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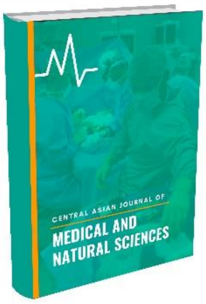

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SYNTHESIS AND LUMINESCENT PROPERTIES OF NANOCRYSTALS IN THE CORE/SHELL

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ABSTRACT: On the basis of a semiconductor material, a hybrid CdSe/ZnS quantum-sized (1-10 nm) hybrid of cadmium selenide with a “core-shell” structure was synthesized. The absorption and luminescence spectra of quantum dots were studied and quantum yield was calculated theoretically. The values of the theoretical and experimental dimensions of CdSe nanocrystals were studied comparatively. Optimal temperature conditions for efficient synthesis were determined. CdSe quantum dots stabilized with oleic acid were obtained by the colloidal method and their optical properties were studied. By growing a ZnS shell onto the surface of CdSe nanoparticles, CdSe/ZnS core-shell hybrid QDs are synthesized. Ligand exchange reactions were carried out under mild conditions using an excess amount of a thiol stabilizer. The fact of the replacement of stabilizers was established by IR spectroscopy.

KEYWORDS: Quantum dot, CdSe, CdSe/ZnS, stabilizer, oleic acid, nanoparticle, size, nanocrystal.

INTRODUCTION

Quantum dots (QDs) - optically active semiconductor nanoparticles are of interest as components of light-emitting devices, solar cells, luminescent sensors and new-generation biomarkers [1]. Quantum dots attract the attention of researchers due to their unique optical and electronic as well as physicochemical properties [2]. These unique features expand their applications in opto-electronic devices, including as base element materials for transistors and solar cells, as well as in high-speed quantum computer chips and various data transmission equipment. It can also be seen that quantum dots are currently used in large-scale biomedical applications [3].

Nowadays, along with the growing demand of mankind for new nanotechnologies, chemical nanotechnologies are also developing rapidly [4]. Therefore, in the field of nanochemistry, the scientific literature pays great attention to the development of nanotechnologies and their application in various fields of human activity [5]. In the last decade, the synthesis of nanocrystals of metals and semiconductors, which defines the main direction of research in the development of chemical nanotechnologies, has become particularly important [6].

Among the well studied nanoparticles are cadmium chalcogenides, which have good luminescent properties over a wide range of electromagnetic spectrum [7]. 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 [8].

QDs are nanoparticles composed of atoms of semiconductor materials whose electronic properties occupy a range of properties of hybrid structures and discrete molecules. These features are related to the onset of the quantum effect level [9]. The electron transfer band of quantum dots depends on their size, chemical composition, and nature. One way to influence the properties of QDs is to add additional atomic ions to their system. The literature analyzes that the conversion of semiconductor cations into atoms of 3D-transition metals or rare earth elements leads to the formation of magnetic properties in them, and on this basis significantly expands the field of application of a new type of composition quantum dots.

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. The nature and composition of a semiconductor as an nucleus play an important role in the synthesis of quantum dots. By changing the composition of the semiconductor, effective luminescence can be achieved in the desired range. Among the most studied nanoparticles among QDs are CdSe nanocrystals with good luminescence properties [10,11].

Numerous studies on the changing of hydrophobic ligand with hydrophilic have been reported in the paper [12-15]. 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.

MATERIAL AND METHODS

Cadmium oxide (99%, pure for analysis), selenium (Se), sulfur (S), zinc oxide (ZnO, 99%, pure for analysis), oleic acid (OA, 98%, pure), 1-octadecene (ODE), 90%, pure for analysis), toluene (99%, chemically pure), ethanol (96%), acetone (99%, chemically pure), oleylamine (ODA, 96%).

Absorption spectra were recorded by a PerkinElmer Lambda 35 spectrophotometer, photoluminescence spectra were recorded by a Varian Cary Eclipse spectrofluorimeter. Hydrodynamic sizes were determined by dynamic light scattering using a Malvern Zetasizer Nano-ZS experimental setup. X-ray diffractograms were recorded by a Bruker D2 Phaser with the use of CoKα radiation. The EPR measurements were performed by an X-band EPR Elexsys E-580 spectrometer (Bruker) with the ER4122 SHQ resonators. The EPR spectra were simulated with the use of the EasySpin package based on the Mathlab system. The elemental composition of experimental samples was determined by a Bruker S2 Picofox instrument. The quantum yield was calculated by a standard method relative to rhodamine 101 (the quantum yield is 96% in ethanol).

Methods for obtaining quantum dots in a colloidal environment allow nanoparticles to form in a highly quantum efficient state over a short-range distribution range. In this case, a stabilizer is selected in organic solvents, such as amines, fatty acids, thiols, which ensure the distribution of quantum dots in different media, depending on the conditions of synthesis, which in turn provides a monodisperse-sized distribution of quantum dots [16].

The synthesis of CdSe/ZnS QDs was carried out with partial modification based on the method described by the authors [17,18]. The synthesis temperature was changed to 260°C. The synthesis was carried out in an argon atmosphere in a colloidal manner. A 1:1 mixture of ethanol and acetone was used to purify the reactants. The mixture was separated in a centrifuge at 10000 rpm for 10 minutes (the cleaning process was repeated 3 times). During high-temperature synthesis, oleic acid (OA) was used as an organic solvent octadecen and stabilizer to obtain CdSe/ZnS nanocrystals. To study the optical properties of the obtained nanocrystals, they were dissolved in an organic solvent.

RESULTS AND DISCUSSION

The obtained nanoparticles have a spectral range of 500-600 nm in the luminescence spectrum. The spectrum shows that the luminescence range is narrow and symmetrical. This suggests that nanocrystals have very few surface defects and are characteristic of colloidal synthesis. The selected synthesis method made it possible to obtain monodispersed quantum dots. The maximum photoluminescence intensity of quantum dots is 555 nm (Figure 2a). The quantum yield of the synthesized hybrid CdSe/ZnS quantum dots was determined by the coumarin method, based on a solution of rhodamine 6G (96%) in ethanol [19]. The quantum yield of hybrid CdSe/ZnS nanocrystals was 19%.

The photoluminescence and absorbance spectra of the QDs was recorded in n-hexane (Fig. 2). The maximum luminescence intensity was at 513 nm at wavelength excitation 350 nm.

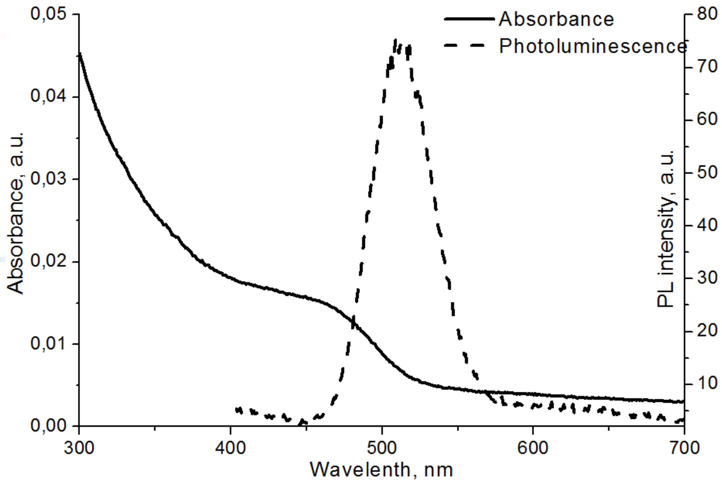
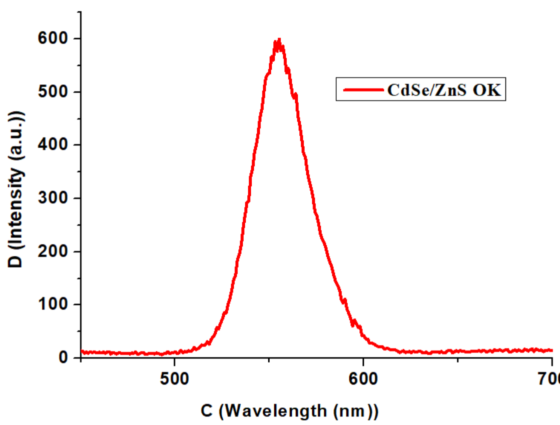
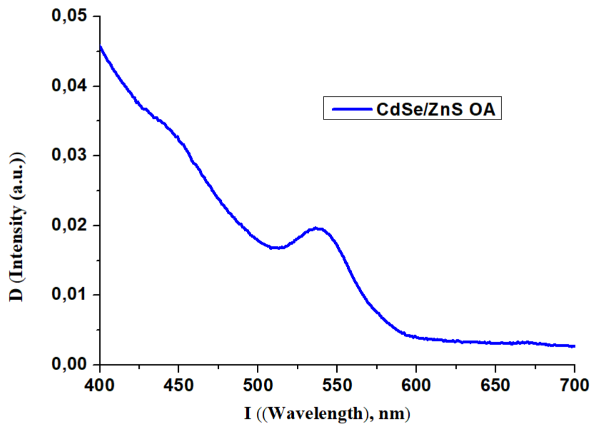


Figure 1. Absorbance and photoluminescence (λ_{ex} = 350 nm) spectra of CdSe QDs.

As can be seen from the absorption spectra of the quantum dots CdSe/ZnS (Figure 2b), an exciton peak of 537 nm is observed in the field of view. The field of view of CdSe quantum dots is 500-600 nm. corresponds to the wavelength.



a)



b)

Figure 2. Luminescence (a) and absorption (b) spectra of CdSe/ZnS QDs

We have investigated the features of the QD surface modification using various types of stabilizers. The molecules of the initial stabilizer (oleic acid) on the surface of the synthesized CdSe/ZnS QDs were replaced by compounds containing a thiol group: L-cysteine (Cis), mercaptopropionic acid (MPA), dodecanethiol-1 (DT), and dodecyl dihydrolipoate (DDL).

The use of L-cysteine and MPA as a stabilizer made it possible to obtain hydrophilic QDs, while the luminescence intensity slightly decreases. It was determined that the substitution of oleic acid (OA) contributes to a slight shift of the emission peak to longer wavelengths. It was shown that, as a result of surface hydrophilization, the hydrodynamic size of nanoparticles increases due to hydration of the QD surface, due to the presence of charged stabilizer ions.

The average size of quantum dots is determined by the following formula, depending on the position of the exciton peak in their absorption spectrum [20]:

$$D = (1.6122 \cdot 10^{-9}) \cdot \lambda 4 - (2.6575 \cdot 10^{-6}) \cdot \lambda 3 + (1.6242 \cdot 10^{-3}) \cdot \lambda 2 - 0.4277 \cdot \lambda + 41.57$$

Here: D-particle size (nm), λ- the wavelength corresponding to the first exciton peak of the absorption spectrum.

The average hydrodynamic size of the nanoparticles was calculated based on the dynamic scattering data of light scattering on the Malvern Zetasizer Nano. According to the literature, the size of the oleic acid molecule used as a stabilizer is 2.35 nm. The size of the quantum point CdSe/ZnS was calculated taking into account the equality of [21]. The mean hydrodynamic (GD) size was 11.3 nm when QDs was stabilized with oleic acid at the surface.

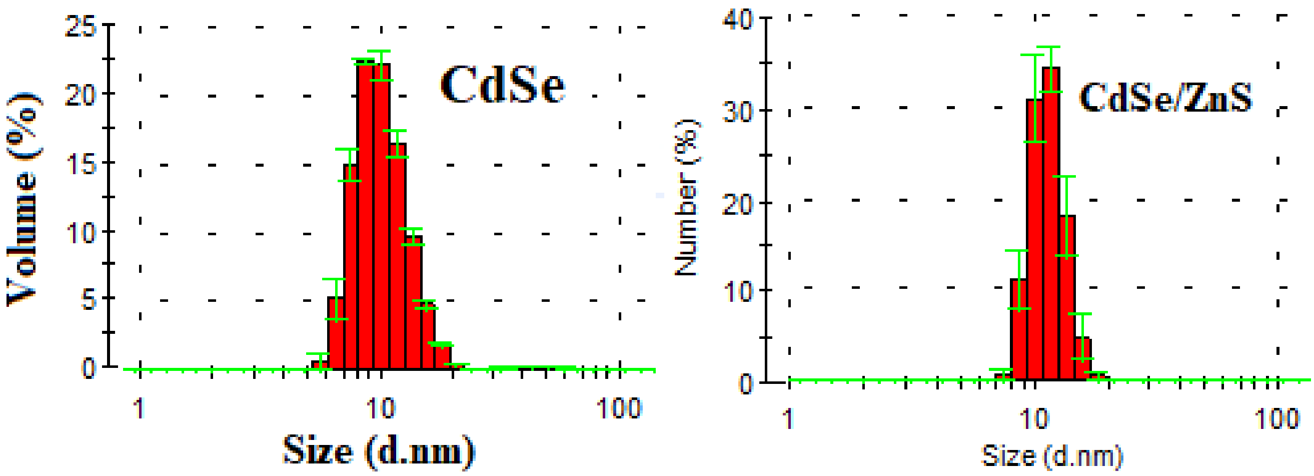


Figure 3. Diagram of the average GD size distribution of the obtained QDs

The results show that the average size of a nanoparticle is 3 min. was 8.4 nm when continued (Figure 4).

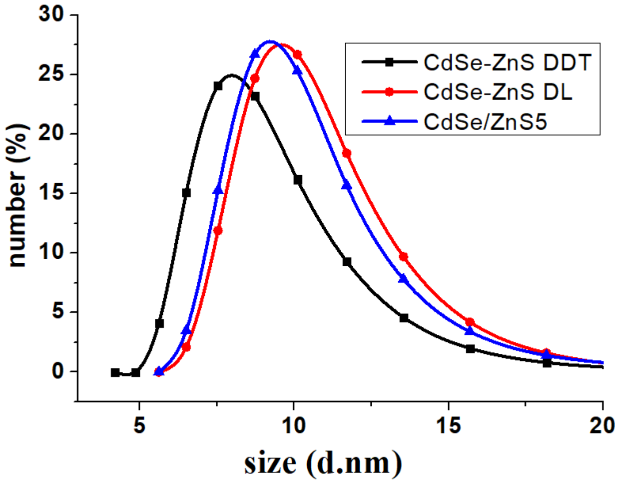


Figure 4. Size distribution diagram of CdSe/ZnS hybrid quantum dots coated with different stabilizers (b)

The CdSe nanoparticles were formed after Se source adding. The reaction time and temperature influenced on the quality and size of the QDs. The optimal reaction time of 1.5 hours at 70 °C allowed to obtain nanoparticles with diameter about 2.5 nm (Fig.5).

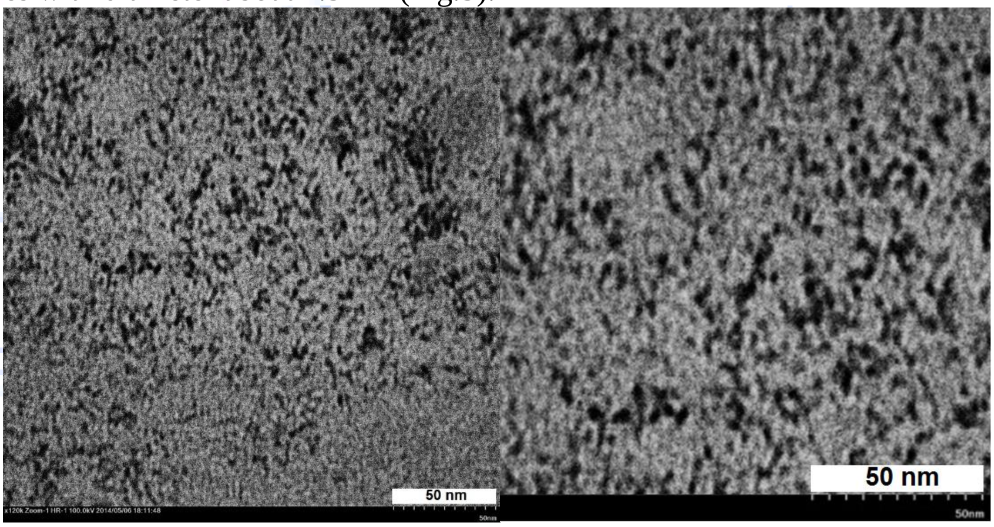


Figure 5. TEM image of colloidal CdSe QDs

The values of quantum dots stabilized with oleic acid based on theoretical calculations and practical results obtained by the method of dynamic scattering of light are given in Table 1.

Table 1. Dimensional characteristics of quantum dots CdSe/ZnS

	Average hydrodynamic size	The size of the CdSe core	The size of the ZnS shell	Stabilizer shell size
CdSe/ZnS (OA)	11,3 nm	2,8 nm	0,9 nm	2,35 nm

CONCLUSIONS

Oleic acid-stabilized hybrid CdSe/ZnS nanocrystals were synthesized in a colloidal manner. The selected synthesis method made it possible to obtain monodispersed quantum dots. The absorption and luminescence spectra of the hybrid CdSe/ZnS quantum dot have moved to a region with shorter wavelengths.

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