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Synthesis of CdSe/ZnS Nanoparticles with Multiple Photoluminescence

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In this work, CdSe/ZnS nanostructures of Core-Shell type, that have multi-wave emission, are described and a scheme of possible electron transitions in the studied system is presented. CdSe nuclei were synthesized by mixing cadmium and selenium precursors without creating an inert atmosphere. The cadmium complex with sulphanilamide was used as a cadmium precursor and simultaneously as a stabilizing ligand. To grow the shell, zinc stearate and thiourea were gradually added to the solution of cadmium selenide nuclei in octadecene at 200°C. The obtained CdSe/ZnS nanoparticles were studied by UV-visible spectroscopy, photoluminescence, TEM, X-ray fluorescence spectroscopy (EDX), and Atomic force microscopy (AFM). The dependence of emission spectra on the excitation wavelength and the time of quantum dot synthesis are analysed for the studied systems. TEM studies show that the obtained CdSe/ZnS nanoparticles have the shape close to tetrahedral with an effective diameter up to 10 nm. The thickness of the ZnS shell is about 3-4 nm. From the absorption spectra of the CdSe/ZnS nanoparticles, it is clear that the shell growth leads to a sharp increase in the absorption in the short wavelength area, which means the formation of a wide gap ZnS material. The size of nanocrystals determined by AFM is 10-14 nm. EDX confirms the presence of zinc, cadmium, sulfur and selenium in the samples.

The obtained CdSe/ZnS nanostructures emit three fluorescence peaks in the visible range. They are attributed to exciton transitions in the nucleus, recombination at defects of the boundary between the core and the shell, and recombination at defects of the shell. Such property provides CdSe/ZnS nanocrystals with a wide range of functionalities.

Keywords: nanostructures, Core-Shell, CdSe, ZnS, quantum dots, photoluminescence.

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Introduction

Among semiconductor nanocrystals, cadmium selenide nanocrystals are of special interest. Such structures demonstrate high photoluminescence (PL) quantum yield in a wide range of the spectrum [1].

To increase the brightness of PL and its stability, CdSe nanoparticles are covered with the shells of a widegap semiconductor, such as ZnS. In the core-shell structure, more widegap semiconductor passivates the surface of the fluorescent nucleus, reducing the number of free valence states through which charge carriers could be recombined nonradiative. Also, the shell spatially separates the nucleus from the environment, as a result, we can reduce the sensitivity of optical properties to the influence of external factors. To grow such shells, the addition of metal and chalcogenide to the core solution at high temperatures it is often used. To avoid defects at the boundary of two crystal lattices of CdSe and ZnS, between them was placed a layer of cadmium sulfide, which has intermediate crystal lattice parameters and bandgap energy [2].

Achievements in the synthesis of quantum dots (QD) heterostructures open up the possibility of producing double-luminescent QD, which can be useful for various applications [3]. Such double PL QD allows us to study the electronic effects of coupling between two subcomponents. It becomes possible due to the spatial separation of the excited wave functions of charge carriers. All this allows both emitters to preserve partially their characteristics.

The first examples of double-luminescent QD were presented by a core/shell structure that contained few shell layers created from the narrow gap semiconductor materials separated by a barrier – widegap material. Such structures are generated either by cation exchange or by consecutive adsorption and reaction of ionic layers (SILAR). In these cases, the precursors are inserting either by an interchange of injections or by slow, continuous addition [4].

Another type of structure that demonstrates double PL is the structure “core - thick shell”. For the first time, such effect was observed in the structures of the CdSe core covered by a thick CdS shell. It is interesting to note that at low excitation intensities, only the red luminescence band was observed, but at higher excitation intensity, the particles also emitted a band in the green region of the spectrum [5].

Nanoparticles "CdSe core-ZnSe thick shell" were first described in 2015 [6]. For them, it was observed a decrease in the effect of "blinking" due to the more complete localization of charge carriers in the nucleus. The authors also predicted the possibility of the formation of the quasi type II core-shell structure in such systems with sufficiently small nucleus sizes (2 - 3 nm). However, in this research work authors did not measure the PL excitation spectrum and the dependence between the spectrum and the excitation intensity.

It is shown in [7] that effective passivation of CdSe crystals with a ZnSe shell, using zinc stearate, increases the photoluminescence quantum yield at room temperature by up to 60 – 85 %.

In our work, we first describe the synthesis of nanoparticles by type CdSe core-ZnS thick shell, which exhibits multicolor photoluminescence

Stable cadmium selenide nanocrystals in organic solvents can be obtained by various methods [8-11]. However, these methods are complicated due to the use of many components, the need for providing an inert atmosphere, and usage of toxic components such as phosphines, selenophen and its derivatives [12].

The feature of the synthesis of nanoparticles using the cadmium complex with 4-aminobenzenesulfamide is the stability of this complex. It does not melt and decompose until 300˚C. This means that under the conditions of synthesis, cadmium is in a bound complex form, whose reactivity is very temperature-dependent [9]. This allows using such complexes for slow down growth of the shell with a single loading of reactant, compared to the SILAR method.

I. Materials and methods of research

The synthesis of cadmium selenide nanoparticles was realized by mixing cadmium and selenium precursors without creating an inert atmosphere. The streptocide cadmium complex was used simultaneously as a cadmium precursor and as stabilizing ligand. The synthesis was made in a 50ml 3-neck flask. The complex with cadmium and streptocide weighing 0.2g was heated together with 26 ml of octadecene up to the synthesis temperature (200°C) and intensively stirred for 60 minutes. A 6ml of selenium precursor, produced by continuous (over 24 hours) mixing of the octadecene-selenium powder mixture (1:30 molar ratio) was injected in the Cd-solution. At stated intervals, aliquots (2 ml) were taken. The total duration of the synthesis was 5 hours.

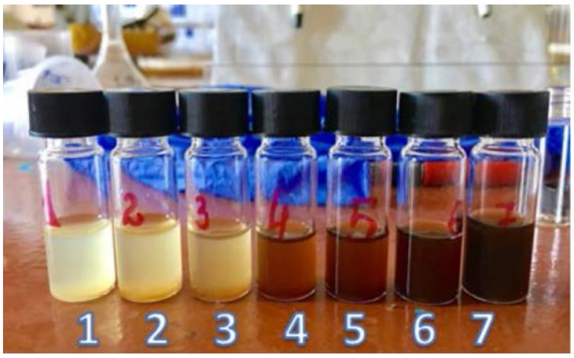

Fig. 1. Photo of aliquots of CdSe nanoparticles selected after the following reaction times: 1 – 15 min, 2 – 30 min, 3 – 75 min, 4 – 135 min, 5 – 195 min, 6 – 255 min, 7 – 315 min.

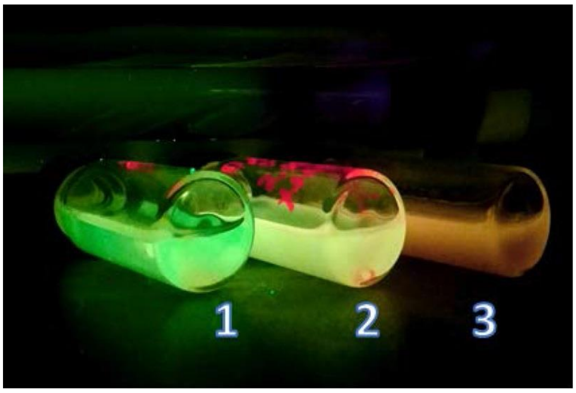

Fig. 2. Fluorescence of solutions illuminated by UV-light: 1 - CdSe quantum dots, 2 - intermediate nanostructures (CdSe + zinc stearate), 3 - CdSe/ZnS nanostructures.

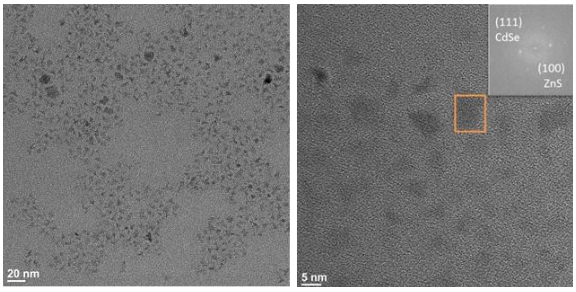

Fig. 3. TEM images of CdSe/ZnS nanostructures. Insertion - Fourier transform of a rectangular fragment of an image with identified indexes.

The formation of CdSe nanocrystals leads to the gradual color change of the reaction solution (Fig. 1):

The absorption spectra of CdSe nanoparticles are typical. The absorption edge is located between 500 - 570nm, which is equivalent to the formation of particles with a diameter ~ 2.5 nm [8]. The peaks of the PL spectra

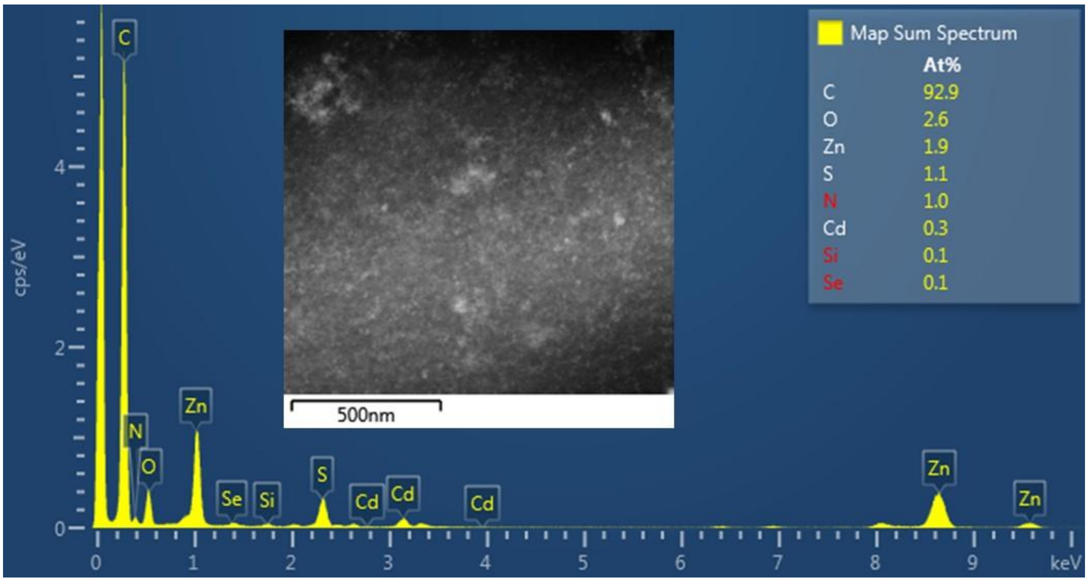

Fig. 4. X-ray fluorescence spectrum (EDX) of CdSe/ZnS nanostructures shown in the insertion.

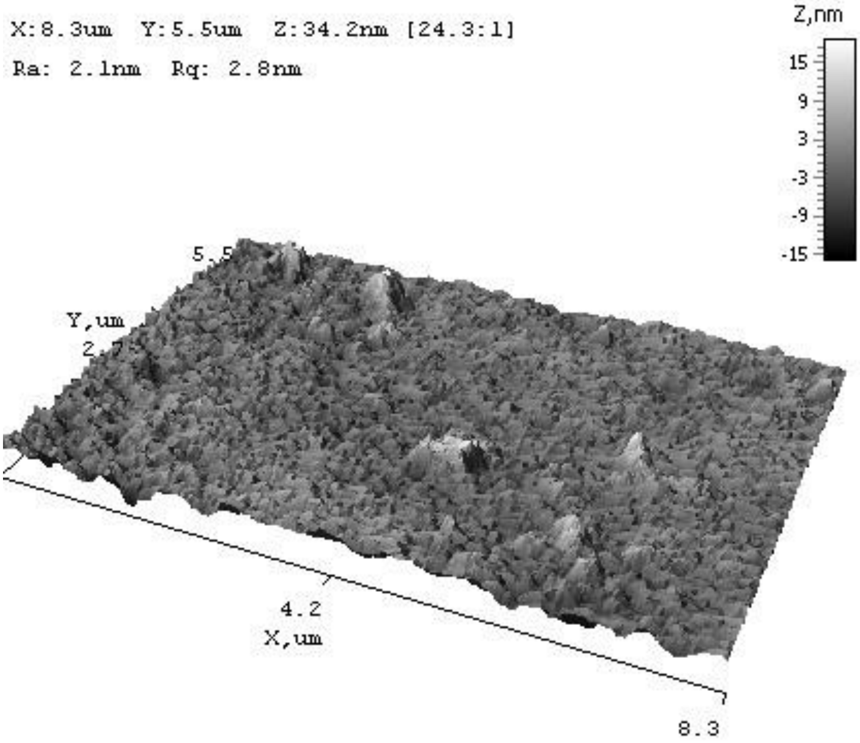

Fig. 5. 3D AFM image of the mica surface covered with CdSe / ZnS nanoparticles.

of the derived nanoparticles are characterized by a bathochromic shift from 500 to 545nm. The full-width – at-the –half-maximum of the peak – is about 100nm.

To grow the shell we gradually added zinc stearate and thiourea to a solution of cadmium selenide nanoparticles in octadecene, at a temperature of 200°C. Aliquots were taken at stated intervals. Total synthesis time – 150 min. CdSe quantum dots, intermediate nanostructures, which were received after zinc stearate addition, and CdSe/ZnS nanostructures exhibit fluorescence of green, yellow, and orange (Fig. 2).

II. Results and discussion

TEM studies show that obtained CdSe/ZnS nanoparticles have a shape close to tetrahedral with an effective diameter up to 10 nm (Fig. 3). Thereout we can conclude that the thickness of the ZnS shell is about 3 - 4 nm. At the same time, the high-resolution TEM analysis of the images allows us to identify interatom spacing – 2.1 - 2.2 A, 3.1 - 3.3 A, 3.5 A attributed to the

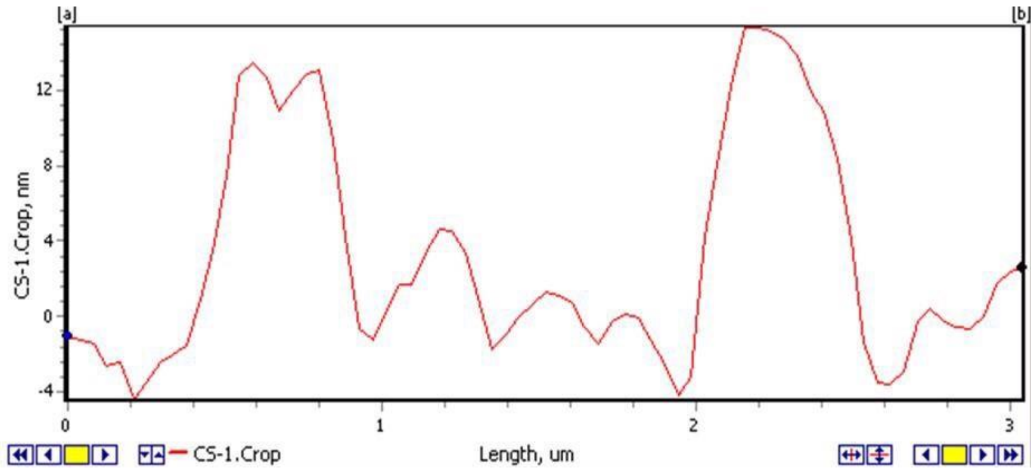

Fig. 6. Schematic representation of the mica surface profile with the adding of CdSe/ZnS nanocrystals.

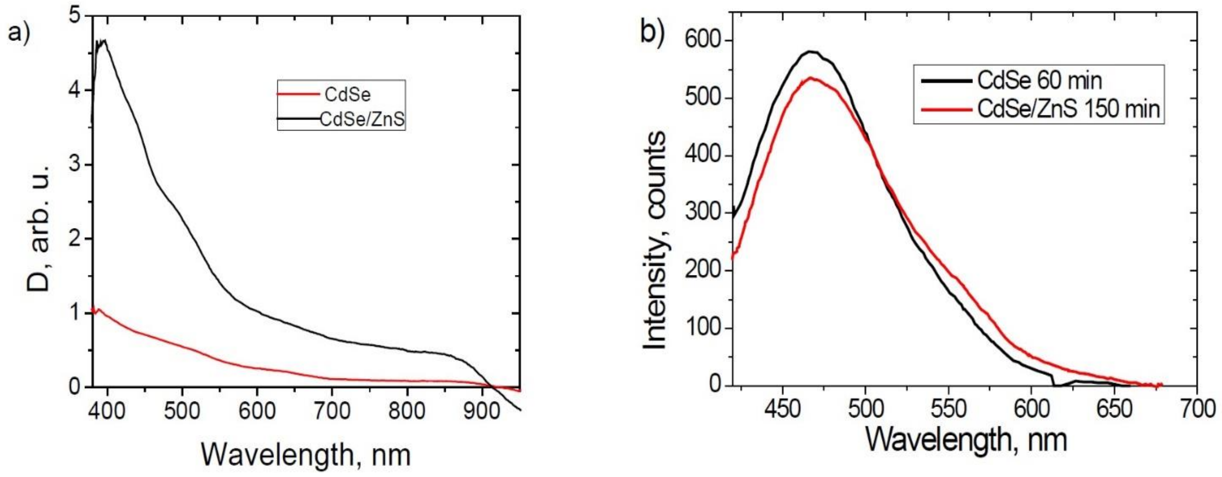

Fig. 7. a) Optical density spectra of CdSe nanoparticles and ZnS-coated CdSe nanoparticles, b) PL spectra of CdSe and CdSe/ZnS nanoparticles solutions after shell upbuilding while 150min.

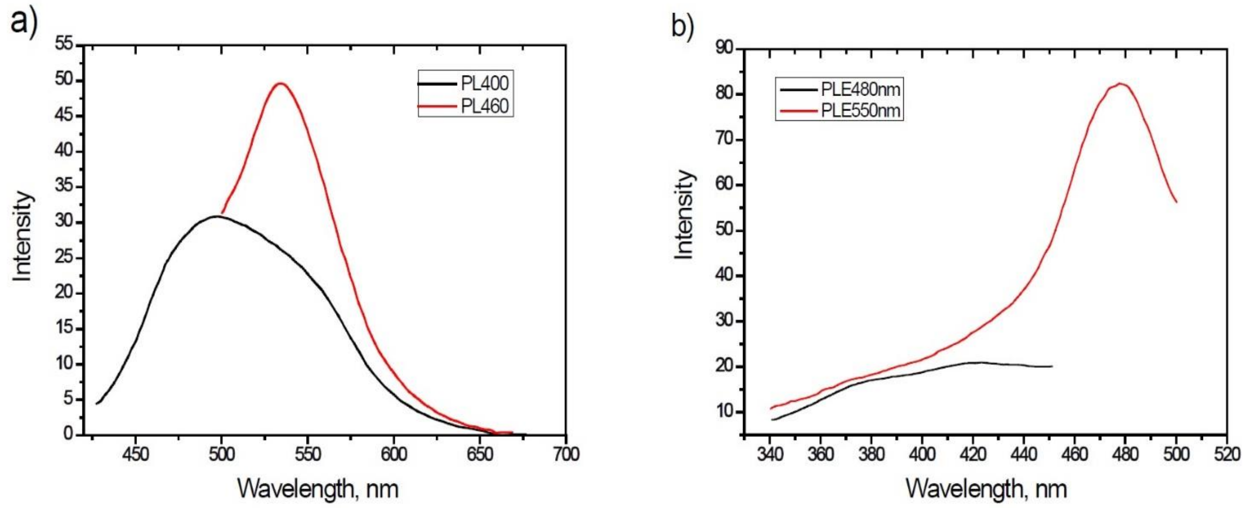

Fig. 8. a) PL spectra of CdSe nanoparticle solutions excited by waves of 460 and 400nm, b). PL excitation spectra of PL at the wavelength of 480 and 550nm.

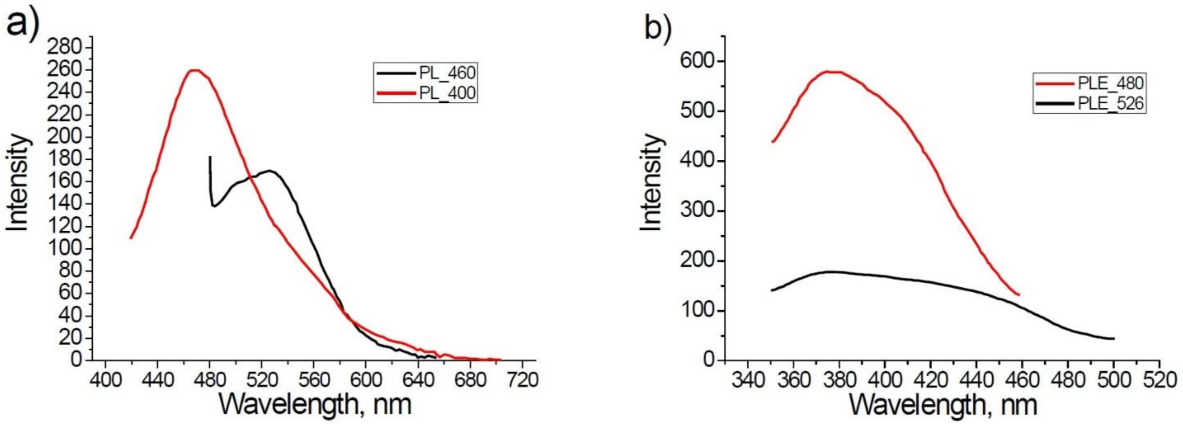

Fig. 9. a) PL spectra of solutions of CdSe+Zn^{2+} nanoparticles excited at the wavelength of 460 and 400 nm. b) PL excitation spectra of PL at the wavelength of 480 and 526 nm.

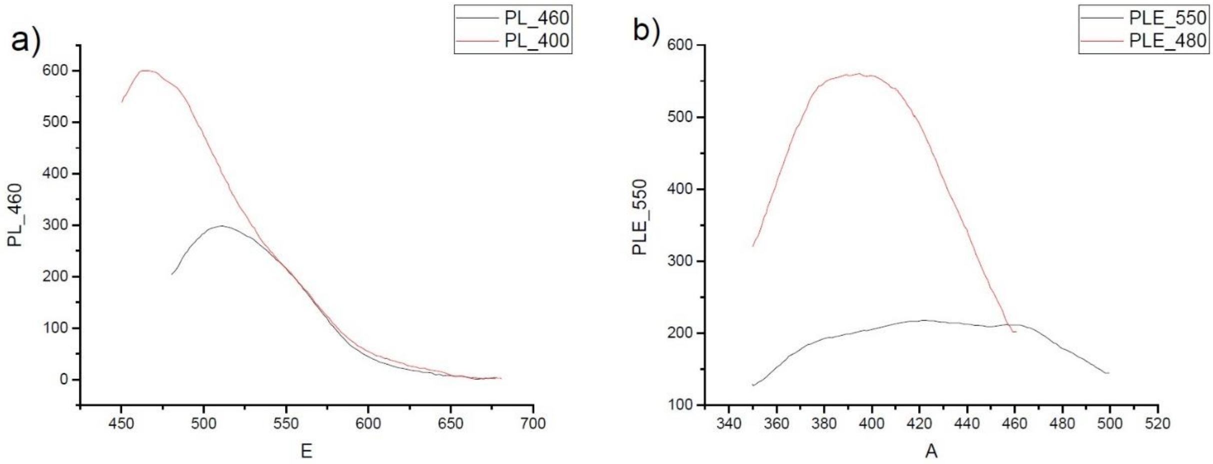

Fig. 10. a) PL spectra of CdSe/ZnS nanoparticle solutions excited by waves of 460 and 400 nm, b) PL excitation spectra at the wavelengths of 480 and 550 nm.

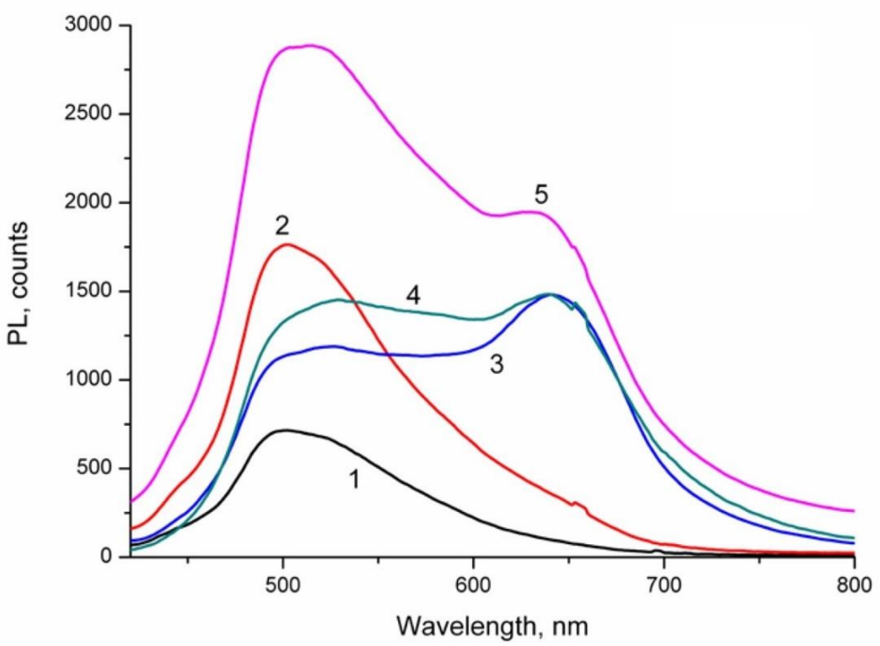

Fig. 11. PL spectra of cadmium selenide nanoparticles excited with 150 mW laser: 1 - before the start of the reaction, 2 - after the addition of zinc stearate (60 min after the start of the reaction), 3,4,5 - after the addition of thiourea (90, 120 and 150 min after the start of the reaction).

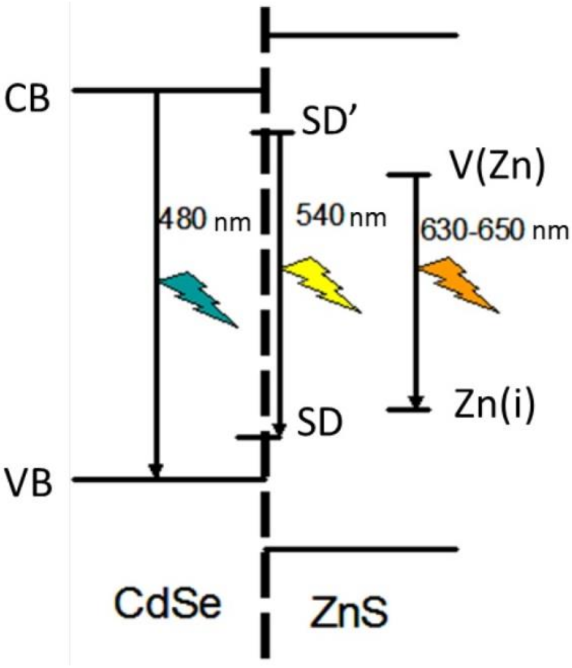

Fig. 12. Energy diagram of CdSe/ZnS nanoparticles. The straight solid arrows indicate the possible emissive recombination of charge carriers. CB, VB – the conduction band and band gap of CdSe, V(Zn) – vacancies of zinc atoms, Zn(i) are interstitial zinc atoms, SD' and SD – defect levels at the core-shell boundary.

planes (102) and (100) for ZnS and (111) for CdSe. The formation of particles with a similar structure was observed in [13].

Qualitative and quantitative analysis realized by the method of X-ray fluorescence spectroscopy (EDX) confirms the presence of zinc, cadmium, sulfur, and selenium in the samples. Noticeable nitrogen and sulfur content indicate that a certain part of the sulphanilamide complex of cadmium and zinc stearate is contained on the surface of the particles.

The presence of formed CdSe/ZnS nanostructures was confirmed by atomic force microscopy. 3D image and image of the surface's contour of mica with nanoparticles supported on it are shown in Fig. 5 and 6. The size of nanocrystals determined by this method is 10-14nm. The shell thickness, computed with TEM and AFM measurements, is larger than the Bohr exciton radius for zinc sulfide (3.8nm) [14], all this leads to the formation of energy levels which is aligned with the massive ZnS.

To study the optical properties of the formed nanostructures, the absorption band and photoluminescence spectrum were measured (Fig. 7) [15].

The growth of the shell leads to a sharp increase of the absorption in the shortwave region (Fig. 7a), which follows the formation of the widegap ZnS material. As you can see from Fig. 7b, this process is also followed by the widening of the right edge of the luminescence spectrum.

The asymmetry of the photoluminescence peak of CdSe nanoparticle solutions indicates that there are several mechanisms of emissive recombination. The low-energy PL maximum at a wavelength of 520 – 560 nm was separately identified by the excitation wavelength of 460 nm (Fig. 8a).

The photoluminescence excitation spectrum of CdSe nanoparticles at two wavelengths of 480 and 550 nm showed that higher energy PL is most effectively excited by waves with a length of 360 – 420 nm, while the excitation of the longwave component is quite effective even with the use of longer waves and get to the peak at 480nm (Fig. 8b).

Addition of Zinc ions and short-term heating of the mixture results to the partial passivation of surface defects, which appears in a significant decrease of the relative intensity of the PL long wavelength (Fig. 9a) in comparison with the short wavelength of the excitonic PL. The PL excitation spectrums are characterized by the same tendency as CdSe nuclei, but the intensity of the excitonic component is higher according to the excitation wave (Fig. 9b).

The similar type of emission spectrum was observed for solutions received after the addition of thiourea (150 min after the start of the reaction) (Fig. 10a and 10b). This indicates that the defective structure of the CdSe nucleus does not change much after the ZnS shell sheathing. Therefore, the relative position of the energy levels remains constant. The energy level, which is slightly below in connection with the level of the conduction band of the cadmium selenide nucleus, be aligned with the surface defects at the CdSe-ZnS boundary. This gives possibilities for the partial transition of excited electrons in the nucleus to the boundary with the shell and their further emissive recombination, which is appeared by a low-grade peak with a longer wavelength [16].

Irradiation of nanoparticles with high-intensity laser leads to the appearance of an additional peak in the photoluminescence spectrum at the wavelengths of 650nm (Fig. 11). This peak is not observed in the spectrum of CdSe nucleus. After the addition of zinc stearate and thiourea, its intensity becomes comparable to the intensity of the main peak at 500nm. With further thermal treatment, the height of this peak decreases.

It is rather obvious, that this PL is defective. It does not appear at low excitation intensities since the probability of recombination between the nucleus and the major ZnS shell levels remains high. The [17] describes the appearance of an orange emission band in the spectrum of ZnS nanoparticles, which the authors relate to transitions between levels which are equivalent to interstitial zinc atoms and vacancies of zinc. The growth of the ZnS shell due to the longer thermal treatment causes the minimizing of its fractional intensity, that coming from a reduction of the number of defects and the increasing of electron-phonon interaction.

Position of energy levels and radiative transitions are summarized in Fig. 12.

Therefore, we have produced CdSe/ZnS nanostructures of the type of Core-Shell, in the emission of which we can clearly distinguish three PL peaks in the visible range. They are explained by the excitonic transitions in the nucleus, recombination at the boundary defect between the nucleus and the shell, and recombination at shell defects. Such emission provides these nanocrystals with a wide range of functionality that can be advantageously used for different types of color LEDs and displays.

Conclusions

A low-temperature technology for synthesis of Core-Shell CdSe/ZnS nanostructures with multicolor emission was developed and a scheme of transitions in the explored system is proposed.

The developed method of synthesis involves the use of less toxic reagents and allows control of both the size of the nucleus and the size of the shell. The spectral analysis shows that all this significantly affects the final parameters of the obtained nanomaterials.

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Синтез наночастинок CdSe/ZnS з мультимодальною фотолюмінесценцією

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У роботі описано наноструктури CdSe/ZnS типу core-shell, які володіють мультихвильовим випромінюванням, та запропоновано схему можливих енергетичних переходів в досліджуваній системі. Синтез ядер CdSe здійснювали змішуванням прекурсорів кадмію і селену без створення інертної атмосфери. Як прекурсор кадмію і одночасно як стабілізуючий ліганд використано комплекс кадмію зі стрептоцидом. Для нарощування оболонки до розчину наночастинок кадмій селеніду в октадецені поетапно додавали цинк стеарат і тіосечовину за температури 200°C. Отримані наночастинки CdSe/ZnS вивчалися за домомогою УФ спектроскопії, фотолюмінесценції, ПЕМ, рентгенофлуоресцентної спектроскопії (EDX), АСМ. Для синтезованих систем проаналізовано залежність спектрів випромінювання та фотолюмінесценції від довжини збуджуючої хвилі та часу синтезу квантових точок. Дослідження ПЕМ показують, що отримані наночастинки CdSe/ZnS мають форму близьку до тетраедричної з ефективним діаметром до 10 нм. Товщина оболонки ZnS становить близько 3-4 нм. Зі спектрів поглинання наночастинок CdSe/ZnS видно, що ріст оболонки призводить до різкого збільшення поглинання в короткохвильовій області, що відповідає утворенню широкозонного матеріалу ZnS. Розмір нанокристалів, визначений за допомогою АСМ, становить 10 - 14 нм. EDX підтверджує наявність цинку, кадмію, сульфуру та селену у зразках.

Для одержаних наноструктур CdSe/ZnS характерні три піки ФЛ у видимому діапазоні. Вони пов’язані з екситонними переходами в ядрі, рекомбінацією на дефектах межі між ядром і оболонкою та рекомбінацією на дефектах оболонки. Таке випромінювання забезпечує нанокристали CdSe/ZnS широким спектром функціональних можливостей.

Ключові слова: наноструктури, Core-Shell, CdSe, ZnS, квантові точки, фотолюмінесценція.