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# Optimization of Synthetic Conditions for the Preparation of Core–Shell Structures of CdTe/ZnSe QDs in Water [†]

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**Abstract:** Quantum dots (QDs) are nanocrystal semiconductors that feature unique optical properties. However, they have a high density of dangling bonds on their surface, causing defects that can compromise their fluorescence. Their superficial passivation using another semiconductor is an alternative to reduce these defects. Herein, CdTe QDs stabilized with mercaptusuccinic acid (MSA) and cysteamine (CYA) were synthesized in water and coated with a ZnSe layer, forming a core–shell heterostructure. An improvement in photoluminescence 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

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## 1. Introduction

Quantum dots (QDs) are semiconductor nanocrystals with sizes between 2 and 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 and emitting a photon with energy close to that of the band gap (Eg), 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 the 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 a core–shell-type heterostructure 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 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 (Eg = 1.49 eV), a layer of ZnSe (Eg = 2.69 eV) was deposited onto CdTe QDs' surface, through synthesis in an aqueous colloidal medium, while studying several experimental conditions, such as reaction time, temperature, the frequency of addition, and the concentration of precursors.

## 2. Materials and Methods

### *2.1. Preparation of CdTe Quantum Dots*

### 2.1.1. CdTe-MSA

Briefly, $CdCl_2$ (0.2 mmol, 99.99% Sigma-Aldrich, Burlington, MA, USA) and mercaptusuccinic acid (MSA, 0.24 mmol, $\geq$ 98% Sigma-Aldrich) were dissolved in 100 mL of ultrapure water. Subsequently, the pH of this mixture was adjusted to ~10.5 with NaOH (2 $mol.L^{-1}$), purged under $N_2$ for 30 min. Then, 5 mL of $Na_2O_3Te$ (0.018 $mol.L^{-1}$, 99.99% Sigma-Aldrich) was added, followed by $NaBH_4$ (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

$CdCl_2$ (4.7 mmol) was dissolved in 125 mL of ultrapure 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 $mol.L^{-1}$), and the system was purged with $N_2$ for 30 min. Then, 23 mL of $Na_2O_3Te$ (0.0019 $mol.L^{-1}$) and $NaBH_4$ (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 $(Zn(CH_3COO)_2)\cdot 2H_2O$ (99.99% Vetec), a stabilizing agent (MSA or CYA), and $Na_2O_3Se$ and $NaBH_4$ 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 | $Zn(OAc)_2$ (mmol) | Stabilizing Agent (mmol) | $NaBH_4$ (mmol) | $Na_2O_3Se$ (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 in a single addition; 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, Waltham, MA, USA) and spectroscopy of electronic fluorescence (fluorimeter LS 55, PerkinElmer, Shelton, CT, USA), 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 CdTe QDs 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 quantum dots were obtained emitting at 590 nm, with a FWHM of 54 nm, and a diameter of 3.15 nm.

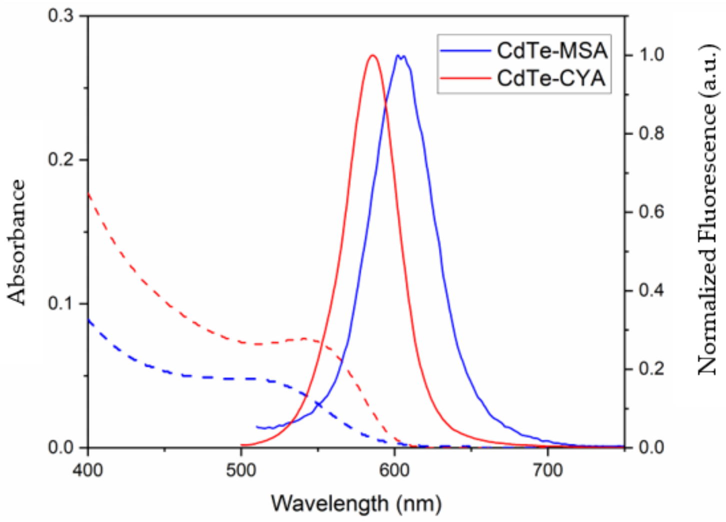

**Figure 1.** Absorption and emission ($\lambda_{exc}$ = 488 nm) spectra of CdTe QDs stabilized with MSA and CYA.

### 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, the concentration of precursors, pH, and the 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 the 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 $NaBH_4$ 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 in 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 $NaBH_4$ quantity (S4) also presented an improvement in the emission intensity (57%). However, the best coating attempt so far was sample S3, with a fluorescence enhancement of 166%. Thus, the subsequent experiments were performed based on the S3 synthetic conditions while maintaining the reaction time at 110 minutes.

It has been reported in the literature that the number of additions can influence shell deposition and growth. Thus, we added the reagents considering the different number of additions (samples S3_1 to S3_4). Among these attempts, sample S3_3 showed the highest enhancement in the emission intensity (376%).

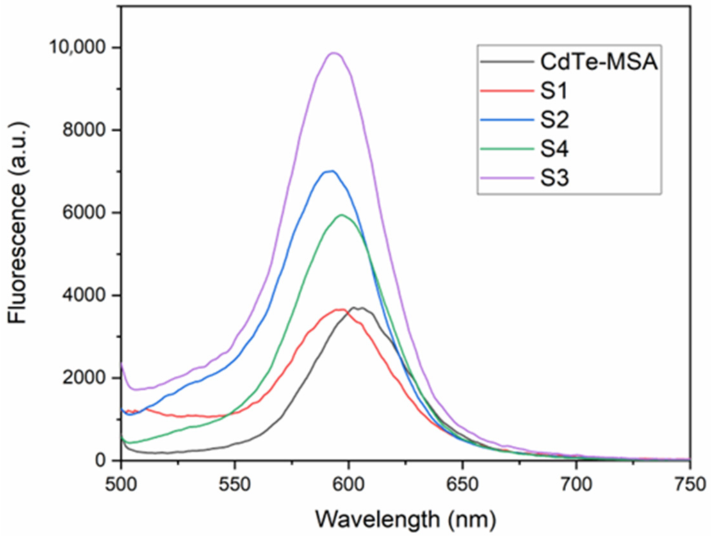

**Figure 2.** Emission spectra ($\lambda_{exc}$ = 488 nm) of original and modified CdTe-MSA (samples S1–S4).

The influence of the reaction temperature in the conditions of samples S3_3 was also studied, from 30 to 90 °C. And an increase of 361% at 30 °C was observed, 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 involved temperatures around room temperature (30 °C) and the reagents' addition divided 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 were initially tested (sample CYA_1). Another test was performed 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, an FWHM similar to that of the original QD, without the displacement of the emission maximum, suggesting that there was only a superficial change (Figure 3).

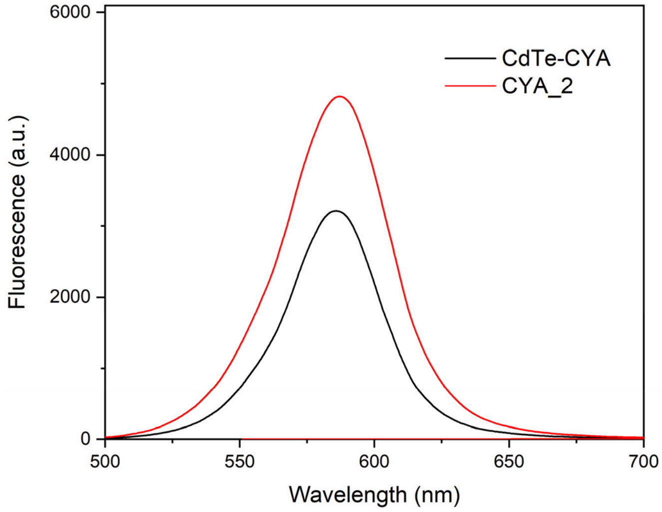

**Figure 3.** Emission spectra ($\lambda_{exc}$ = 488 nm) of original and modified CdTe-CYA.

## 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 (~30 °C), with pH ~10.5 and the precursors being 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, albeit 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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