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## Investigation of the optical properties of quantum dots depending on the nature and number of additional semiconductor layers

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**Abstract.** The present study aims to investigate the properties of quantum dots (QDs) depending on the nature and number of additional semiconductor layers. The analysis of spectral data showed that when CdTe QDs are coated with a ZnS shell, a bathochromic shift of the exciton peak and maximum of fluorescence is observed due to the restriction of charge carriers in the nucleus. However, the build-up of the additional shell leads to a decrease in the quantum yield, which may be due to the difference in the parameters of the crystal lattices to CdS and ZnS and the occurrence of defects in the crystal structure. In contrast, CdTe QDs coated with a CdS shell increased the quantum yield and shifted the peak of fluorescence to a longer wavelength region.

**Keywords:** quantum dots, nanoparticles, bandgap, synthesis, core, shell

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## Исследование оптических свойств квантовых точек в зависимости от природы и количества дополнительных полупроводниковых слоев

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**Аннотация.** Данное исследование направлено на изучение свойств квантовых точек (КТ) в зависимости от природы и количества дополнительных полупроводниковых слоев. Анализ спектральных данных показал, что при покрытии CdTe КТ оболочкой из ZnS наблюдается bathochromic сдвиг экситонного пика и максимума флуоресценции из-за ограничения носителей заряда в ядре. Однако наращивание дополнительной оболочки приводит к снижению квантового выхода, что может быть связано с различием параметров кристаллических решеток CdS и ZnS и наличием дефектов в кристаллической структуре. Напротив, у CdTe КТ после покрытия оболочкой CdS, увеличивается квантовый выход и сдвигается пик флуоресценции в более длинноволновую область.

**Ключевые слова:** квантовые точки, наночастицы, запрещенная зона, синтез, ядро, оболочка

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## Introduction

Currently, semiconductor nanostructured materials are much in demand due to their unique properties. Nanostructured materials exhibit specific optical and electronic properties when their size changes in the range of 1–100 nm. Depending on the dimension, they can be classified as twodimensional (thin films or quantum wells); one-dimensional (quantum wires); zero-dimensional (quantum dots) ones [1]. Thus, a QD is a zero-dimensional system and has a limited number of atoms forming discrete energy states. QDs have a surface effect and a quantum restriction which affect their atomic-like properties [2]. The quantum restriction results in specific size- and shapedependent optoelectronic properties.

Colloidal chemistry techniques allow the synthesis of multicomponent QDs from semiconductors with different characteristics, primarily with different band gap widths. A special place in this group is occupied by core/shell QDs, consisting of a core of one semiconductor covered by a shell of another [3]. Due to the low luminescence of the QD nuclei themselves, hybrid structures consisting of a nanoscale semiconductor core and their shell are often created for practical purposes. By selecting the type of shell material and its thickness, the maximum luminescence enhancement effect can be achieved [4]. Such a QD structure is called a “core/shell” structure. Additional shell build-up significantly improves the fluorescence quantum yield and photostability of quantum dots. The proper choice of the shell material and its thickness are important factors affecting the overall properties of QDs. If the core and shell structures have a huge lattice mismatch, this leads to lattice deformation and defective states occur inside or at the core/shell interface. In addition, a thicker semiconductor shell creates mismatch dislocations, which also reduces the fluorescence quantum yield due to the non-radiative process [5].

The present study aims to investigate the properties of quantum dots depending on the nature and number of additional semiconductor layers. QDs with a CdTe core and additional semiconductor shells were synthesised in the study. The material of the semiconductor shells is selected so that the difference between the crystal lattices of the core-shell-shell is minimal. The layer size is controlled by the synthesis time. As the size of the semiconductor layer increases, the quantum yield increases to a certain size, then decreases sharply with a further increase in the layer size, which is demonstrated in [6]. In order to increase stability, additional shells from wider-band ZnS and CdS semiconductors were built up on CdTe QDs. The analysis of spectral data showed that when CdTe QDs are coated with a ZnS shell, a bathochromic shift of the exciton peak and maximum of fluorescence is observed due to the restriction of charge carriers in the nucleus. However, the build-up of the additional shell leads to a decrease in the quantum yield, which may be due to the difference in the parameters of the crystal lattices to CdS and ZnS and the occurrence of defects in the crystal structure. In contrast, CdTe QDs coated with a CdS shell increased the quantum yield and shifted the peak of fluorescence to a longer wavelength region.

## Synthesis of CdTe/CdS/ZnS-TTK-(L-cys) QDs

The synthesis of multilayer CdTe/CdS/ZnS-TGA-(L-cys) QDs was carried out in three steps in an inert atmosphere and at 98 °C.

To obtain CdTe QDs a solution of cadmium precursor with stabilizer was prepared and a freshly prepared solution of sodium hydrotelluride NaHTe (tellurium precursor) was quickly added under

constant stirring, with Cd:Te ratio of 1:0.3. Powder of tellurium Te (0.387 mmol) and sodium borohydride  $\text{NaBH}_4$  (1.692 mmol) were mixed, and cadmium chloride  $\text{CdCl}_2$  (0.2 mmol) was dissolved in water with added stabilizer to obtain tellurium precursor. TGA (0.6 mmol) was used as stabilizer. The pH of the solutions obtained was adjusted to 9.2 with a sodium hydroxide solution with a concentration of 0.5 M to obtain the TGA salt.

To cover CdTe QDs with CdS layer, Cd precursor and S precursor were slowly added to the solution stabilized by TGA QDs using syringes, the reaction mixture was boiled under stirring with reflux for 2 hours (borate buffer (5 mmol) with  $\text{pH} = 10$  was used as reaction medium).

The synthesis of CdTe/CdS-TGA QDs with a CdTe:CdS ratio of 1:1.5 was carried out as follows. To prepare the Cd precursor, a 0.15 mmol sample of  $\text{CdCl}_2$  was placed in a 25 ml beaker and dissolved in 10 ml of deionized water. To the obtained solution 0.45 mmol of TGA was added and the mixture was stirred for 5 min. Then the pH of the resulting solution was adjusted to 10 with 0.5 M NaOH. Precursor S was prepared by dissolving 0.150 mmol of thiourea in 5 ml of deionized water. QDs with a CdTe:CdS ratio of 1:3 and 1:3.75 were prepared according to the same algorithm.

The synthesised CdTe/CdS QDs were coated with ZnS, where L-cys was used as a stabiliser for further use of the QDs in bioassay. The order of ZnS coating is similar to that of CdS coating. To prepare the Zn precursor, a suspension of L-cys (0.300 mmol) was placed in a beaker, dissolved in 10 ml of deionized water, and diluted with 0.5 M NaOH to  $\text{pH} = 9$ . To the obtained stabilizer solution, 1 ml of solution containing (0.150 mmol)  $\text{ZnCl}_2$  was slowly added under stirring and the mixture was stirred for 5 min. After that the pH of the resulting solution was adjusted to 10. The precursor S was prepared by dissolving 0.150 mmol of thiourea in 5 ml of deionized water.

#### Purification of QDs

The resulting QDs were precipitated with isopropanol in a centrifuge at 8000 rpm for 15 minutes, and the liquid was decanted. The procedure was carried out twice. After that, the deposited QDs were dried at 50 °C in air.

#### Results and Discussion

The key to the use of QDs in bioassays is that they must have hydrophilic properties. Importantly, QDs produced by high-temperature organometallic synthesis are hydrophobic, and further application in aqueous media requires additional hydrophilization of their surface, which is usually accompanied by deterioration of optical properties.

QDs produced by aqueous colloidal synthesis (ACS) are hydrophilic and immediately suitable for use. Also, this synthesis is carried out at low temperatures and using relatively environmentally friendly reagents.

CdTe QDs obtained by ACS were used as nuclei for multilayer QDs, where TGA was chosen as a stabilizer. The synthesis was carried out for 60 minutes. The mole ratios of Cd:Te, Cd:TGA are given in Table 1.

Table 1

The mole ratios of Cd:Te, Cd:TGA

	Mole ratios	
	Synthesis of CdTe-TGA QDs	Cd:Te
Cd:TGA		1:3
Synthesis of CdTe/CdS-TGA QDs	CdTe:CdS	1:1.5
		1:3
		1:3.75

Cadmium sulphide was used as a second layer in order to eliminate defects that may appear as a result of the large mismatch of CdTe and ZnS crystal lattices. The mole ratios of CdTe:CdS during the QDs syntheses were 1:1.5, 1:3 and 1:3.75 (Table 1). The CdS precursor concentrations were varied to study the effect of layer thickness on the optical properties of the QDs.

The third layer was the wide band semiconductor ZnS. The bandgap width of zinc sulphide is larger than that of the core, which allows the charge carriers to be kept inside the core without allowing them to interact with the dispersion medium, which has a positive effect on the quantum yield. In addition, zinc sulphide is more resistant to oxidation and has a

higher affinity to thiolcontaining stabilizers, which improves the colloidal stability of QDs [7].

The synthesis revealed that, after coating CdTe/1.5CdS-TGA QDs with ZnS shell, the luminescence of QDs completely disappeared. Therefore, a decision was made to increase the thickness of the CdS shell to move the crystal lattices of CdTe and ZnS further away from each other.

The synthesized CdTe/1.5CdS-TGA, CdTe/3CdS-TGA и CdTe/3.75CdS-TGA QDs were studied by spectral methods of analysis. From the fluorescence spectra (Figure 1), it can be observed that the fluorescence peak of CdTe/3.75CdS-TGA QDs is flatter and narrower compared to the peaks of CdTe/1.5CdS-TGA and CdTe/3CdS-TGA QDs, indicating high dispersion of QDs in size [4].

One of the most important characteristics of a QD is the quantum yield of luminescence.

Therefore, the quantum yield of QDs was calculated. The quantum yield of luminescence was determined by comparison method, where Rhodamine 6J was used as a reference. The quantum yield of luminescence of CdTe/1.5CdS-TGA, CdTe/3CdS-TGA and CdTe/3.75CdS-TGA QDs was 8%, 10% and 13%, respectively. From which it can be concluded that the quantum yield increased when the shell thickness was increased.

The successful coating of QDs with ZnS layer and the improved QDs characteristics depend on the thickness of the second layer - CdS. The synthesized CdTe/1.5CdS-TGA, CdTe/3CdS-TGA and CdTe/3.75CdS-TGA QDs were further coated with a ZnS layer.

The spectral studies showed that the CdTe/1.5CdS-TGA QDs after coating with an additional layer of ZnS completely disappeared fluorescence, while QDs with CdTe:CdS ratios of 1:3 did not lose fluorescence due to the reduced effect of CdTe and ZnS lattice mismatch. The presented spectra (Figure 2) show that the additional ZnS envelope leads to a bathochromic shift of the exciton peak and the fluorescence maximum.

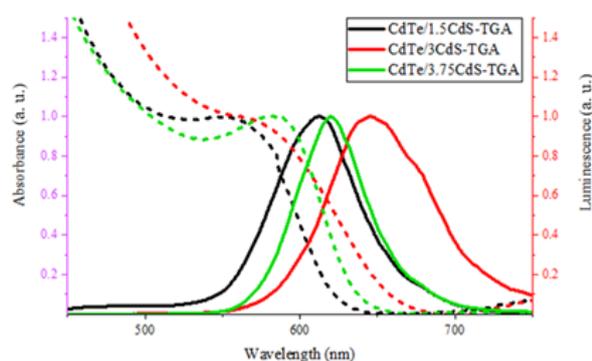


Fig. 1. Normalized absorption and fluorescence spectra of CdTe/1.5CdS-TGA, CdTe/3CdS-TGA and CdTe/3.75CdS-TGA QDs

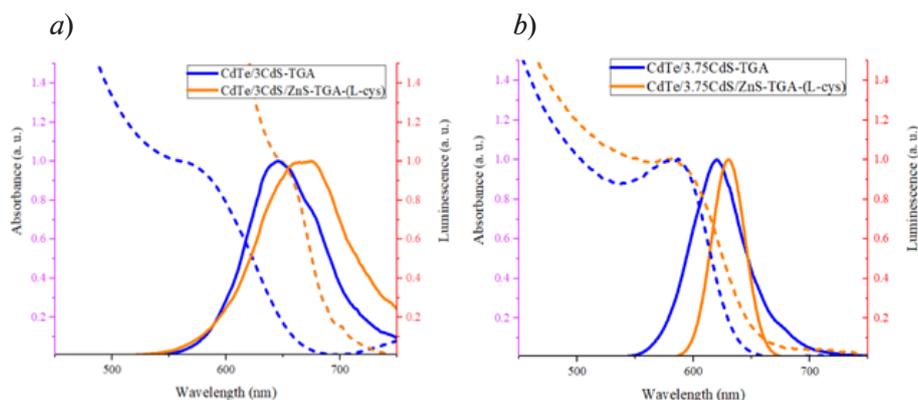


Fig. 2. Normalized absorption and fluorescence spectra of a) CdTe/3CdS-TGA, CdTe/3CdS/ZnS-TGA-(L-cys) QDs, b) CdTe/3.75CdS-TGA и CdTe/3.75CdS/ZnS-TGA-(L-cys) QDs

When coated with a ZnS layer, the quantum yield of CdTe/3CdS/ZnS-TGA-(L-cys) and CdTe/3.75CdS/ZnS-TGA-(L-cys) QDs luminescence was strongly reduced in both cases, which was 3.8% and 1.3%.

Thus, in further studies, it is proposed to continue increasing the CdS shell to improve the optical properties of QDs. But it should be considered that the effects of crystal lattice mismatch between the two materials begin to affect at high shell thicknesses, which leads to the appearance of mechanical stresses that relax with the formation of structural defects, reducing the quantum yield of particles [8].

### Conclusion

The influence of CdS layer thickness on QDs optical properties was studied. The results of this study showed that the optimum thickness of CdS layer was obtained with CdTe:CdS ratio of 1:3.75 because these QDs have better optical characteristics, and also have the highest quantum yield of luminescence in comparison with QDs with other ratios.

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