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MODIFIED HYBRID CdSe/ZnS QUANTUM DOTS AND THEIR SIZE DEPENDENT UNIQUE CHARACTERISTICS

A.F. Ishankulov[1], **R.R. Shamilov**[2], **Yu.G. Galyametdinov**[2], **N.K. Mukhamadiev**[1]

EMAIL: ishankulov-alisher@mail.ru

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[1]Samarkand State University, University boulevard. 15, 140104, Samarkand, Uzbekistan
[2]Kazan National Research Technological University, Karl Marx 68, 420015 Kazan, Russia

ABSTRACT: In this study, CdSe-based hybrid CdSe/ZnS quantum dots were synthesized. Their optical properties have been proven using absorption and luminescence spectroscopy methods. After the ZnS shell was grown on the surface shell of CdSe nanoparticles, the photoluminescence stability and shelf life of the quantum dots increased significantly. The energy of the outer shell has increased. Absorption and luminescence spectra shifted to a shorter wavelength range. The size of the nucleus decreased from 3.7 nm to 2.8 nm. The surface was stabilized with oleic acid as an active ligand. After stabilization with the surfactant, the average total hydrodynamic size of the nanoparticles increased.

KEYWORDS: hybrid CdSe/ZnS, unique characteristic, optical properties.

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 InAs, Si, InP, CdSe/ZnS and other simple semiconductor materials (consisting of several tens, hundreds of atoms) [1-3].

Among the well studied nanoparticles are cadmium chalcogenides, which have good luminescent properties over a wide range of electromagnetic spectrum [4]. 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 [5].

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 [6,7].

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 [8,9].

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 [10-14].

Numerous studies on the changing of hydrophobic ligand with hydrophilic have been reported in the paper [15-18]. 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%).

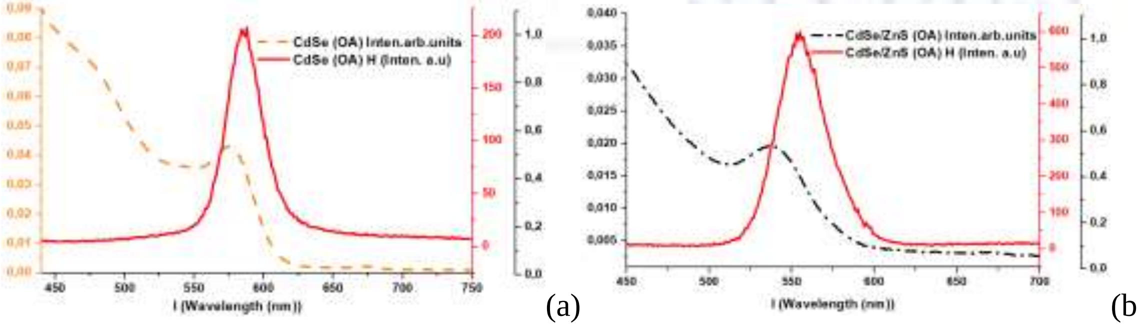
CdSe nanoparticles were synthesized according to the methods described in the authors' work [19-22]. The process was as follows. The synthesis was provided with a three-neck glass flask, and the solution temperature was controlled by a thermometer immersed in the solution. A magnetic stirrer was used to achieve uniformity of heating and distribution of the components in the dispersion medium. A condenser was used to maintain a constant volume of solution. To prevent oxidation of the reagents, the synthesis was carried out in an inert gas argon medium. In high-temperature synthesis, 1-octadecene as an organic solvent and oleic acid as a stabilizer were used to obtain cadmium selenide nanoparticles. Initially, 5.04 ml of oleic acid and 20 ml of ODE mixture were dissolved in 0.256 g of cadmium oxide in a 3-neck glass flask to obtain cadmium precursors at 260°C for the required time. Se precursors were then prepared by dissolving 0.158 g of selenium and 10 ml of ODE at 200˚C.

To prepare a solution of zinc oleate (0.1 M), 0.045 g of ZnO was prepared by heating a solution of 1.41 ml of oleic acid and 3.6 ml of ODE at a temperature of 260˚C. 0.016 g of sulfur in 5 ml of ODE at 200˚C dissolved to obtain a sulfur precursor (0.1 M). A 20 ml solution was prepared by adding 5 ml of ODE to a solution of CdSe ($6.6 \cdot 10^{-6}$ mol / l) QDs in toluene. The toluene in the mixture was then heated to 200°C until it evaporated. Then 2 ml of oleylamine and 4.7 ml of zinc oleate solution were added and 4.7 ml of sulfur precursor solution was infused over a period of time using the SILAR method.

The photoluminescence and photoluminescence excitation spectra of QDs were detected by the Cary Eclipse (Varian) fluorescence spectrophotometer. Optical absorption spectra were measured with a two-beam spectrometer Perkin Elmer Instrumental LAMBDA 35. QDs size were evaluated by dynamic light scattering with Malvern Zetasizer Nano which was equipped with a narrow filter at 632.8 nm. The average size of the QDs was estimated to be of 9.3 nm.

RESULTS AND DISCUSSION

From the absorption spectra of the obtained hybrid CdSe/ZnS QDs (Figure 1 a), it can be seen that as the ZnS shell grows, the maximum of the excitation peak in the spectrum shifts toward the short-wavelength region. The emission spectrum of CdSe QDs is symmetrical, with a peak in the 587 nm range (Figure 1 a). We have obtained hybrid CdSe/ZnS QDs by preliminary formation of CdSe core and growing a ZnS shell on them. The formation of the shell leads to a shift of the excitation peak of CdSe core to shorter wavelengths. According to calculations, during the formation of the ZnS layer, the size of the CdSe core decreases from 3.7 to 2.8 nm due to the replacement of surface atoms of cadmium by zinc. In this case, the QD luminescence peak is also shifted to the short-wavelength region (Figure 1 b). The quantum yield, which was 4.9% for CdSe nanoparticles, increased to 19% after the growth of the ZnS shell. This indicates that the yield of a quantum dot obtained on the basis of a hybrid CdSe/ZnS increases with decreasing particle size.



(a) (b)

Figure 1. Absorption and emission spectra of CdSe (a) and CdSe/ZnS (b) QDs ($\boldsymbol{\lambda}_{ex} = 400$ nm)

Absorption spectroscopy data also allow the calculation of the extinction coefficient and the concentration of nanoparticles. The extinction coefficients for CdSe and hybrid CdSe/ZnS nanocrystals were determined by the following formula.

$$\varepsilon = 5857 \cdot (D)^{2,65}$$

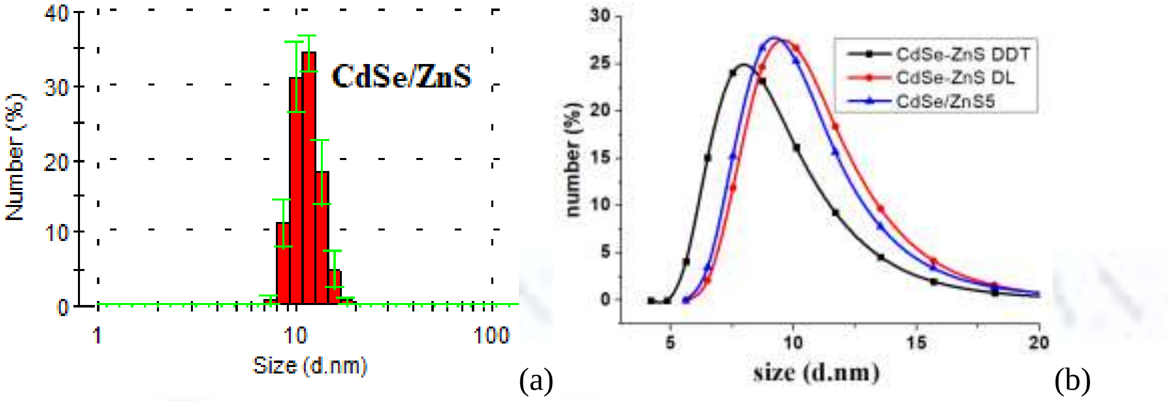
In this D is the diameter of the nanoparticle, ε = extinction coefficient ($M^{-1} \cdot cm^{-1}$), CdSe QD extinction coefficient for 187676,4 ($M^{-1} \cdot cm^{-1}$), for hybrid CdSe/ZnS QDs, 89669.34 ($M^{-1} \cdot cm^{-1}$) equality was determined.

In turn, the nanoparticle concentration in the solution was determined using the following formula using Lambert-Beer's law.

$$C_M = \frac{A_{max,abs}}{\varepsilon \cdot l}$$

Where C_M is the quantum dot concentration (mol/l), $A_{max,\ abs}$ – the maximum absorbance, *l* – surface shell layer.

The average hydrodynamic size of the nanoparticles was determined based on the dynamic scattering method of light in a Malvern Zetasizer Nano instrument. The results show that the average size of a nanoparticle is 3 min. was 8.4 nm when continued (Figure 2 b).



(a) (b)

Figure 2. Mean hydrodynamic size distribution of hybrid CdSe/ZnS quantum dots (a). Size distribution diagram of CdSe/ZnS hybrid quantum dots coated with different stabilizers (b)

The mean hydrodynamic size of the synthesized hybrid CdSe/ZnS nanocrystals was 11.2 nm, taking into account the stabilizer shell (Figure 2 a). From this, it can be determined that the thickness of the ligand shell is 2.35 nm, given that the size of the core of the hybrid CdSe/ZnS QDs is 2.8 nm.

In the infrared spectra of CdSe/ZnS hybrid quantum dots stabilized with oleic acid, intense symmetrical and asymmetric stretching signals of the oleate anion COO^- group are present in the 1546 and 1456 cm^{-1} ranges (Figure 6). In turn, the presence of a strong signal with a value of 1734 cm^{-1} in the -COOR group in the DDL molecule and the bending mode intensity in C-O are in the range of 1249 and 1174 cm^{-1}. The stretching signals 2922, 2854, and 1461 cm^{-1} belong to groups C–H. The complex ether bond signals in the DDL-modified CdSe/ZnS QDs correspond to 1734 cm^{-1}, 1248 cm for the C-O bond, and 1171 cm^{-1}, respectively. In this case, the stretching signals of the oleate anion 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 $-COO^-$ 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 cease the ligand exchange process, it is necessary to increase the concentration of the replaced ligand or repeat the reaction step several times.

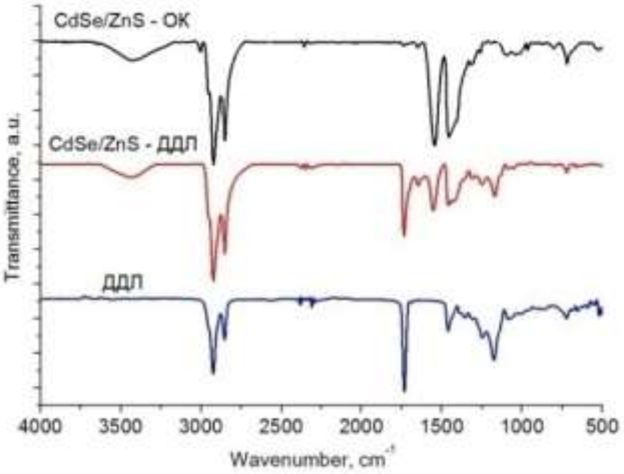


Figure 3. IR spectra of CdSe/ZnS QDs and DDL

When the surface is modified with dodecanethiol and dodecyl dihydrolipoate, the QD surface remains hydrophobic. In this case, a high luminescence intensity is maintained and the peak position does not shift. According to IR spectra, a small part of oleic acid molecules on the QD surface remains unsubstituted. The hydrodynamic particle size is slightly reduced as a result of the modification, due to the smaller length of the stabilizer molecules in comparison with oleic acid.

CONCLUSIONS

The results of the study showed that the absorption and emission spectra of CdSe and hybrid CdSe/ZnS QDs were studied. The absorption and luminescence spectra of the hybrid CdSe/ZnS quantum dots shifted to a shorter wavelength. The monodispersity of the obtained QDs and the radiation efficiency were found to depend on the molar ratio of cadmium to selenium. Excess cadmium and selenium led to high quantum yield. In this case, the excessive increase in the amount of selenium facilitated the synthesis of particles with high efficiency over a long period of time for the reaction. Luminescence quantum yield was found to increase from 4.9% to 19%.

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