

## Synthesis And Modification Of Hybrid Cdse/Zns Quantum Dots

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### Abstract

*The CdSe quantum dots (QD) synthesized by the colloidal method were stabilized with oleic acid (OA) and their optical properties were studied. The average size of the detected nanoparticles, depending on the peak of exciton absorption, was 3.7 nm. CdSe/ZnS hybrid core-shell quantum dot nanocrystals were synthesized by depositing a ZnS shell on the surface of CdSe nanoparticles. At the same time, the quantum yield of luminescence increased from 1.5 to 19%. As a result of the exchange of cadmium ions for zinc ions on the surface of the core of hybrid quantum dots, the size of the CdSe nucleus decreased to 2.8 nm. As a result, the absorption of the CdSe/ZnS hybrid quantum dot and the peak of the spectral wavelengths of luminescence moved to a short region. After growing the ZnS shell, a slight increase in the total hydrodynamic quantum dot particle size was observed. The effect of the nature of stabilizers on the synthesis of nanoparticles is studied. This process was carried out by surface alteration reactions. Molecules retained by the thiol group, which are strongly bound to the surface of nanocrystals, have been found to have effective exchange properties of dodecyl esters of dodecanthiol-1 and dihydrolipoic acid. It is proved by infrared (IR) spectroscopy that stabilizers were replaced. The optical-dimensional properties of stabilized quantum dots were studied.*

**Keywords:** quantum dots, colloidal synthesis, cadmium selenide, zinc sulfide, “core shell”, nanoparticles, luminescence, photoluminescence, ligand, precursor.

### 1. INTRODUCTION

Colloidal quantum dots are semiconductor nanocrystals stabilized by surfactant molecules. The typical dimensions of quantum dots are 1–10 nm, but these limits depend significantly on the nature of the material and the electronic properties of the particle structure. Quantum dots are large associates, consisting mainly of CdSe, ZnS, InAs, Si, InP and other simple semiconductor materials (consisting of several tens, hundreds of atoms) [1-3].

The following promising areas of application of quantum dots in optoelectronic systems are developing: the development of laser environments [4], light-emitting diodes (LEDs) [5], displays [6], solar cells [7], biomarkers and others [8,9].

Among the well studied nanoparticles are cadmium chalcogenides, which have good luminescent properties over a wide range of electromagnetic spectrum [10]. The development of a hybrid “core/shell” type quantum dots can lead to a further increase in the luminescence intensity. In particular, quantum dots consisting of elements group II and VI have a wide band gap and have high photoluminescence efficiency at room temperature [6].

The synthesis of quantum dots with a core/shell structure is formed by the growth of monolayers by adding precursors to the reaction medium. The thickness of the shell is one of the important parameters determining the properties of the crystal, which allows one to determine the yield, stability, and other properties of quantum dots [11,12].

It should be noted that CdSe/ZnS quantum dots has a high luminescence property [13]. The ZnS shell fills the crystal lattice and reduces defects on the core surface. In addition, it localizes the charges inside the core, limiting their nanoparticles to the surface and bonding fluorescent particles. In addition, the shell increases the chemical photostable stability of quantum dots.

It is known that colloidal synthesis methods allow the production of high quantum efficient nanoparticles with a short size distribution. Depending on the synthesis conditions, the stabilizers are selected from fatty acids, amines, thiols and various organic solvents that provide distribution in

different environments. They are adsorbed on the phase boundary, creating a barrier that prevents the accumulation of nanoparticles and passivates the surface energy state of the nanocrystals, which in turn provides monodisperse-sized, stabilized quantum dots [14,15].

Changing the surface area of quantum dots is usually done by means of a ligand (stabilizer). For example, quantum dots with good luminescent properties obtained in an organic medium are transferred to an aqueous medium as a result of the replacement of surface stabilizers. Also, different molecules or compounds exhibit different beneficial biological properties on the surface due to changes in surface condition [16,17].

To dissolve particles in polar solvents, it is recommended to change the layer of stable molecules on the surface of quantum dots. This can be solved by using long-chain thiols, obtaining nanoparticles in an aqueous medium, and replacing stabilizer molecules on the surface of a quantum dot with molecules obtained in an organic medium. Therefore, during the exchange of ligands, the quantum dots are stabilized with fatty acids or amines, which are then replaced by molecules retained by the thiol group.

Numerous studies on the changing of hydrophobic ligand with hydrophilic have been reported in the paper [18-21]. According to them, the transfer of the obtained quantum dots to the aqueous medium is easier in hydrophilic stabilizers.

To this end, the task was set to develop a method for the conversion of hydrophobic ligand to hydrophilic in the process of synthesis of hybrid quantum dots. Through this process, nanoparticles with multifunctional properties can also be obtained.

Molecules containing dodecanthiol-1 and dodecyl ester of dihydrolipoic acid, stored by the thiol group, were used as model stabilizers. To carry out ligand replacement, CdSe and hybrid nanoparticles with CdSe/ZnS “core / shell” quantum dots, previously stabilized with oleic acid, were synthesized.

## 1. EXPERIMENTAL

### Chemical reagents, materials and equipment

Cadmium oxide (CdO, 99%, Vecton, Russia), selenium (Se, 99%, Reakhim, Russia), sulfur powder (S, Lenreaktiv, Russia), zinc oxide (ZnO, 99%, Rekhim, Russia), oleic acid (OA, 98%, Ekos, Russia), oleilamine (ODA, 90%, Acros, Belgium), rodamin 6G (96%, Ekos, Russia), 1- octadecen (ODE, 90% Acros, Qatar), dodecanethiol-1 (DT, 98%, Alfa Aesar, UK), dodecyl ether of dihydrolipoic acid (DDL, 96%, Alpha Aesar, UK), toluene (99%, Vecton, Russia), ethanol (96%, Vecton, Russia), acetone (99%, Ecos, Russia) were used without any further purification.

### Instruments

Absorption spectra were obtained on a “Perkin Elmer Instrumental LAMBDA 35” spectrophotometer, and luminescence spectra were recorded on a “Cary Eclipse” (Varian) spectrometer. Measurements were made at 25°C.

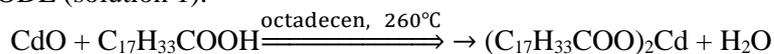
IR spectra were obtained with a Bruker Alpha-T FT-IR spectrometer. TP-350-E (Mirlab) magnetic mixer was used.

The calculation of the quantum yield of the luminescence of quantum dots was performed with respect to a solution of rhodamine 6G in ethanol. A Malvern Zetasizer Nano analyzer (dynamic scattering of light scattering) was used to determine the hydrodynamic size of a quantum dot particle. Measurements were made at 25°C.

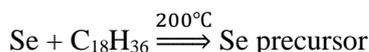
### Synthesis of CdSe and CdSe / ZnS “core/shell” quantum dots

The synthesis of CdSe quantum dots was carried out with partial modifications based on the method described elsewhere [22-24].

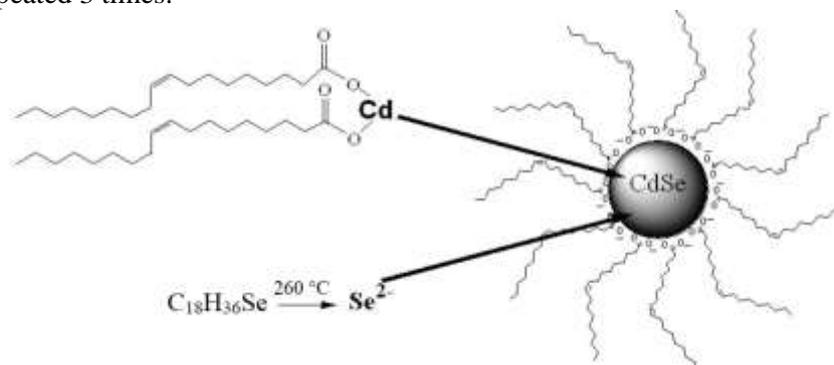
In argon atmosphere, mixture of 0.256 g (2 mmol) of CdO with 5.04 ml of oleic acid was dissolved in 20 ml of ODE (solution 1).



0.158 g (2 mmol) of selenium was dissolved in 10 ml of ODE at 200°C in argon atmosphere (solution 2).



The process of synthesizing CdSe quantum dots was carried out by mixing solutions 1 and 2 at 260°C for 3 min. To fast cooling the resulting mixture, 10 ml of ODE and 10 ml of toluene were added to the solution. Ethanol and acetone are added to the solution until tarnished to clear the mixture of unaffected precursors. The mixture was then centrifuged at 6000 rpm for 20 minutes and separated into separate phases. The resulting precipitate was dissolved in toluene. The cleaning process was repeated 3 times.



**Figure 1. The mechanism of formation of CdSe quantum dots**

The method proposed by the authors in their work [25 - 28] was used to grow the ZnS shell around the CdSe core.

Therefore, in the preparation of a solution of zinc oleate (0.1 M), 0.0405 g of ZnO was prepared by dissolving a mixture of 1.41 ml of oleic acid and 3.6 ml of ODE at a temperature of 260°C. Dissolving 0.016 g of sulfur in 5 ml of ODE at the temperature 200°C, solution (precursor) of sulfur (0.1 M) was obtained.

20 ml solution was prepared by adding 5 ml of ODE to quantum dot solution of CdSe ( $6.6 \cdot 10^{-6}$  mol/l) in toluene and heated to 200°C until the toluene in the mixture evaporated. Then 2.2 ml of oleilamine and 4.7 ml of zinc oleate solution were added and mixed for 15 min. Thereafter, a total of 4.7 ml of sulfur solution (precursor) was added to the reaction mixture every 15 minutes. The mixture was stirred in a magnetic stirrer for 30 min at 200°C to allow the components in the mixture to fully react. The purification process was performed in the same manner as for CdSe quantum dots.

### The process of ligand exchange at CdSe/ZnS quantum dots

The previously synthesized CdSe/ZnS quantum dot was added to 1 ml ( $4.35 \cdot 10^{-5}$  mol/l) toluene solution of the corresponding ligands (25  $\mu$ l DT and 16 mg DDL) and mixed at 80°C for 2 h. The mixture then centrifuged by adding ethanol until it becomes cloudy. The resulting quantum dot precipitate was dissolved in toluene. The process was repeated 3 times.

### Calculation of the quantum yield of nanocrystals

The quantum yield of the synthesized CdSe and hybrid CdSe/ZnS nanocrystals was determined by the coumarin method, based on the solution of rhodamine 6G (96%) in ethanol [29,30]. The quantum yield of luminescence was determined in quartz cuvettes. An alcohol solution of rhodamine 6G was used as a reference sample. Quantum dot samples were diluted to the desired optical density value, and then photoluminescence spectra were obtained. Quantum yield was determined using the following equation:

$$QY = QY_{\text{rhod}} \cdot S_{\text{QD}}/S_{\text{rhod}}$$

In this case, QY is the quantum yield,  $QY_{\text{rhod}}$  – the quantum yield of rhodamine 6G (96%),  $S_{\text{rhod}}$  – the field surface of the luminescence spectra of rhodamine 6G,  $S_{\text{QD}}$  – the field surface of the luminescence spectra of a quantum dot sample. Because the refractive indices ( $n_d$ ) of alcohol ( $n_d - 1.3611 \cdot 10^{20}$ ), hexane ( $n_d - 1.3749 \cdot 10^{20}$ ) and toluene ( $n_d - 1.4960 \cdot 10^{20}$ ) were close to each other, their effects were not considered.

## 2. Results and discussion

CdSe quantum dots was synthesized at high temperatures in an octadecene environment and oleic acid was used as a stabilizer.

The excitation maximum of the obtained CdSe quantum dots is appeared at a wavelength of 576 nm (Fig. 2). The average particle size (3.7 nm) was calculated based on the position of the excitation peak [31].

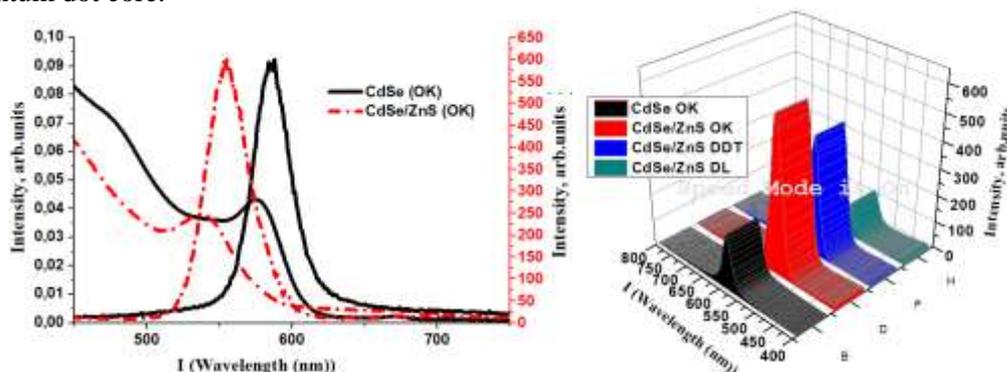
Obtaining high luminescence quantum yields for hybrid quantum dots is important for research. This can be achieved by growing a thin layer of ZnS shell on the surface of the semiconductor CdSe quantum dots.

Therefore, the shell growth method was used in this study [32]. To do this, metal and chalcogenide precursors were added to the CdSe quantum dot solution at high temperature, respectively [33].

The amount of zinc and ions of sulfur atoms in the precursors needed to grow the required ZnS shell was calculated by the method of the authors [7,34–36].

From the obtained absorption spectra (Fig. 2) it can be seen that as the ZnS shell grows, the maximum of the excitation peak in the spectrum shifts towards the short-wavelength region. It is estimated that during the growth of the ZnS shell, the size of the CdSe core decreased from 3.7 to 2.8 nm as a result of the exchange of cadmium atoms on the surface of the core with ions of zinc atoms.

The emission spectrum of CdSe quantum dots is symmetrical, with its peak in the 587 nm range (Figure 2). The quantum yield of quantum dot nanoparticles relative to rhodamine 6G was 1.5%. The growth of the shell around the core led to a significant increase in luminescence intensity, and a quantum yield increase of up to 19% was observed for hybrid CdSe/ZnS QDs. Also, the emission peak moved to the range up to 555 nm. This phenomenon is associated with a decrease in the size of the quantum dot core.



**Figure 2. Absorption and emission spectra of CdSe and CdSe / ZnS quantum dots ( $\lambda_{exc} = 350\text{nm}$ )**

The average hydrodynamic size of the obtained CdSe quantum dots was 8.4 nm, taking into account the stabilizing shell (oleic acid) (Figure 3). From this it can be determined that the thickness of the ligand shell is 2.35 nm, given that the size of the CdSe quantum dot core is 3.7 nm. However, the growth of the ZnS shell resulted in an increase in the hydrodynamic size of the particles to 9.3 nm (Figure 3). According to the absorption spectra, the size of the CdSe core decreased to 2.8 nm because the thickness of the stabilizer shell remained unchanged. Therefore, the ZnS shell thickness increased by 0.9 nm.

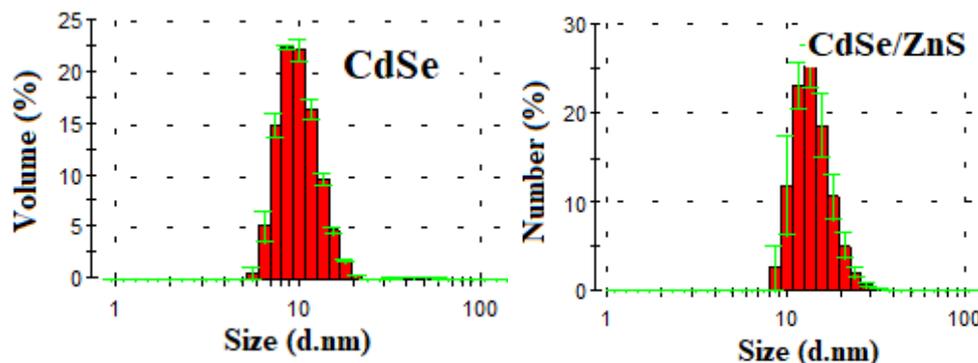


Figure 3. The average hydrodynamic size distribution diagram of the obtained quantum dots

A ligand exchange reaction was applied at the resulting CdSe/ZnS hybrid quantum dot. In the replacement of ligands (qualitatively) were chosen molecules of similar nature, i.e. dodecanthiol-1 (Figure 4) and dodecyl ester of dihydrolipoic acid (DDL) (Figure 5), which retain the thiol group, because the molecules of these substances form a strong bond on the nanoparticle surface.

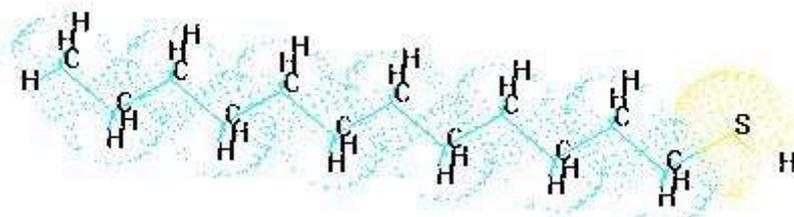


Figure 4. Dodecanthiol-1

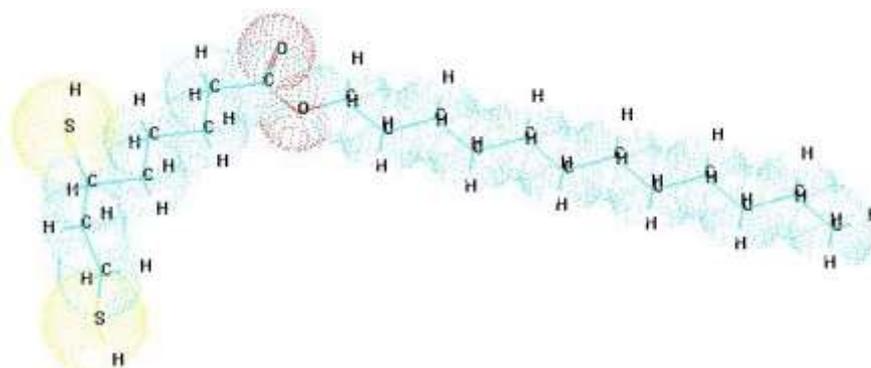
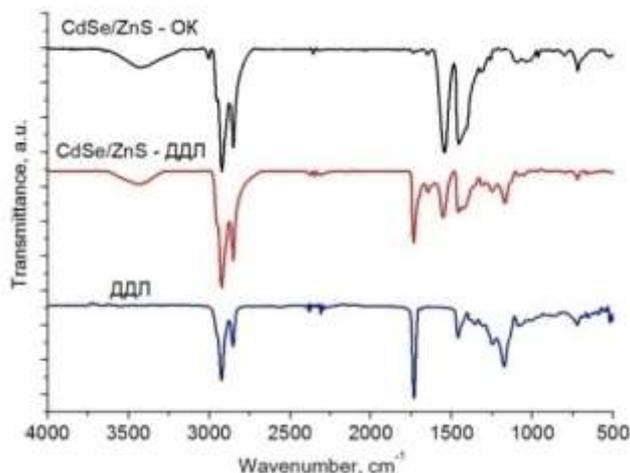


Figure 5. Dodecyl ester of dihydrolipoic acid

In the choice of ligands, an excess amount of stabilizer obtained for the replaced one. For this purpose, the concentration of quantum dots and the specific surface area were determined, as well as the number of moles of oleic acid (OA) molecules bound to the surface of nanoparticles and the amount of moles [37,38]. Five times the amount of thiol stabilizers was used to qualitatively replace oleic acid molecules.

In the infrared spectra of CdSe/ZnS hybrid quantum dots stabilized with oleic acid, intense symmetrical and asymmetric oscillation signals of the oleate anion  $\text{COO}^-$  group are present in the  $1546$  and  $1456\text{ cm}^{-1}$  ranges (Figure 6). In turn, the presence of a strong signal with a value of  $1734\text{ cm}^{-1}$  in the  $-\text{COOR}$  group in the DDL molecule and the bending mode intensity in C-O are in the range of  $1249$  and  $1174\text{ cm}^{-1}$ . The valence vibration signals  $2922$ ,  $2854$ , and  $1461\text{ cm}^{-1}$  belong to groups C-H. The complex ether bond signals in the DDL-modified CdSe/ZnS quantum dots correspond to  $1734\text{ cm}^{-1}$ ,  $1248\text{ cm}^{-1}$  for the C-O bond, and  $1171\text{ cm}^{-1}$ , respectively. In this case, the valence oscillation signals of the oleate anion  $\text{COO}^-$  group are significantly reduced. In the IR spectrum of dodecanthiol-modified quantum dots, it was observed that the value of the vibration signals of the  $-\text{COO}^-$  group decreased in the same way. Thus, an exchange between the ligands occurred during the reaction, but

only a small fraction of the oleic acid molecules remained unchanged. To stop the ligand exchange process, it is necessary to increase the concentration of the replaced ligand or repeat the reaction step several times.

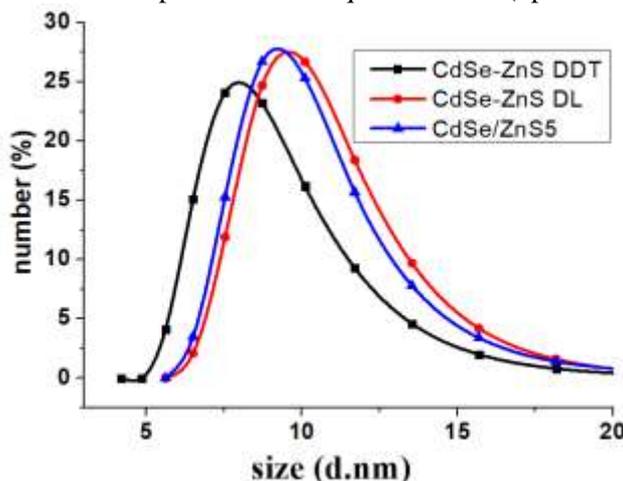


**Figure 6. IR spectra of CdSe/ZnS quantum dots and DDL**

No significant changes were observed in the absorption and luminescence spectra of the modified hybrid CdSe/ZnS quantum dots with dodecanthiol and DDL. However, the luminescence quantum yield (in value) of quantum dots modified by dodecanthiol was slightly reduced (up to 15%).

However, for CdSe quantum dots, a complete decrease in intensity in the luminescence spectra was observed when oleic acid was replaced by dodecanthiol. In summary, the ZnS shell plays an important role in the localization of charge carriers in the CdSe core and limits their access to the quantum dot surface. However, in the process, there are many defects, and molecules (thiols, oxygen, water, etc.) that suppress luminescence are also involved.

Based on the dynamic scattering data of light scattering, the change in the surface area of the quantum dot also leads to a change in the hydrodynamic size of the nanoparticles (Figure 7). The average hydrodynamic size of dodecanthiol-coated quantum dots is 8 nm, which is smaller than that of CdSe/ZnS quantum dots (9.3 nm). The reason for the reduction in nanoparticle size is in the small size of the dodecanthiol molecule relative to the molecular length of oleic acid. The use of DDL as a stabilizer has led to an increase in the particle size of quantum dots (up to 9.6 nm).



**Figure 7. Size distribution diagram of CdSe/ZnS hybrid quantum dots coated with different stabilizers**

The values of the quantum dots stabilized with different stabilizers on the basis of theoretical calculations and from the practical results obtained by the method of dynamic scattering of light are given in Table 1:

**Table 1. Dimensional characteristics of hybrid CdSe/ZnS quantum dots**

	CdSe (OA)	CdSe/ZnS (OA)	CdSe/ZnS (DT)	CdSe/ZnS (DDL)
<b>The mean hydrodynamic size of CdSe quantum dots</b>	8.4 nm	9.3 nm	8 nm	9.6 nm
<b>CdSe core size (nm)</b>	3.7 nm	2.8 nm	2.8 nm	2.8 nm
<b>ZnS shell size</b>	-	0.9 nm	0.9 nm	0.9 nm
<b>Stabilizer shell size</b>	2.35 nm (OA)	2.35 nm (OA)	1.7 nm (DT)	2.5 nm (DDL)

### 3. Conclusions

Synthesis of oleic acid-stabilized CdSe and its hybrid CdSe/ZnS quantum dots was performed and their optical-dimensional properties were studied.

Surface stabilizers for quantum dots were modified with hydrophilic thiol ligands. Based on the IR spectra, it was found that a certain proportion of the initial oleic acid stabilizer molecules remained unchanged. The presence of the ZnS shell allowed the luminescence of the modified quantum dots to be modified with thiol stabilizers.

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