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Method of Obtaining and Studying the Optical Properties of Carbon Quantum Dots

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The proposed method of synthesis of CQDs on the basis of nanoporous carbon obtained from plant raw materials. It is established that in the short-wave region a band is registered, which is due to the exciton mechanism of recombination, whereas in the long-wavelength region it is related to the state of defects. The kinetics of PL extinction is not strictly exponential, which most likely indicates the distributed nature of fading from individual emitters.

Keywords: porous carbon material, carbon quantum dots, photoluminescence, quantum-dimensional effect.

Introduction

Carbon Quantum Dots (CQDs) [1] represent a new class of carbon nanomaterials with apparent fluorescence consisting of discrete, quasiparticle carbon nanoparticles with dimensions less than 10 nm. CQDs integrate the unique optical properties of quantum dots with special electrical properties of sp^2-carbon materials, which makes them different from traditional semiconductor quantum dots or other carbon nanotubes (eg, graphene and carbon nanotubes).

Quantum dots of carbon are often described in terms of a carbonogenic nucleus with surface functional groups. Most carbon quantum dots consist of an amorphous to a nanocrystalline nucleus with predominantly sp^2 carbon hybridization, whose lattice distances are consistent with graphite or turbostatic carbon. At the same time, CQDs, as a rule, end with oxygen fractions (content 5 - 50 mass%) on their surface, [2, 3], which provide high solubility in aqueous solutions and provide a potential for further functionalization in comparison with other carbon nanomaterials.

Carbon is usually a black material, and is characterized by weak fluorescence. However, quantum dots with a carbon nanoclay attract great attention because of their strong luminescence.

Different methods of synthesis of CQDs, such as laser ablation, arc discharge, electrochemical methods, hydrothermal method, ultrasonic method, acid dehydration method and pyrolysis method have been developed. The application of quantum dots of carbon lies in the area of optometrists, materials for solar cells, which use dyes, organic solar cells, super-capacitors, as well as light emitters and catalysts.

"Carbon dots" is a complex term for various nanoscale carbon materials. In a broad sense, all nanoscale materials, which consist mainly of carbon, can be called carbon points. Carbon dots always have at least one size smaller than 10 nm in size and fluorescence, as their instinctive properties. The structure of the CQDs consists of sp^2/sp^3 carbon and oxygen-nitrogen groups or polymer aggregates. CQDs mainly include graphene quantum dots, carbon nanotubes and polymer dots. Graphene quantum dots have one or more layers of graphene and associated chemical groups at the edges. They are anisotropic with lateral dimensions larger than their height. Carbon nanoparticles are always spherical, and they are divided into carbon nanoparticles that do not have a crystalline lattice, and CQDs that have an obvious crystalline lattice. As a result, the center of photoluminescence (PL) is very different for different types of carbon nanotubes. Polymer dots are aggregated or crosslinked polymers derived from linear polymers or monomers. In addition, the carbon core and the bound polymer chains can be assembled in their own form in the form of polymeric dots. Due to the variety of carbon dots, there are many approaches to their obtaining, the most common of which are "top to bottom" cutting from different sources of carbon and "bottom-up" synthesis of organic molecules or polymers and modification of

surface functionality or passivation [4].

I. Experiment

Activated charcoal production

The most common methods of obtaining porous carbon material (PCM) are the physical or chemical activation of carbonaceous raw materials. Chemical activation usually occurs at temperatures (400-800 ºC) and is accompanied by the use of dehydrating agents (phosphoric acid, zinc chloride, potassium hydroxide).

Chemical activation is considered as a reaction between a solid precursor (a waste of coffee grounds) and a chemical reagent (orthophosphoric acid). The weight of the final product and its structure depend on the concentration and ratio of the initial components, temperature and activation time. A prerequisite for chemical activation is the removal of residual activation reagents and inorganic residues contained in the original carbonaceous material [5].

Orthophosphoric acid acts as an activating agent and promotes the dehydration of the primary material, which leads to a decrease in the temperature of degradation of the material, an increase in the mass of carbon dioxide produced and promotes the formation of its porous structure.

When activated carbon is obtained by chemical activation of the raw material with orthophosphoric acid, the ratio between the amount of acid and the raw material is important:

$$Y = \frac{m(H_3PO_4)}{m(BC)} \qquad (1)$$

which was 1,25:1; 1,00:1; 2,00:1.

Before the experiment began, the sample mass was measured to within 10^{-3} g using analytical weights.

The following activation steps were performed according to the method of obtaining acid-activated carbon materials []. For this, the coffee grounds were dried and ground to a fraction of 2.5 - 4 cm, the resulting material was divided into portions and mixed with orthophosphoric acid at concentrations of 4 to 32 %, with a step of 4 %. The resulting mixture was thoroughly stirred for 1 to 2 hours, after which the samples were dried at 100°C. for 24 hours until a constant mass. The resulting carbon dioxide carbon material was placed in a vertical cylindrical furnace and heated to 450°C., 500°C. and 550°C. at a rate of 10°C./min. in an argon atmosphere at a flow rate of gas of 30 ml / min. When the desired temperature was reached, the isothermal exposure was carried out for 60 min. After cooling the resulting material to room temperature, hot-distilled water was washed to neutral pH and dried at 80 ° C. until constant mass was obtained.

The obtained carbon materials were indicated according to the time of isothermal aging (t) and the ratio of the mass of orthophosphoric acid and the raw material (Table 1.).

For the synthesis of CQDs, we used the PCM.

In general, the synthesis of dominant carbon points includes one molecular precursor that provides the basic structure of carbon, while another molecular precursor introduces other elements into the structure. The most

Table 1
The ratio of the mass of acid to the mass of the raw material and the temperature of heat treatment

$Y = \dfrac{m(H_3PO_4)}{m(BC)}$	1,25	1,00	2,00
Sample	C_1	C_2	C_3

common combination in this regard is citric acid as a source of carbon in combination with molecules containing nitrogen, for example, ethylenediamine or urea.

Sample 1

0.8 g of carbon C1 (coffee 1.25), 1.6 g of citric acid ($C_6H_8O_7$), 50 ml. water and 30 ml of C_2H_5OH were mixed and heated to a temperature of t = 170 ° C for 4.5 h.

After natural cooling to room temperature, the resulting solution was extracted with dichloromethane (CH_2Cl_2), followed by drying for 12 h.

Sample 2

0.8 g of carbon C1 (coffee 1.25), 0.8 g of citric acid ($C_6H_8O_7$), 50 ml. water and 30 ml of C_2H_5OH were mixed and heated to a temperature of t = 170 ° C for 4.5 h.

After natural cooling to room temperature, the resulting solution was extracted with dichloromethane (CH_2Cl_2), followed by drying for 12 h.

II. Results and discussion

The PL spectra, its excitation and the kinetics of luminescence decay were investigated in unpolarized light at room temperature.

In the process of photoluminescence, the transformation of the absorbed light energy into the energy of luminescent radiation occurs. Absorption capacity of a substance is characterized by absorption spectrum. Waves whose absorption luminescence occurs, form a band of excitation. There may be several such bands. The sum of all excitation bands forms an excitation spectrum (PLE). In this paper, in both cases, the excitation spectrum is represented by only one band with a narrow maximum in the visible range of the spectrum with λ_m = 351 nm (sample 1) and λ_m = 355 nm (sample 2).

The spectrum of PL of both samples is a superposition of two channels of radiative recombination due to annihilation of excitons and recombination through surface levels created by defects. The PL spectrum is a band that occurs as a result of overlapping of two individual luminescence bands, localized in two regions of the visible range. In the short-wave region, the band is recorded, due to the exciton mechanism of recombination, and in the long-wavelength band associated with defective states. The samples contain a large number of particles of different sizes, resulting in a dimensional shift of the line is heterogeneously widespread.

The analysis of the obtained results allows us to conclude that in both cases the same type of structure is
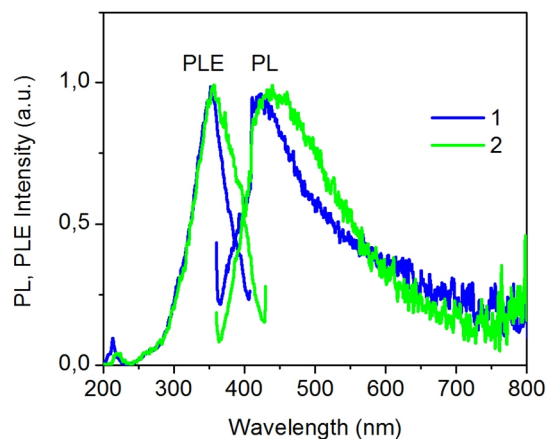
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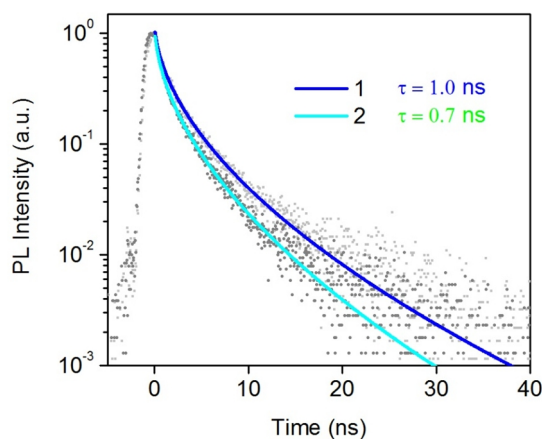**Fig. 1.** Spectra of radiation PL C_1 -1, C_2 – 2.

Fig. 2. Fluorescent kinetics of extinction CQDs C_1-1, C_2 – 2.

formed, but the second sample is characterized by a wider distribution of particles in size and size of the particles of the main fraction.

Fluorescent fading of identical fluorophores in the system should be strictly exponential, provided that they interact equally with the environment and do not participate in the reactions of excited states. The results obtained by us show the kinetics of fading, which is strictly non-exponential (Figure 2). The absence of a noticeable dependence of the kinetics of extinction on the wavelength of excitation does not explain the results previously obtained. This behavior indicates the "distributed" nature of extinction from individual emitters, due to their continuous distribution, which demonstrates a change in the rate of extinction.

It is known that the non-exponential behavior of fluorescence fading also occurs when the fluorophore shows any excited state of reactions such as charge transfer or FRET (from the English Förste rresonance energy transfer). These reactions occur with decreasing energy of the donor and its partial absorption by the acceptor in the longer wavelength range of the spectrum. If these effects are present, they should disappear when excited in the red area. Thus, only the FRET acceptor should be excited in this case and the kinetics of fading should be different from that which would be observed at the maximum of the excitation of the fluorophore or in the blue range. However, such results were not observed.

Consequently, this indicates a lack of FRET or other excited states.

Therefore, it can be assumed that the fast and slow components of the kinetics of the PL correspond to the decay of PL carbons with a larger and smaller number of surface defects. Therefore, the fast component of the kinetics of the PL corresponds to the radiationless absorption of charge carriers for surface defects, and the slow - to the radiative recombination of excitons (this hypothesis in the literature confirms the results obtained from the analysis of kinetics at other photon energies within the spectrum of PL).

In cases there is a rapid anisotropy of fading fluorescence. The high initial anisotropy decreases somewhat over time due to the loss of the initial orientation of the particle as a result of rotational diffusion or transfer of energy to other emitters. The obtained results show that for all investigated systems there is a rapid anisotropy of fading.

The value of the fluorescence lifetime is one of the main characteristics of the fluorophore, indicating its stability and promising use. The analysis of the results showed a rush from 0.7 to 1 ns, which correlates with the previously obtained data. The absence of the dependence of the emission intensity on the lifetime of the fluorophore was established.

Conclusions

The re-constructed fluorescence emission of carbon quantum dots can be achieved either by controlling the size of the domain sp^2 of conjugation or modification of the chemical groups formed on the surface of carbon nanotubes.

When obtaining carbon quantum dots, small molecules of fluorophore are formed at low reaction temperatures. As the carbonization temperature increases, the carbon core is formed by dehydrating the parent molecules or by consuming the formed fluorophore. These carbon nanoparticles exhibit strong releases of high quantum-PL fluids, while the carbon-core state has low-level PL fluency behavior with high photostability.

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Методика отримання та дослідження оптичних властивостей вуглецевих квантових точок

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Запропонована методика синтезу ВКТ на основі нанопористого вуглецю отриманого із рослинної сировини. Встановлено, що у короткохвильовій області реєструється смуга, зумовлена екситонним механізмом рекомбінації, тоді як у довгохвильовій області вона пов'язана станом дефектів. Кінетика згасання ФЛ не є строго експоненційною що найбільш ймовірно свідчить про розподілений характер згасання від окремих емітерів.

Ключові слова: пористий вуглецевий матеріал, вуглецеві квантові точки, фотолюмінісценція, квантово-розмірний ефект.