1	0.22
CNDs (h)1:4	0.4	CNDs (m)1:4	0.55
CNDs (h)1:5	0.43	CNDs (m) 1:5	0.49
CNDs (h)1:6	0.34	CNDs (m) 1:6	0.47



1 — CNDs 1:1; 2 — CNDs 1:4; 3 — CNDs 1:5; 4 — CNDs 1:6.

Figure 7. Fluorescence spectra of CNDs obtained by hydrothermal (a) and microwave (b) methods, with different ratios of citric acid and urea under photoexcitation at 350 nm.

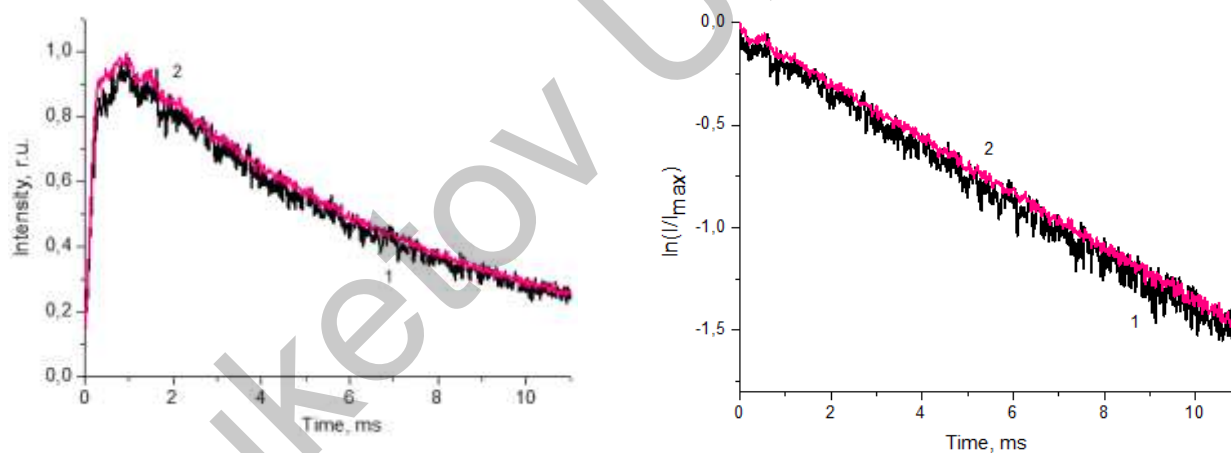


Figure 8. Normalized fluorescence decay kinetics of CND(m) 1:1 and CND(m) 1:4 under the registration at 440 nm.

The fluorescence lifetime of the studied carbon nanodots was estimated from the decay kinetics, approximated with monoexponential law. The measurements showed (Fig. 8, Table 3) that the average fluorescence lifetime in CNDs is 7.4 ns.

Table 3

Fluorescence lifetime of CNDs(m) of various composition quantum yields of synthesized CNDs

Solution	τ , ns
CNDs 1:1	7.3
CNDs 1:4	7.4
CNDs 1:5	7.4
CNDs 1:6	7.4

Conclusions

The influence of the composition of precursors and synthesis conditions on the structural and optical properties of carbon dots, prepared by microwave and hydrothermal synthesis, was studied. Their structural properties showed that a change in the ratio of precursors does not significantly affect the size and morphology of carbon dots. The sizes of synthesized CNDs after dialysis were varied from 2 to 8 nm. The maximum fluorescence intensity of both types of CNDs was observed upon excitation at 350 nm. The highest fluorescence quantum yield (55 %) is exhibited by CNDs synthesized by the microwave method. The fluorescence lifetime averages ≈ 7.4 ns for all studied solutions.

Acknowledgments

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Г. Аманжолова, Е. Селиверстова, Н. Ибраев, Е.И. Теруков

Азот атомдары енгізілген лимон қышқылына негізделген көміртекті нанонүктелердің құрылымдық және оптикалық қасиеттері

Лимон қышқылы мен мочевинадан микротолқынды және гидротермиялық синтездеу әдістері арқылы алынған көміртекті нанонүктелердің люминесценттік қасиеттерін зерттеу жұмыстары жүргізілді. Алынған нанобөлшектер трансмиссиялық электронды микроскопия, жарықтың динамикалық шашырауы және Фурье түрлендіруі бар инфрақызыл спектроскопия арқылы сипатталды. Диализден кейін алынған көміртекті нанонүктелердің өлшемдері 2 нм-ден 8 нм-ге дейін өзгереді. Алынған ерітінділер құрамында оттегі атомы бар ОН, CN және -NH топтарының болуын Фурье түрлендіруі бар инфрақызыл спектрлері растайды. Барлық зерттелген көміртекті нанонүктелер үшін флуоресценцияның максималды интенсивтілігі 350 нм толқын ұзындығында қоздыру кезінде байқалады. Сонымен қатар, прекурсорлардың молярлық қатынасы мен синтездеу әдісінің өзгеруіне байланысты зерттелген үлгілер үшін флуоресценция спектрі толқын ұзындығы шкаласы бойынша өз орнын өзгертпейді. Флуоресценцияның ең үлкен кванттық шығымы микротолқынды синтездеу әдісімен алынған лимон қышқылы мен мочевина қатынасы 1:4 болатын көміртекті нанонүктелер үшін алынды. Азот атомдары енгізілген көміртекті нанонүктелердің флуоресценциясының өмір сүру уақыты орта есеппен 7,4 нс тең. Прекурсорлардың молярлық қатынасының өзгеруі көміртекті нанонүктелердің мөлшері мен морфологиясына айтарлықтай әсер етпейтіні көрсетілді.

Кілт сөздер: көміртекті нанонүктелер, микротолқынды синтез, гидротермиялық синтез, оптикалық қасиеттері, лимон қышқылы, мочевина.

Г. Аманжолова, Е. Селиверстова, Н. Ибраев, Е.И. Теруков

Структурные и оптические свойства углеродных наноточек на основе лимонной кислоты, допированных атомами азота

Проведено исследование люминесцентных свойств углеродных наноточек, полученных микроволновым и гидротермальным методами синтеза из лимонной кислоты и мочевины. Наночастицы были охарактеризованы с помощью просвечивающей электронной микроскопии, динамического рассеяния света и инфракрасной спектроскопии с преобразованием Фурье. Размеры полученных углеродных наноточек после диализа варьируются от 2 до 8 нм. ИК спектры с Фурье преобразованием подтверждают наличие кислородсодержащих ОН и CN, -NH групп в полученных растворах. Для всех исследованных углеродных наноточек максимальная интенсивность флуоресценции наблюдается при возбуждении на длине волны 350 нм. Спектр флуоресценции не изменяет своего положения по шкале длин волн для исследуемых образцов от изменения молярного соотношения прекурсоров и метода синтеза. Наибольший квантовый выход флуоресценции наблюдается у углеродных наноточек с соотношением лимонной кислоты и мочевины 1:4, полученных микроволновым методом синтеза. Время жизни флуоресценции допированных атомами азота углеродных наноточек в среднем составляет 7,4 нс. Показано, что изменение соотношения прекурсоров не оказывает заметного влияния на размеры и морфологию углеродных наноточек.

Ключевые слова: углеродные наноточки, микроволновый синтез, гидротермальный синтез, оптические свойства, лимонная кислота, мочевина.