

# Optimization of Synthetic Conditions for the Preparation of Core-Shell Structures of CdTe/ZnSe QDs in Water <sup>†</sup>

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**Abstract:** Quantum Dots (QDs) are nanocrystals of semiconductors that feature unique optical properties. However, they have high density of dangling bonds on their surface, causing defects that can compromise their fluorescence. Their superficial passivation with another semiconductor is an alternative to reduce these defects. Herein, CdTe QDs stabilized with mercaptosuccinic acid (MSA) and cysteamine (CYA) were synthesized in water and coated with a ZnSe layer, forming a core-shell heterostructure. A photoluminescence improvement greater than 300% was obtained for CdTe/ZnSe-MSA. However, for CdTe/ZnSe-CYA the emission enhancement was around 55%. This study reinforces the importance of the experimental conditions to optimize QDs' emission.

**Keywords:** semiconductors; fluorescence; mercaptosuccinic acid; cysteamine

## 1. Introduction

Quantum Dots (QDs) are semiconductor nanocrystals with sizes between 2–10 nm and unique optical properties, which are related to their composition and diameter. When semiconductors enter the quantum confinement regime, and end up with a diameter close to or smaller than the Bohr radius of the exciton, some changes in their physical-chemical properties occur when compared with bulk materials [1,2].

QDs have a wide application area ranging from optoelectronics devices to biological applications. However, these nanomaterials have a high superficial area/volume ratio, and consequently, a higher amount of unsaturated bonds at their surface due to fewer adjacent coordination atoms, generating intrinsic surface defects. These defects cause an inefficiency in the luminescent properties of these nanocrystals, because the electron when excited instead of relaxing emitting a photon with energy close to that of the band gap (E<sub>g</sub>), can be trapped for a long time on the electronic surface defects and cause a decrease in the luminescence efficiency of the QDs, and can also provoke an asymmetric broadening of the emission band [3,4].

Methods to overcome these issues and improve QDs' photostability and quantum yields have been developed, such as silanization, photoactivation, and the formation of a shell with another semiconductor. Emphasizing the last one, the formation of the heterostructure of the core-shell type has aroused a lot of interest, since it consists of coating the nanocrystal (core) with another semiconductor forming a shell. The formed material has the same optical characteristics as the nucleus, but with the modified surface, the frequency of excitonic recombination and, therefore, the luminescence intensity of the QDs is increased. For cadmium-based QDs, the formation of a core-shell structure can also

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reduce their toxicity. The QDs' surface coating with a second semiconductor can be a challenge, mainly for aqueous colloidal synthesis [4].

The first works focused on the application of core-shell quantum dots date back to the mid-1990s. Since then, the synthesis of these materials has been gradually increasing. In this work, aiming to optimize the optical properties of aqueous CdTe QDs ( $E_g = 1.49$  eV), a layer of ZnSe ( $E_g = 2.69$  eV) was deposited in CdTe QDs' surface, through synthesis in an aqueous colloidal medium, studying several experimental conditions, such as reaction time, temperature, frequency of addition and concentration of precursors.

## 2. Materials and Methods

### 2.1. Preparation of CdTe Quantum Dots

#### 2.1.1. CdTe-MSA

Briefly, CdCl<sub>2</sub> (0.2 mmol, 99.99% Sigma-Aldrich) and mercaptosuccinic acid (MSA, 0.24 mmol,  $\geq 98\%$  Sigma-Aldrich) were dissolved in 100 mL of ultra-pure water. Subsequently, the pH of this mixture was adjusted to  $\sim 10.5$  with NaOH (2 mol.L<sup>-1</sup>), purged under N<sub>2</sub> for 30 min. Then, 5 mL of Na<sub>2</sub>O<sub>3</sub>Te (0.018 mol.L<sup>-1</sup>, 99.99% Sigma-Aldrich) was added, followed by NaBH<sub>4</sub> (3 mmol, 99.99% Sigma-Aldrich) diluted in 5 mL of water. The mixture was allowed to stir for 5 h at 90°C under inert atmosphere.

#### 2.1.2. CdTe CYA

CdCl<sub>2</sub> (4.7 mmol) was dissolved in 125 mL of ultra-pure water, and cysteamine hydrochloride (CYA, 5.7 mmol,  $\geq 98\%$  Sigma-Aldrich) was added. The pH was adjusted to 5.6 - 5.8 with NaOH (2 mol.L<sup>-1</sup>) and the system was purged with N<sub>2</sub> for 30 min. Then, 23 mL of Na<sub>2</sub>O<sub>3</sub>Te (0.0019 mol.L<sup>-1</sup>) and NaBH<sub>4</sub> (0.46 mmol dissolved in 1 mL of ultrapure water) were injected. The system was maintained at 90 °C for 5 h under inert atmosphere.

### 2.2. Preparation of CdTe/ZnSe Core-Shell Structures

The core-shell structures were prepared using the method of Li et al. [5] with modifications. To 10 mL of CdTe were added (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (99.99% Vetec), stabilizing agent (MSA or CYA), Na<sub>2</sub>O<sub>3</sub>Se and NaBH<sub>4</sub> alternatively, divided in several additions (Table 1). After all the additions, the solution was kept under stirring between 90 and 110 min without heating.

**Table 1.** Synthetic parameters tested for the synthesis of CdTe/ZnSe-MSA.

Sample	Zn(OAc) <sub>2</sub> (mmol)	Stabilizing Agent (mmol)	NaBH <sub>4</sub> (mmol)	Na <sub>2</sub> O <sub>3</sub> Se (mmol)	Reaction Time (min)	Number of Additions
S1	0.04	0.05	3.7	0.5	90	2
S2	0.04	0.1	3.7	0.5	90	2
S3	0.04	0.05	3.7	0.5	110	2
S4	0.04	0.05	1.85	0.5	90	2

To study the influence of the reagent addition, the shell precursors were added in the following manner: sample S3\_1 - each precursor was added at once; S3\_2 - the volume of precursor solutions was divided into 2 additions; S3\_3 - the volume of precursors was divided into 5 additions; and S3\_4 - the volume of precursors was divided into 10 additions.

### 2.3. Optical Characterization

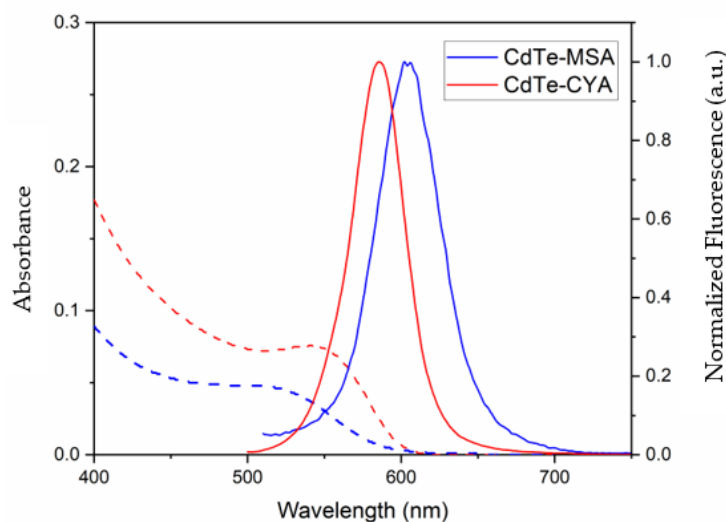
All samples were submitted to optical characterization, by electronic absorption spectroscopy in the UV-Vis region (Evolution 600 spectrophotometer, Thermo Scientific) and spectroscopy of electronic fluorescence (fluorimeter LS 55, PerkinElmer), with excitation

at 488 nm. The CdTe diameter was estimated according with the equations proposed by Dagtepe et al. [6].

### 3. Results and Discussion

#### 3.1. Preparation of CdTe Quantum Dots

The QDs of CdTe stabilized with MSA and CYA were obtained successfully. The absorption and electron emission profiles of the QDs are presented in Figure 1. CdTe-MSA presented an emission maximum at around 600 nm, with a full-width at half-maximum (FWHM) of 61 nm, and an average size of 3.20 nm. CdTe-CYA were obtained emitting at 590 nm, with a FWHM of 54 nm, and a diameter of 3.15 nm.



**Figure 1.** Absorption and emission ( $\lambda_{exc} = 488$  nm) spectra of CdTe QDs stabilized with MSA and CYA.

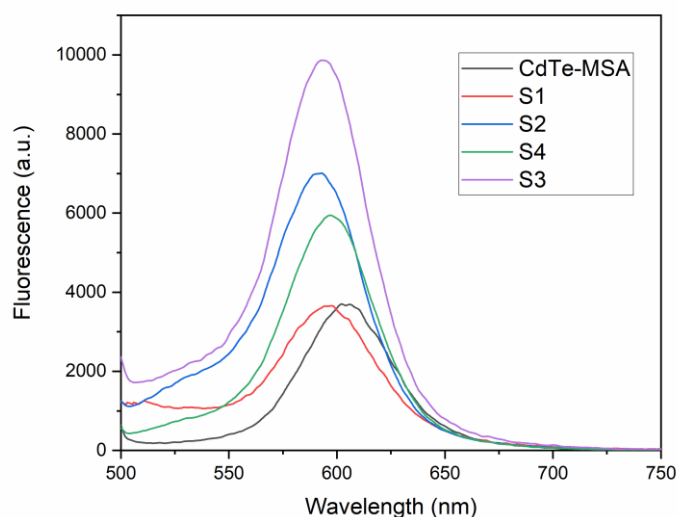
#### 3.2. Preparation of Core-Shell Structures of CdTe/ZnSe Stabilized with MSA

The first attempts to form the ZnSe layer on the CdTe particles resulted in unstable suspensions, which precipitated at the end of the synthesis, leading to the need for adjustments in the methodology. Some factors, such as temperature, concentration of precursors, pH, volume of additions can affect colloidal stability during the process. The literature describes that the temperature, for example, directly affects the deposition of the semiconductor on the QDs, since the temperature influences the kinetics of material formation, where temperatures below 100 °C are preferable, since high temperatures can affect the adsorption of the stabilizer on the surface of the QD, and there may be changes in the QD during the procedure [7].

To optimize the CdTe-MSA QDs' emission after deposition of a ZnSe layer, some experimental parameters were studied. During these experiments, we observed that carrying out the reaction at room temperature and without an inert atmosphere, maintained the QDs' colloidal stability. Then, we studied the influence of the MSA stabilizer concentration (samples S1 and S2), reaction time (sample S3), and the NaBH<sub>4</sub> concentration (sample S4).

For all these samples (S1–S4) no significant shift in the absorption maximum was observed, indicating that the CdTe core was not affected during the QDs' passivation. Comparing sample S1 with the starting QD, it was verified that there was a blue-shift of 9 nm the emission band, but no significant change in the emission occurred (Figure 2). Increasing the MSA quantity (S2) a 87% increase in the QDs' emission intensity was observed (Figure 2), indicating that the stabilizer plays an important role in the shell formation.

Reducing the  $\text{NaBH}_4$  quantity (S4) presented also a improve in the emission intensity (57%). However, the best coating attempt so far was sample S3, with a fluorescence enhancement of 166%. Thus, the further experiments were done based on S3 synthetic conditions, maintained the reaction time at 110 minutes.



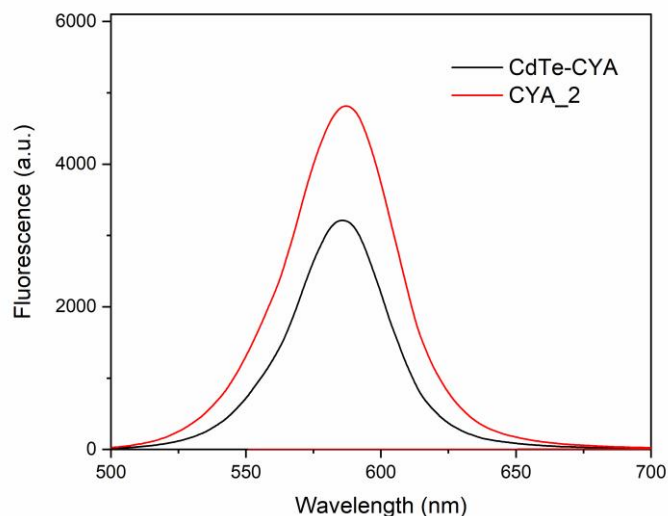
**Figure 2.** Emission spectra ( $\lambda_{\text{exc}} = 488 \text{ nm}$ ) of original and modified CdTe-MSA (samples S1–S4).

It has been reported in the literature that the number of additions can influence the shell depositions and growth. Thus, we added the reagents considering different number of additions (samples S3\_1 to S3\_4). Among these attempts, sample S3\_3 showed the higher enhancement in the emission intensity (376%).

The influence of the reaction temperature in the conditions of samples S3\_3 was also studied, from 30 to 90 °C. And, it was observed an increase of 361% at 30 °C, suggesting that the condition with the lowest temperature was more efficient for this procedure. Therefore, the best synthetic parameters for the formation of CdTe/ZnSe-MSA with improved fluorescence intensity involve temperature around room-temperature (30 °C) and divide the reagents addition in several fractions. Then, the best conditions were also tested with a positively-charged CdTe QD.

### 3.3. Preparation of Core-Shell Structures of CdTe/ZnSe Stabilized with CYA

Two tests were performed using CdTe QDs stabilized with cysteamine (CYA), which are cationic nanoparticles at approximately pH 5.8–6.0. The best coating conditions obtained for MSA stabilized quantum dots was initially tested (sample CYA\_1). Another test was done without the presence of borohydride (CYA\_2). In the CYA\_1 attempt, after the addition of borohydride, the nanoparticles precipitated and this can be explained by the increase in the pH of the suspension, which leads to a decrease in the stability of the QDs. Furthermore, it was observed that the emission spectrum of the CYA\_2 sample presented an increase of more than 55% in the emission intensity, maintaining however the FWHM similar to the original QD, without displacement of the emission maximum, suggesting that there was only superficial change (Figure 3).



**Figure 3.** Emission spectra ( $\lambda_{\text{exc}} = 488 \text{ nm}$ ) of original and modified CdTe-CYA.

#### 4. Conclusions

From the results obtained in this work, we concluded that the best condition for the formation of a shell of ZnSe on CdTe-MSA QDs was at room temperature ( $\sim 30^\circ \text{C}$ ), with pH  $\sim 10.5$  and the precursors added in five aliquots. Using these conditions, a spectral enhancement greater than 350% was obtained. For the system with CdTe-CYA, a behavior similar to CdTe-MSA was observed, however with a lower fluorescence enhancement (55%). Thus, this study reinforces the importance of studying the experimental conditions to control the surface modification process of QDs for an optimized emission.

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