SYNTHESIS OF NANOCRYSTALS IN THE CORE/SHELL

Ishankulov A.F., Mukhamadiev N.K.
Samarkand state university, Uzbekistan.
e–mail: Ishankulov-alisher@mail.ru

Annotation: 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.

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

Nowadays, along with the growing demand of mankind for new nanotechnologies, chemical nanotechnologies are also developing rapidly [1]. 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 [2]. 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 [3].

Semiconductor nanocrystals or quantum dots (QDs), which exhibit luminescence properties, have become a promising material for use in a variety of fields due to their unique optical properties. QDs are used as biomarkers in the manufacture of light-emitting diodes, displays, lasers, solar cells, and in the study of cells [4,5].

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.

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 [6].

The synthesis of CdSe/ZnS QDs was carried out with partial modification based on the method described by the authors [7,8]. 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.

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 1a). 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 [9]. The quantum yield of hybrid CdSe/ZnS nanocrystals was 19%.

As can be seen from the absorption spectra of the quantum dots CdSe/ZnS (Figure 1b), 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.
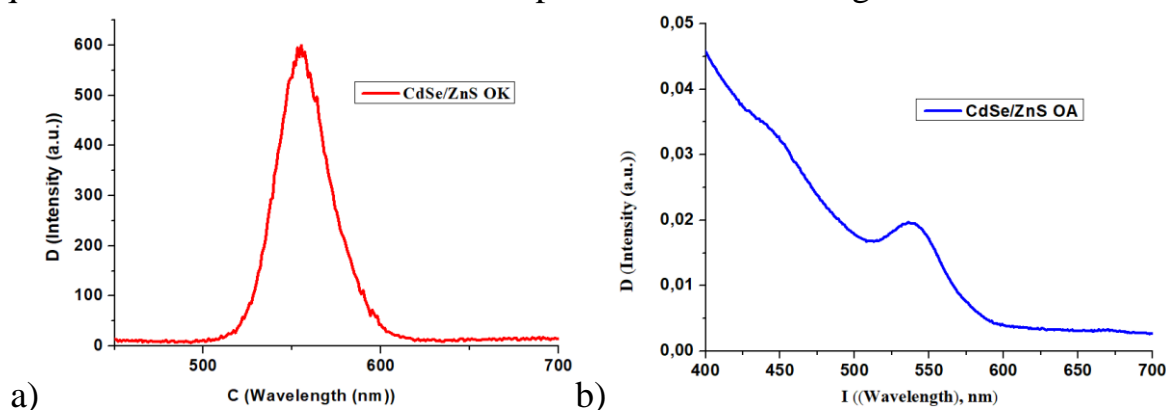

Figure 1. Luminescence (a) and absorption (b) spectra of CdSe/ZnS QDs

The average size of quantum dots is determined by the following formula, depending on the position of the exciton peak in their absorption spectrum [10]:

$$D = (1.6122 \cdot 10^{-9}) \cdot \lambda4 - (2.6575 \cdot 10^{-6}) \cdot \lambda3 + (1.6242 \cdot 10^{-3}) \cdot \lambda2 - 0.4277 \cdot \lambda + 41.57$$

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 [11]. The mean hydrodynamic (GD) size was 11.3 nm when QDs was stabilized with oleic acid at the surface.
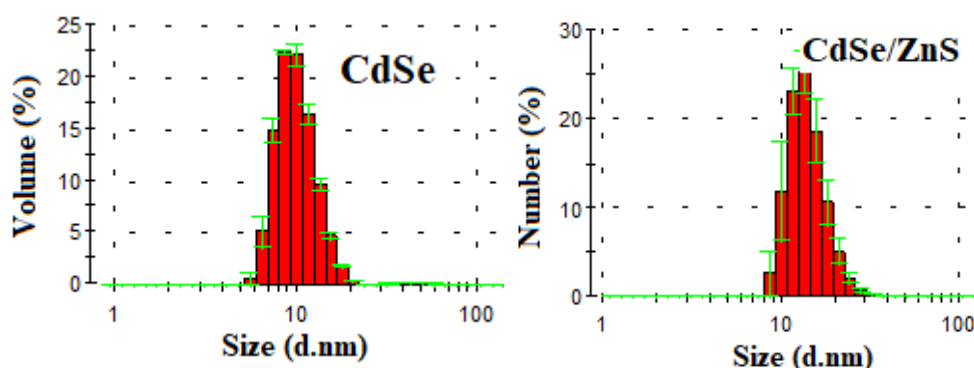

Figure 2. Diagram of the average GD size distribution of the obtained QDs

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.

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 3 b).
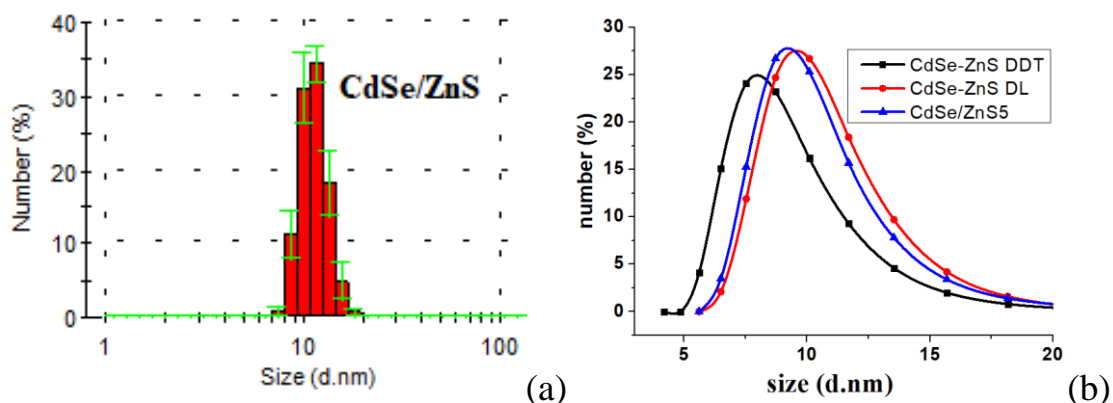
Figure 3. Mean hydrodynamic size distribution of hybrid CdSe/ZnS quantum dots (a). Size distribution diagram of CdSe/ZnS hybrid quantum dots coated with different stabilizers (b)

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

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

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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