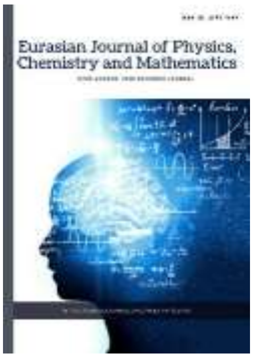

Modification of Polymethyl Methacrylate Based on Hybrid CdSe/ZnS AND CdSe/CdS/ZnS Quantum Dots

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ABSTRACT

CdSe quantum dots obtained by the colloid method were stabilized with oleic acid and their optical properties were studied. By growing a ZnS shell on the surface of CdSe nanoparticles, a hybrid CdSe/ZnS "core-shell" nanoparticle was synthesized. At the same time, the luminescence quantum yield increased from 1.5 to 19%. As a result, the luminescence spectral wavelength peak of the CdSe/ZnS quantum point shifted to a shorter region. 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.

Keywords: Quantum dots, colloid synthesis, cadmium selenide, zinc sulfide, "core/shell", nanoparticles, luminescence, precursor.

Introduction

In recent years, much attention has been paid to the study of composite organic-inorganic materials. Quantum dots (QDs) are nanosized semiconductor nanoparticles with fluorescent properties whose optical properties change depending on their chemical composition, size and shape. The incorporation of quantum dots into monodisperse polymer microspheres can produce materials with reproducible properties, which can be used in applications such as optical coding, biological analysis, optical data storage, and sensing [1-3].

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%).

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.

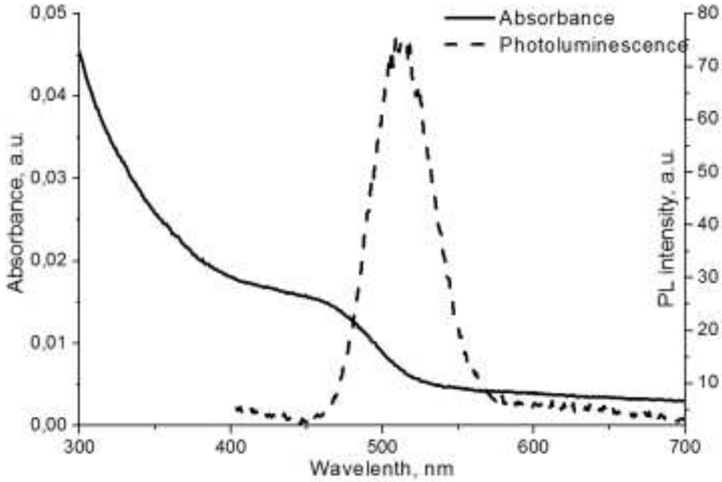


Figure 1. Absorbance and photoluminescence (λ_{ex} = 350 nm) spectra of CdSe QDs.

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.

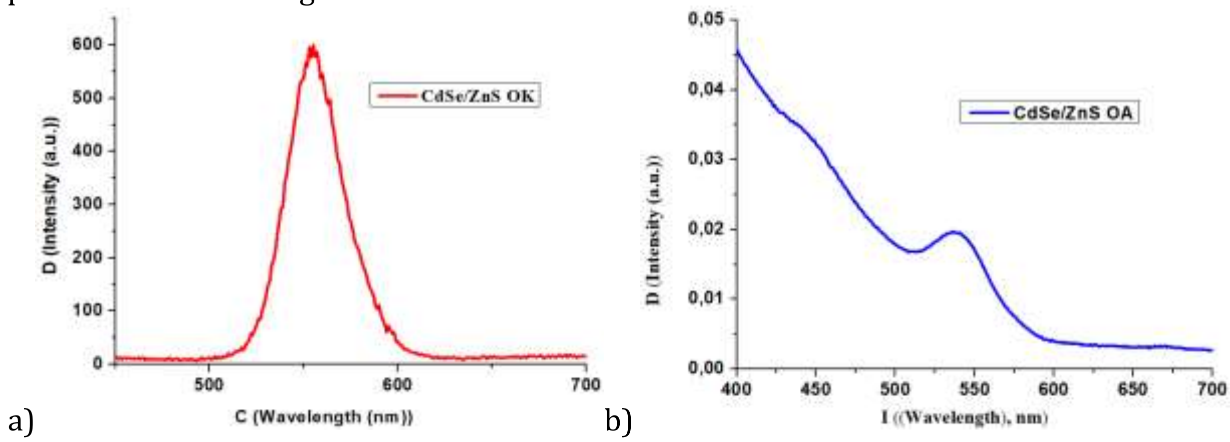


Figure 2. Luminescence (a) and absorption (b) spectra of CdSe/ZnS QDs

The synthesis of CdSe QDs was performed with partial modifications based on the method described by the authors [6,7].

The method recommended by the authors [8,9] was used to grow the ZnS shell around the CdSe nucleus.

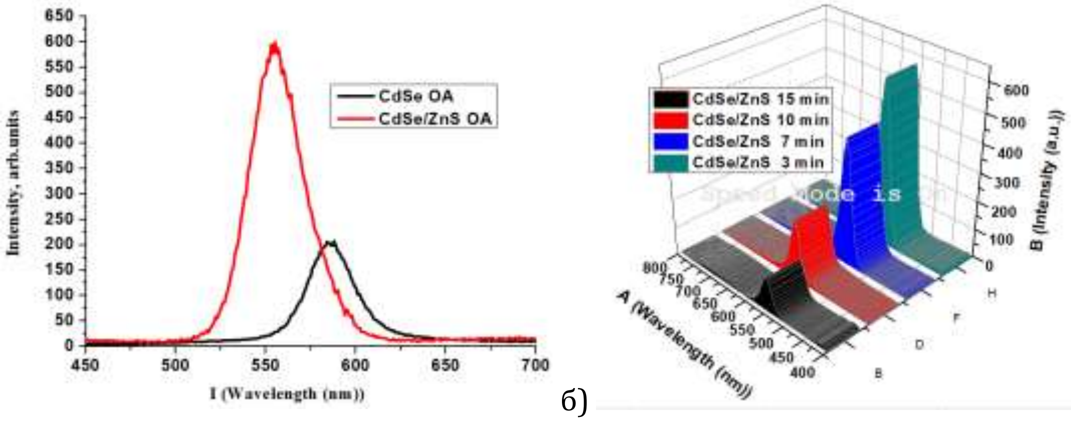
To prepare a solution of zinc oleate (0.1M), a solution prepared from a mixture of 1.41 ml of oleic acid (OA) of 0.0405 g ZnO and 3.6 ml of octadecene was prepared by heating at 260°C. A precursor of a sulfur (0.1M) solution was obtained by dissolving 0.016 g of sulfur in 5 ml of octadecene at 200°C.

A 20 ml solution was prepared by adding 5 ml of octadecene to a solution of CdSe ($6.6 \cdot 10^{-6}$ mol/l) QD 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. A total of 4.7 ml of sulfur precursor solution was added to the reaction mixture every 15 minutes. The mixture is stirred in a magnetic stirrer for 30 min at 200°C so that the components in the mixture are fully reactive. The purification process is performed in the same order as for CdSe quantum dots.

Synthesis was performed on the surface of CdSe nanocrystals based on changes in the addition time of sulfur precursors (for 3, 7, 10, 15 minutes) during ZnS shell growth.

Oleic acid was used as a stabilizer in the synthesis of CdSe QDs and was synthesized at high temperatures in an octadecene medium.

The luminescence intensity spectrum of CdSe QDs is symmetrical, with its peak in the 587 nm range (Figure 3a). The surface defects in the synthesized nanoparticles were very small, and the chosen synthesis method made it possible to obtain monodispersed quantum dots. The quantum yield of nanoparticles of CdSe QDs relative to rhodomine 6G was 1.5%. The growth of the shell around the nucleus leads to a significant increase in luminescence intensity, and a quantum yield increase of up to 19% is observed for hybrid CdSe/ZnS QDs. Also, the luminescence spectrum shifted to the region up to 555 nm. This phenomenon is associated with the QD nucleus dimension. Furthermore, when the addition time of sulfur precursors during the growth of ZnS shell on the surface of CdSe nanocrystals changed (for 3, 7, 10, 15 minutes), a decrease in the peak state of luminescence intensity was observed with increasing time (Fig. 3b).



a) б)

Figure 3. Luminescence spectra of CdSe and CdSe/ZnS QDs (a) and three-dimensional coordinate images at different synthesis times (b) (motion = 350nm)

Synthesis of hybrid CdSe/ZnS quantum dots stabilized with oleic acid was performed. The luminescence spectra of CdSe/ZnS QDs were studied. The absorption and luminescence spectra of the hybrid CdSe/ZnS quantum point moved to the short region of the wavelength peak. An increase in luminescence quantum yield was observed to be 1.5–19%.

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.

References

1. A.V. Barve, S.J. Le, S.K. Noh, S. Krishna, Review of current progress in quantum dot infrared photodetectors, Laser Photon. Rev. 4 (2010) 738–750.
2. H.K. Jun, M.A. Careem, A.K. Arof, Quantum dot-sensitized solar cells-perspective and recent developments: a review of Cd chalcogenide quantum dots as sensitizers, Renew. Sustain. Energy Rev. 22 (2013) 148–167.
3. H. Shin, D. Jang, Y. Jang, M. Cho, and K. Park, "High resolution imaging analysis of CdSe/ZnS core-shell quantum dots (QDs) using Cs-corrected HR-TEM/STEM," Journal of Materials Science: Materials in Electronics, vol. 24,no. 10,pp. 3744–3748, 2013.
4. A.M. Kelley, Q. Q. Dai, Z.-J. Jiang, J.A. Baker, and D. F. Kelley, "Resonance Raman spectra of wurtzite and zincblende CdSe nanocrystals," Chemical Physics, vol. 422, pp. 272–276, 2013.
5. Chang, J., Waclawik, E.R., "Colloidal semiconductor nanocrystals: controlled synthesis and surface chemistry in organic media," RSC Adv. 4(45), 23505-23527 (2014).
6. W. Zhang, C. Jin, Y. Yang, and X. Zhong, "Noninjection facile synthesis of gram-scale highly luminescent CdSe multipod

nanocrystals," Inorganic Chemistry, vol. 51, no. 1, pp. 531–535, 2012

7. R.R. Shamilov, A.F. Ishankulov, Yu.G. Galyametdinov "Size-optical characteristics of CdSe/Zns quantum dots modified by thiol stabilizers T.23, №3, 19-23 (2020).
8. Xinyue Liu, Yixuan Liu, Shu Xu, Chong Geng, Yangyang Xie, Zi-Hui Zhang, Yonghui Zhang, and Wengang Bi. Formation of "Steady Size" State for Accurate Size Control of CdSe and CdS Quantum Dots. The Journal of Physical Chemistry Letters 2017, *8* (15), 3576-3580. DOI: 10.1021/acs.jpclett.7b01238.
9. Quantum Dots: research, technology and applications. Ed. by R.W. CDoss. Nova Science Publishers, Inc. New York. 2008.
10. J. Chen, J.L. Song, X.W. Sun, W.Q. Deng, C.Y. Jiang, W. Lei, J.H. Huang, R.S. Liu. // Applied physics letters. 2009. V. 94. P. 153115-3.
11. N. Tessler, V. Medvedev, M. Kazes, S. Kan, U. Banin. // Science. 2002. V. 295. P. 1506 – 1513.
12. Nayak A P, Yuan Z, Liu J, Wu J, Moran S T, ... & Lin J F 2015 Pressure-modulated conductivity, carrier density, and mobility of multilayered tungsten disulfide. *ACS nano* 9(9) pp 9117-9123.
13. Mikhailov I I, Tarasov S A, Solomonov A V, Matyushkin L B, & Mazing D S 2014 The investigation of the luminescence properties of colloidal quantum dots based on cadmium chalcogenides *Functional materials*.
14. Qin W, Shah R A, & Guyot-Sionnest P 2012. CdSeS/ZnS alloyed nanocrystal lifetime and blinking studies under electrochemical control *ACS nano* 6(1) pp 912-918.
15. Shamilov R R, Ishankulov A F, Galyametdinov Yu G 2020 Size-optical characteristics of CdSe/ZnS quantum dots modified by thiol stabilizers [in Russian] *Technological University Bulletin* 23(4) pp 19-22.
16. Aderhold J, Davydov V Y, Fedler F, Klausing H, Mistele D, Rotter T, ... & Graul J 2001 InN thin films grown by metalorganic molecular beam epitaxy on sapphire substrates *Journal of crystal growth* 222(4) pp 701-705.
17. Van Embden J, Jasieniak J, & Mulvaney P, 2009 Mapping the optical properties of CdSe/CdS heterostructure nanocrystals: the effects of core size and shell thickness *Journal of the American Chemical Society* 131(40) pp 14299-14309.
18. Hofman E, Robinson R J, Li Z J, Dzikovski B, Zheng W, Controlled Dopant Migration in CdS/ZnS Core/Shell Quantum Dots *Chemistry of Materials* 2017 139 pp 8878–8885.
19. Huang X, Parashar V K, & Gijs M A, 2018 Nucleation and Growth Behavior of CdSe Nanocrystals Synthesized in the Presence of Oleylamine Coordinating Ligand. *Langmuir* 34(21) pp 6070-6076.
20. Rogach A L, Kornowski A, Gao M, Eychmüller A, & Weller H, 1999 Synthesis and characterization of a size series of extremely small thiol-stabilized CdSe nanocrystals *The Journal of Physical Chemistry* 103(16) pp 3065-3069.
21. Farmonovich A I, Rashitovich R Sh, Faxritdinovich Q X, Gennadievich Yu G, Kurbonalievich N K 2020 Synthesis and optical-dimensional properties of hybrid CdSe/ZnS nanocrystals *Jour of adv research in dynamical & control systems* 12(7) pp 2201-2205.