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Colloidal synthesis and optical properties of ultra-small CdTe quantum dots

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In this work, we report on the colloidal synthesis of CdTe nanocrystals (NCs) in a reactor whose reaction medium consists of a solution of CdI₂ salt, thioglycolic acid (TGA), and NaOH alkali. The gaseous precursor H₂Te, which was obtained electrochemically in a galvanostatic cell, was passed through this solution. The size of the synthesized NCs was varied by regulating the flow of hydrogen telluride from the galvanostatic cell. In turn, the outflow of hydrogen telluride depends on the current that passes through the cell electrodes. The growth rate of nanocrystals is determined by the rate of precursor feeding into the reactor. Studies have shown that this synthesis usually produces CdTe NCs of different sizes. To separate the colloidal solution into fractions, a centrifugation method was proposed, which allowed to isolate ultra-small quantum dots (USQDs) of CdTe with dimensions of about 2 nm. To obtain QDs of ultra-small size, we used low current values (up to 100 mA), a short synthesis time (0.5-1 min), and high pH values (8-11) of the reaction medium. The study of the absorption spectra of CdTe NC samples taken from the fraction with the smallest size separated by centrifugation showed that the energy of the corresponding transitions significantly exceeds the band gap of bulk CdTe (1.5 eV), and which correspond to CdTe USQDs (clusters). Our study of the size of CdTe on the Zetasizer Nano ZS confirmed the presence of USQDs with dimensions of approximately 2 nm. It has been shown that the photoluminescence of the USQDs is mainly due to surface defects.

Keywords: synthesis technology, ultrasmall quantum dots, centrifugation, absorption spectra, photoluminescence, photoluminescence excitation spectra.

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Introduction

Ultra-small quantum dots (USQDs) of semiconductor compounds A₂B₆ (with dimensions ≤ 2 nm) are characterized by unique properties, in particular, light absorption with a sharp high-frequency edge and almost entirely surface luminescence. It is known that such USQDs are promising for use in light-emitting devices, solar energy, and medicine - for "contrasting" in magnetic resonance imaging and as a material for targeted drug delivery to diseased cells. In the field of information technology, USQDs are promising for use in devices for storing and processing data with high density and high speed of information processing [1, 2]. To date, a significant part of the work is devoted to the study of CdS and CdSe USQDs [3-5]. At the same time, CdTe USQDs

have been studied much less, although this compound is important for the development of long-wavelength photodetectors [6]. Highly luminescent CdTe quantum dots are synthesized in a mixture of Tri-octylphosphine (TOP) and Dodecylamine (DDA) [7]. In this case, the formation of ultra-small CdTe clusters from Cd and Te precursors is observed for the reaction mixture at room temperature, and at temperatures $T > 145$ °C the growth of CdTe nanoparticles occurs and their diameter becomes > 2 nm.

Chemically synthesized CdTe quantum dots are usually characterized by a wide size distribution [8, 9]. The absorption spectrum of such QDs is quite broad even at low temperature [10], which makes it difficult to determine the resonant position of the absorption peak.

Photoluminescence excitation (PLE) spectroscopy is

used to determine the energy levels of absorption and emission of QD. This technique provides information about the size and size distribution of nanoparticles that cannot be obtained by standard measurements of photoluminescence (PL) or absorption spectra. In [11], PLE spectroscopy was used to determine

the size of CdS NCs embedded in the Ormosil matrix. It was found that the obtained values of the dimensions of CdS NCs are consistent with the data obtained by X-ray diffraction analysis, absorption, PL, and CdS NCs transmission electron microscope (TEM) spectra. In work [12], the effect on the size of PL of CdTe NCs obtained by the organometallic synthesis method using PL and PLE was investigated. It was found that the emission of such NCs significantly depends on the energy of the excitation quantum, in particular, in resonant emission, a spectral shift and line narrowing were detected at a decrease in the energy of the excitation quantum.

Therefore, today it is of considerable interest to synthesize USQDs CdTe by colloidal synthesis and study their electronic characteristics by optical methods: absorption, photoluminescence, and excitation of photoluminescence spectra, which is the aim of this work.

I. Synthesis of CdTe nanocrystals

CdTe nanocrystals are produced using a variety of chemical synthesis methods organometallic synthesis, synthesis in micelles and vesicles, in reverse microemulsions, in the pores of polyacrylamide gels, solvothermal synthesis, sol-gel synthesis, synthesis in aqueous and non-aqueous media using thiol stabilizers. One of the simplest and most accessible methods for the production of cadmium telluride NCs is liquid-phase synthesis. Reverse micelles and colloidal synthesis are very promising, since by changing the synthesis conditions, one can influence the size of NCs, their shape, and structure.

Colloidal synthesis is one of the available and inexpensive synthesis methods. In our experiments of colloidal synthesis of CdTe NCs, the reaction chamber was a 500 mL reactor equipped with partitions and valves, a thermometer, and an electromagnetic stirrer, into which we loaded a mixture of compounds that cause nucleation and growth of NCs [13,14]. During the synthesis of NCs in aqueous solution, each of the atomic species involved in the formation of nanocrystals is introduced into the reactor in the form of precursors, which are molecules (complexes) and contain one or more atomic species necessary for the growth of NCs. The reaction medium of the reactor consists of a solution of CdI₂ salt, a certain

amount of TGA (thioglycolic acid), and NaOH alkali. Argon was passed through this solution for 15 minutes to remove residual oxygen. Then, along with the argon stream, the gaseous precursor H₂Te was passed, which was obtained electrochemically in a galvanostatic cell. The size of the synthesized NCs was varied by adjusting the flow of hydrogen telluride from the galvanostatic cell. In turn, the flux of hydrogen telluride depends on the current that passes through the electrodes of the cell, and the rate of argon supply to the reaction mixture. We selected the argon flow in such a way that it remained constant for all cases of synthesis, so the rate of hydrogen telluride supply to the reactor was regulated solely by the amount of current passing through the electrodes of the electrostatic cell. With an increase in the current, the intensity of hydrogen formation on the cell's tellurium electrode increased. Thus, by changing the current strength, it is possible to set the size of the formed CdTe NCs. The size of the synthesized NCs can also be controlled by the duration of the synthesis process (the time of passage of H₂Te through the CdI₂ solution), the pH of the solution in the reactor, and the amount of stabilizer, in this case, TGA. During the synthesis, as a rule, we obtain CdTe NCs of different sizes and, by selecting specific conditions, it is possible to obtain nanoparticles of predominantly the same size with a slight scatter. Using an ultracentrifuge, the obtained colloidal solutions were separated into fractions. For this purpose, an OPN-12 centrifuge with a digital indication of centrifugation speed duration, and a maximum magnitude factor was used. The latter allowed the isolation of ultra-small size CdTe NCs (approximately 2 nm). To obtain ultra-small NPs, low current values (up to 100 mA), a short synthesis time (0.5 - 1 min), and high pH values (8-11) of the reaction medium are used. Table 1 shows the synthesis conditions of CdTe NCs colloidal solutions used for the subsequent study.

To obtain very small NCs, an ultrasonic bath was also used to grind large particles into smaller ones, but it is worth noting that this process is poorly controlled, as it leads to the destruction of the stabilizer shell around the NC.

In the process of synthesizing CdTe NCs and for their further efficient storage and use, the nature of the particle surface formed by the TGA stabilizer is of great importance. The stabilizing coating prevents the aggregation of particles in the dispersed phase and is therefore a crucial component of the formation of CdTe NCs at the initial stage of synthesis. TGA is also responsible for the stability of NCs in an aqueous dispersion medium because, in the absence of a stabilizer, the resulting particles aggregate instantly. The interaction

Table 1.

Synthesis conditions of the studied samples of CdTe NCs

Sample No.	CdI ₂ Initial solution	U (V) Voltage	I (A) Current strength	Synthesis time	Ripening time at 90 °C
1	40 ml	10	0.15	1 min	20 days (t=20° C) +30 min
2	40 ml	18	0.4	45 sec	1 hour
3	20 ml	12	0.1	2 min	1 hour
4	20 ml	15	0.12	1 min	1 hour
5	40 ml	12	0.1	4 min	1 hour

of Cd²⁺ cations with H₂Te in the presence of TGA leads to the formation of transparent CdTe ash, which retains aggregate stability for several years.

Colloidal solutions of CdTe/TGA NCs obtained in a neutral medium have a characteristic dark orange color and in an alkaline medium – a light yellow color. This is direct proof that an increase in the pH of the reaction medium leads to a decrease in the average size of CdTe NCs, which is also confirmed by studies of their optical properties.

II. Absorption spectra

Fig. 1 shows the absorption spectra of CdTe NC samples taken from the fraction with the smallest size separated by centrifugation and synthesized under different technological conditions (Table 1). The maximum absorption bands lie in the region of 300 nm - 310 nm (4.13 - 4.00) eV. The energy of these transitions significantly exceeds the band gap of bulk CdTe (1.5 eV). This means that the detected high-energy transitions correspond to ultra-small quantum dots (clusters) of CdTe with dimensions ≤ 2 nm.

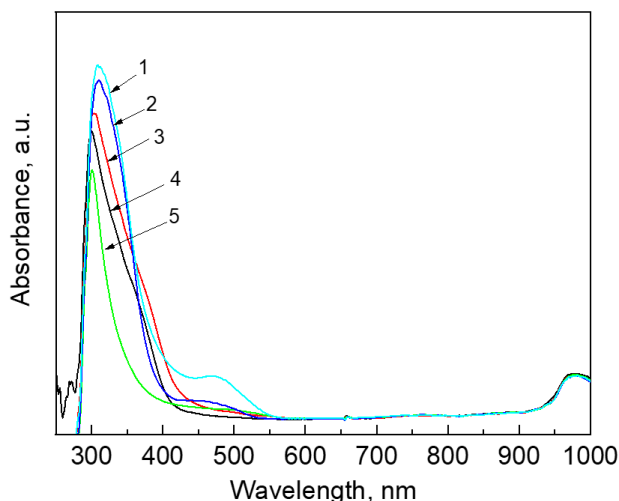


Fig. 1. Optical absorption spectra of CdTe NC samples No.1-5 synthesized under different process conditions (see Table 1). The curve numbers correspond to the sample numbers.

It should be noted that the scatter of absorption peaks (300 - 310) nm, and hence the size of CdTe clusters, depends on a combination of technological factors (voltage, current, synthesis time, maturation time – see Table 1). The smallest wavelength of the maximum absorption band (300 nm) and, accordingly, the smallest size of the CdTe cluster was found for sample No. 5: U = 12 V, I = 0.1 A, synthesis time 4 min, maturation time at 900 °C 1h. For the CdTe clusters studied by us, different synthesis modes were used, which caused different degrees of their passivation.

Our quantitative studies of the size of CdTe CTs on the Zetasizer Nano ZS confirmed the presence of USQDs from 2 nm. For the measurements, the synthesized colloidal solutions were diluted 1000-fold and transferred to the measurement cuvette. The data obtained were

analyzed using Zetasizer software and the following results were obtained (Fig. 2):

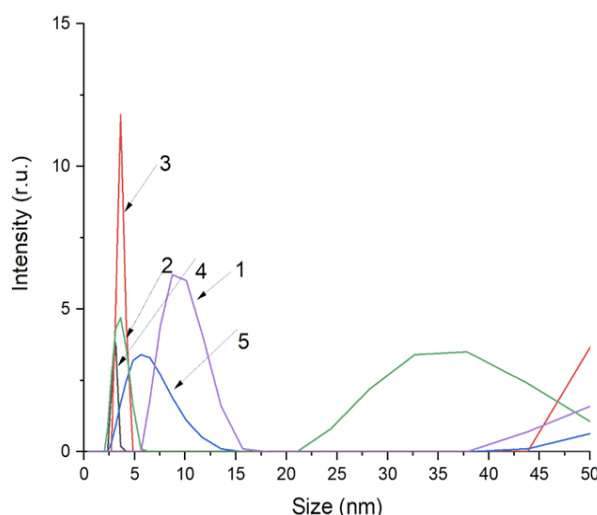


Fig. 2. Size distribution of CdTe NCs No. 1-5 (see Table 1).

According to Figure 2, the synthesized colloidal solutions of CdTe NCs contain small particles (2 nm and more).

Figure 3 shows the presence of USQDs in each sample, according to the characteristics given in Table 1. In this experiment, in order to form a larger number of USQDs, the most favorable synthesis conditions were selected for samples No.3 and No.5.

III. Photoluminescence spectra

Fig. 4 shows the photoluminescence (PL) spectra of the studied CdTe NC samples No.1-5. A characteristic feature of these spectra is the large spread of the PL maxima in the range of 517 nm - 541 nm, in contrast to the absorption spectra, in which the spread of the maxima is much smaller and is only 10 nm. This fact indicates that the studied USQDs (clusters) exhibit mainly surface PL caused by surface defects, some of which may be stored and thus not appear in the PL spectra. In our case, the degree of passivation by thioglycolic acid molecules depends on the technological conditions of synthesis of the studied samples, which explains the significant variation in the energy position of the PL bands.

IV. Excitation spectra of photoluminescence

Figure 5 shows the photoluminescence excitation spectra for colloidal solutions of CdTe nanocrystals. Sample 1 is characterized by a broad PLE with a maximum at 360 nm (~3.44 eV) and a shoulder at 410 nm (~3.02 eV). A band with a maximum at 532 nm (2.33 eV) is also observed. Sample No.2 is characterized by excitation with higher energies than sample No.1 (>3.44 eV). A band with a maximum at 510 nm (~2.43 eV) is also observed. Samples 3-5 are characterized by excitation light with a quantum energy > 3.44 eV. In the photoluminescence excitation spectra for these samples, a shoulder in the region of 400 nm (3.1 eV) is observed. Thus, the excitation spectra of the

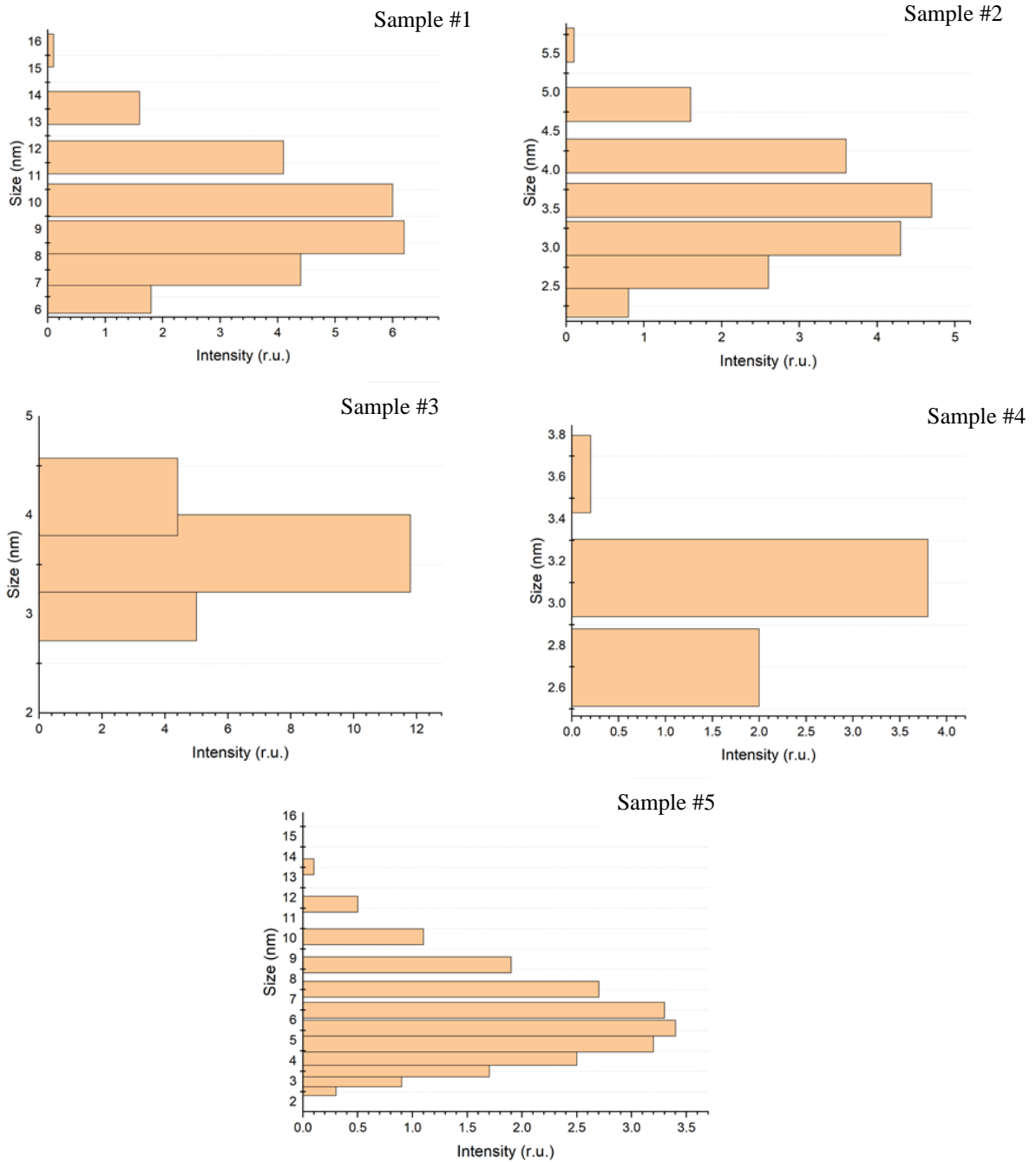


Fig. 3. Dimensions of CdTe NC samples No. 1-5 (see Table 1).

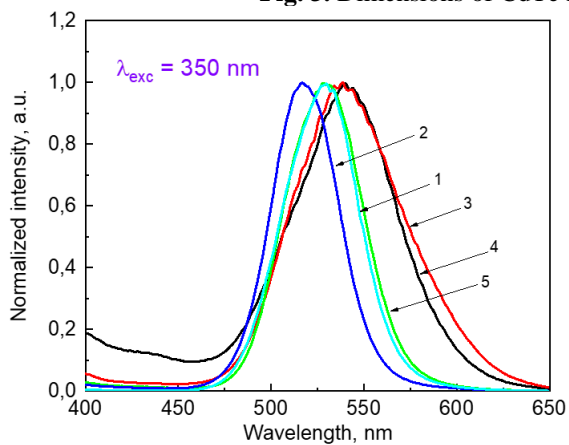


Fig. 4. Photoluminescence normalized spectra of CdTe NCs samples No. 1-5.

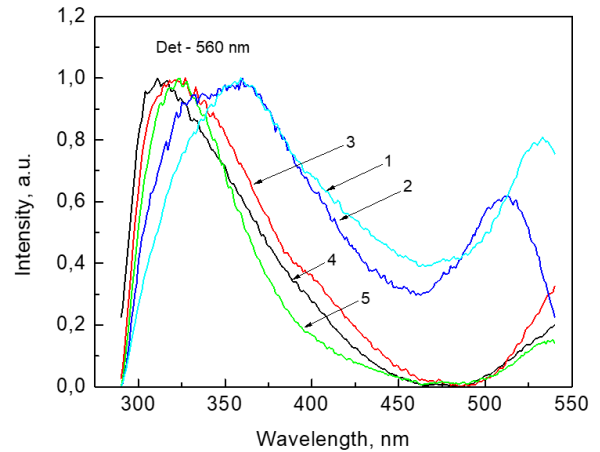


Fig. 5. Excitation spectra of photoluminescence of CdTe NCs samples No. 1-5.

PL of USQDs samples are determined by the peculiarities of the technological modes of their synthesis.

show that their size is ~ 2 nm. The presence of such USQDs is confirmed by our direct studies of the size of CdTe QDs on the Zetasizer Nano ZS. It was found that the photoluminescence of the USQDs is mainly due to surface defects.

Conclusions

A technology for colloidal synthesis of CdTe nanocrystals has been developed. It has been shown that the surface structure formed by the TGA stabilizer is of great importance for their further effective use. The stabilizing coating prevents the aggregation of parts of the dispersed phase and is therefore a crucial component of the formation of CdTe NCs. To obtain USQDs, a method of separating the colloidal solution into fractions by centrifugation is proposed. The optical absorption spectra and photoluminescence excitation spectra of the USQDs

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Колоїдний синтез та оптичні властивості ультрамалих квантових точок CdTe

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В даній роботі повідомляється про колоїдний синтез нанокристалів (НК) CdTe в реакторі, реакційне середовище якого складається з розчину солі CdI₂, тіогліколевої кислоти (ТГК) і лугу NaOH. Через такий розчин пропускали газоподібний прекурсор H₂Te, який отримували електрохімічно у гальваностатичній комірці. Розміри синтезованих НК варіювали, регулюючи потік телуроводню з гальваностатичної комірки. В свою чергу, потік телуроводню залежить від сили струму, який проходить через електроди комірки. Швидкість росту нанокристалів обумовлюється швидкістю подачі прекурсорів в реактор. Дослідження показали, що при такому синтезі, як правило, отримуємо НК CdTe різного розміру. Для розділення колоїдного розчину на фракції запропоновано метод його центрифугування, що дозволило виділити ультрамалі квантові точки (УМКТ) CdTe з розмірами приблизно 2 нм. Для отримання НК ультрамалих розмірів використовували малі значення сили струму (до 100 мА), незначну тривалість синтезу (0,5-1 хв) та високі значення рН (8 – 11) реакційного середовища. Дослідження спектрів поглинання зразків НК CdTe, взятих з виділеної методом центрифугування фракції з найменшими розмірами, показали, що енергія відповідних переходів значно перевищує ширину забороненої зони об'ємного CdTe (1,5 еВ), і які відповідають УМКТ (кластерам) CdTe. Проведені нами дослідження розмірів КТ CdTe на Zetasizer Nano ZS підтвердили наявність УМКТ з розмірами приблизно 2 нм. Показано, що фотолюмінесценція УМКТ зумовлена головним чином поверхневими дефектами.

Ключові слова: технологія синтезу, ультрамалі квантові точки, центрифугування, спектри поглинання, фотолюмінесценція, спектри збудження фотолюмінесценції.