Modified hybrid CdSe/ZnS quantum dots and their size dependent unique characteristics

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Abstract. In this study, CdSe-based hybrid CdSe/ZnS quantum dots were synthesized. Their optical properties have been characterized using the absorption and luminescence spectroscopy methods. When the ZnS shell was grown on the surface shell of CdSe nanoparticles, the photoluminescence stability and the shelf life of the quantum dots increased significantly. The energy of the outer shell has increased. The 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 a surfactant, the average total hydrodynamic size of the nanoparticles increased.

1. Introduction

Colloidal quantum dots are semiconductor nanocrystals stabilized by surfactant molecules. 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 (QDs) are large associates consisting mainly of InAs, Si, InP, CdSe/ZnS and other simple semiconductor materials and containing tens and hundreds of atoms [1-3].

Cadmium chalcogenides, which have good luminescent properties over a wide range of the electromagnetic spectrum, are among the well studied nanoparticles [4]. The development of hybrid “core/shell” type quantum dots can lead to a further increase in the luminescence intensity. In particular, quantum dots consisting of elements of groups II and VI have a wide band gap and possess high photoluminescence efficiency at room temperature [5].

The synthesis of quantum dots with a core/shell structure is carried out 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 control 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, 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 the surface condition [10,11].

Numerous studies on the changing of a hydrophobic ligand with a hydrophilic one have been reported in papers [12-15]. According to them, the transfer of the obtained quantum dots to an aqueous medium is easier in hydrophilic stabilizers.

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

2. 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), dodecanethiol-1 (DT, 98%, Alfa Aesar, UK), dodecyl ether of dihydrolipoic acid (DDL, 96%, Alpha Aesar, UK), toluene (99%, chemically pure), ethanol (96%), acetone (99%, chemically pure), oleylamine (ODA, 96%) were used for the experiments.

CdSe nanoparticles were synthesized according to the methods described in the authors' work [16,17]. 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 a uniformity of heating and distribution of the components in the dispersion medium. A condenser was used to maintain a constant volume of the 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. Sulfur in the quantity of 0.016 g in 5 ml of ODE at 200°C was 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 \times 10^{-6} \text{ 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 a Cary Eclipse (Varian) fluorescence spectrophotometer. Optical absorption spectra were measured with a Perkin Elmer Instrumental LAMBDA 35 two-beam spectrometer. QDs size were evaluated by dynamic light scattering with a Malvern Zetasizer Nano which was equipped with a narrow filter at 632.8 nm. The average size of the QDs was estimated to be 9.3 nm.

3. 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 near 587 nm (figure 1 a). We have obtained hybrid CdSe/ZnS QDs by a 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 cadmium atoms on the surface by zinc atoms. 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 the quantum dot obtained on the basis of hybrid CdSe/ZnS increases with decreasing particle size.

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

The absorption spectroscopy data also allow the calculation of the extinction coefficient and concentration of nanoparticles. The extinction coefficients for CdSe and hybrid CdSe/ZnS nanocrystals were determined by the following formula [18]:

$$\varepsilon = 5857 \times (D)^{2.65},$$

where $D$ is the diameter of the nanoparticle, $\varepsilon$ the extinction coefficient $(\text{M}^{-1} \cdot \text{cm}^{-1})$. From this formula, the extinction coefficients of 187676.4 $\text{M}^{-1} \cdot \text{cm}^{-1}$ for CdSe QDs and 89669.34 $\text{M}^{-1} \cdot \text{cm}^{-1}$ for hybrid CdSe/ZnS QDs were determined.

In turn, the concentration of nanoparticles in the solution was determined using the following formula based on the Lambert-Beer law [19]:

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

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

The average hydrodynamic size of the nanoparticles was determined basing on the method of dynamic scattering of light on a Malvern Zetasizer Nano instrument. 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 use of DDL as a stabilizer has led to an increase in the particle size of quantum dots (up to 9.6 nm) (figure 2 b).

**Figure 2.** Mean hydrodynamic size distribution of hybrid CdSe/ZnS quantum dots (a) and 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 range from 1546 to 1456 cm\(^{-1}\) (figure 3). 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 between 1249 and 1174 cm\(^{-1}\). The stretching signals at 2922, 2854, and 1461 cm\(^{-1}\) belong to groups C–H. The ester bond signals in the DDL-modified CdSe/ZnS QDs correspond to 1734 cm\(^{-1}\) stretching mode signals of C-O and 1248 cm\(^{-1}\), and 1171 cm\(^{-1}\) to the bending mode signals of C-O bond, 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.](image)

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.

### 4. Conclusions

Synthesis of oleic acid-stabilized CdSe and its hybrid CdSe/ZnS quantum dots was performed and their optical-dimensional properties 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. An excess of cadmium and selenium led to a high quantum
yield. In this case, an excessive increase in the amount of selenium facilitated the synthesis of particles with high efficiency over a long period of time for the reaction. The luminescence quantum yield was found to increase from 4.9% to 19%.

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References
[1] Barve A V, Lee S J, Noh S K and Krishna S 2010 Laser & Photonics Reviews 4(6) 738-50.
[2] Galyametdinov Y G, Sagdeev D O, Voronkova V K, Sukhanov A A and Shamilov R R 2017 Materials Research Express 5(7) 075009
[3] Das D, Aiello A, Guo W and Bhattacharya P 2020 IEEE Transactions on Nanotechnology 19 571-4
[4] Ishankulov A F, Shamilov R R, Halilov K F, Galyametdinov Yu G and Mukhamadiev N K 2020 International Journal of Advanced Science and Technology 29(9) 2140-8
[5] Hernández-Gordillo A, Acevedo-Peña P, Bizarro M, Rodil S E and Gómez R 2018 Journal of Materials Science: Materials in Electronics, 29(9) 7345-55
[6] Nayak A P et al 2015 ACS Nano 9(9) 9117-23.
[7] Mikhailov I I, Tarasov S A, Solomonov A V, Matyuşkin L B and Mazing D S 2014 Functional Materials 21(2) 186-9
[8] Qin W, Shah R A and Guyot-Sionnest P 2012 ACS Nano 6(1) 912-8
[9] Shamilov R R, Ishankulov A F and Galyametdinov Yu G 2020 Technological University Bulletin 23(4) 19-22 [in Russian]
[10] Aderhold J, Davydov V Y, Fedler F, Klausing H, Mistele D, Rotter T and Graul J 2001 Journal of Crystal Growth 222(4) 701-5
[11] Van Embden J, Jasieniak J, and Mulvaney P 2009 Journal of the American Chemical Society 131(40) 14299-309
[12] Hofman E, Robinson R J, Li Z J, Dzikovski B and Zheng W Chemistry of Materials 2017 139 8878–85
[13] Guo W and Peng X 2003 Chemistry of Materials 15(14) 2854-60
[14] Huang X, Parashar V K and Gijs M A 2018 Langmuir 34(21) 6070-6
[15] Rogach A L, Kornowski A, Gao M, Eyehmuller A and Weller H 1999 The Journal of Physical Chemistry 103(16) 3065-9
[16] Farmonovich A I, Rashitovich R Sh, Faxritdinovich Q X, Gennadievich Yu G and Qurbanalievich N K 2020 Jour of Advanced Research in Dynamical & Control Systems 12(7) 2201-5
[17] Ghosh Chaudhuri R and Paria S 2012 Chemical Reviews 112(4) 2373-433
[18] Wang Y, Suna A, McHugh J, Hilinski E F, Lucas P A and Johnson R D 1990 The Journal of Chemical Physics 92(11) 6927-39
[19] Kim D, Miyamoto M, Mishima T and Nakayama M 2005 Journal of Applied Physics 98(8) 083514