

Supplementary Material: Water-Soluble CdTe/CdS Core/Shell Semiconductor Nanocrystals: How Their Optical Properties Depend on the Synthesis Methods

Brener R. C. Vale, Fernanda O. Silva, Melissa S. Carvalho, Ellen Raphael, Jefferson L. Ferrari and Marco A. Schiavon

1. How to Determine the Amount of Precursors of Cd²⁺ and S²⁻ to Grow Core/Shell

To determine the amount of Cd and S precursors necessary to grow each CdS monolayer, we used the Lambert-Beer law to calculate the CdTe nanocrystals concentration. To this end, we first determined the CdTe nanocrystals size using the relationship existing between λ_{abs} , obtained from the UV-vis absorption spectrum, and the nanocrystals diameter (D) (Equation (1)). Then, we verified the molar extinction coefficient (ϵ) for CdTe according to Equation (2) [1].

$$D = (9.8127 \times 10^{-7}) \lambda_{abs}^3 - (1.7147 \times 10^{-3}) \lambda_{abs}^2 + (1.0064) \lambda - (194.84) \quad (1)$$

$$\epsilon = 10043(D)^{2.12} \quad (2)$$

Knowing ϵ , we employed the Lambert-Beer law (Equation (3)) to determine the concentration of the solution containing the CdTe nanocrystals, where A , ϵ , c and l represent the absorbance (dimensionless), the molar absorptivity coefficient ($L \cdot mol^{-1} \cdot cm^{-1}$), the nanocrystals concentration ($mol \cdot L^{-1}$), and the path length (cm) of the cell used during analysis, respectively.

$$A = \epsilon cl \quad (3)$$

Finally, by determining the CdTe nanocrystals size and the molar concentration of the solution containing the nanocrystals, we were able to calculate the amount of Cd and S precursors that would be necessary to grow between one and five CdS monolayers around the CdTe nanocrystals using the following equations [2]:

$$V_{CD}(ML_x) = \frac{4}{3} \pi [(r_{AB} + xD)^3 - r_{AB}^3] \quad (4)$$

$$n_{CD}(ML_x) = \rho_{CD} C + V_{CD}(ML_x) \cdot 10^{-27} / m_{CD} \quad (5)$$

$$n_{CD} = n_{AB} n_{CD}(ML_x) \quad (6)$$

Where V_{CD} corresponds to the volume of the shell containing x monolayers (nm^3), r_{AB} is the core nanocrystal radius (nm), and d is the thickness of one monolayer, which can be defined as half of the parameter of the network constituting the shell. In this case, the CdS network parameter was $6.714 \text{ \AA}$, so the mean thickness of a monolayer was 0.35 nm [2]. In Equation (5), $n_{CD}(ML_x)$ represents the number of monomer units of the shell constituents in x monolayers (with no dimension), ρ_{CD} is the density of the shell constituent ($kg \cdot m^{-3}$), and m_{CD} is the mass of one monomer in the shell constituent. For CdS, we have that $\rho_{CD} = 4820 \text{ kg} \cdot m^{-3}$ [3] and $m_{CD} = 0.1444 \text{ kg}$. Finally, in Equation (6), n_{CD} represents the molar quantities of the Cd and S precursors that are necessary to grow x monolayers ($mmol$). It was possible to obtain this value by using the nanocrystals concentration in the core, n_{AB} ($mmol$), calculated by the Lambert-Beer law, and the number of monomer units in the shell constituent, $n_{CD}(ML_x)$, determined according to Equation (5). Table S1 lists data relative to the molar quantities of the Cd and S precursors necessary to grow between one and five CdS monolayers on the CdTe nanocrystals— 2.17 nm obtained at 30 min of synthesis.

Table S1. Molar quantities of the Cd and S precursors necessary to grow between one and five CdS layers around CdTe nanocrystals—2.17 nm.

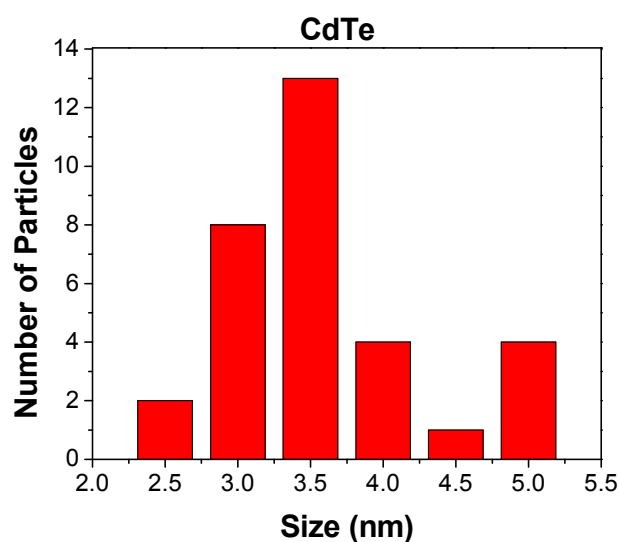
Number of CdS Layers	n_{CD} Cd and S/mmol
1	0.02580
2	0.03820
3	0.05303
4	0.07028
5	0.10116

Table S2. Molar quantities of the Cd and S precursors necessary to grow between one and five CdS layers around CdTe nanocrystals—3.10 nm.

Number of CdS Layers	n_{CD} Cd and S/mmol
1	0.02009
2	0.02743
3	0.03590
4	0.04553
5	0.07150

Table S3. Molar quantities of the Cd and S precursors necessary to grow between one and five CdS layers around CdTe nanocrystals—3.45 nm.

Number of CdS Layers	n_{CD} Cd and S/mmol
1	0.01881
2	0.02511
3	0.03231
4	0.04043
5	0.06529

**Figure S1.** Histogram of the particle size distribution of CdTe obtained with 4 h of synthesis.

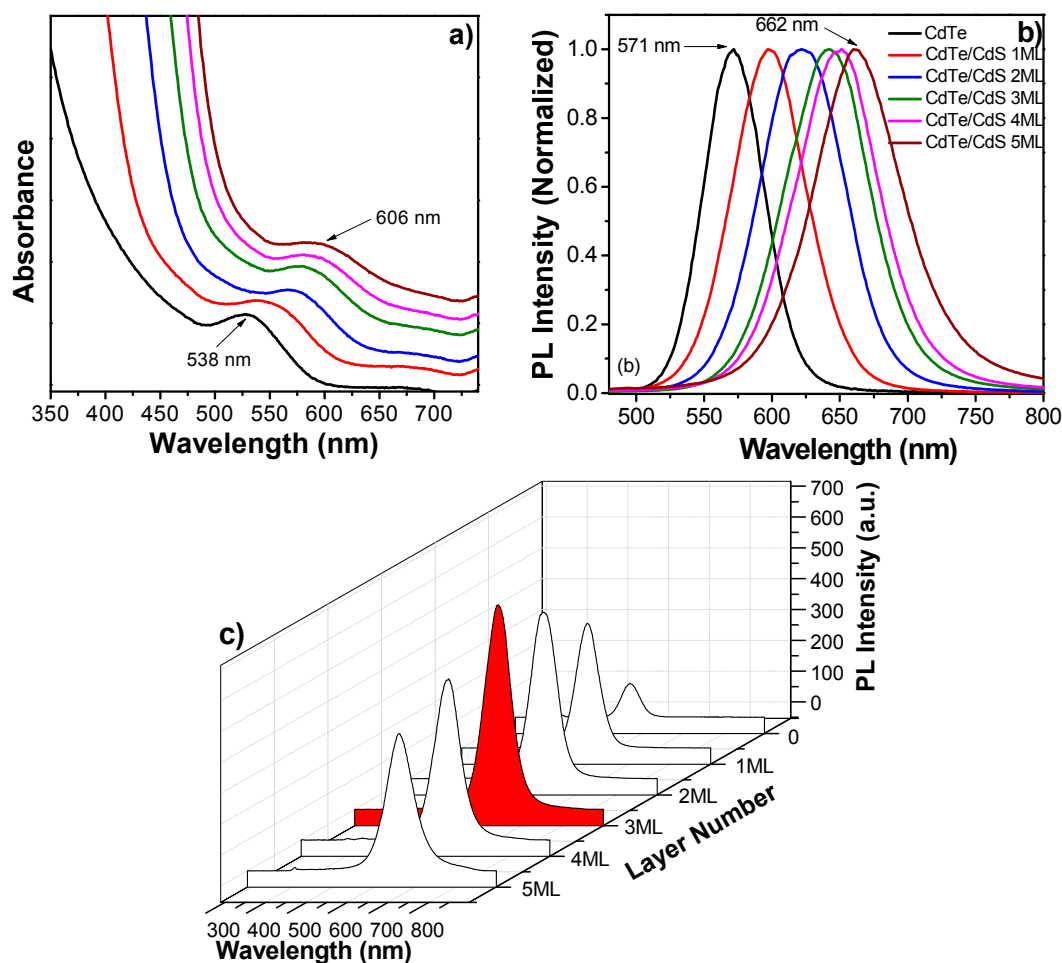


Figure S2. UV-vis absorption (a) and PL (b) and (c) spectra of CdTe/CdS QDs prepared with 1 to 5 monolayers of CdS, and CdTe nanocrystals—3.10 nm.

2. Determination of the Fluorescence Quantum Yield (QY)

In this work, we determined QY for the CdTe/CdS QDs by the comparative method of Willians et al. [4], using rhodamine 101 (QY = 1.0) as standard. Initially, we prepared a rhodamine stock solution by dissolving it 4.8×10^{-3} mmol in 50 mL of water. Then, we removed aliquots (0.02, 0.03, 0.04, 0.05, 0.06, 0.07 and 0.08 mL) from this solution, and obtained the absorption and emission spectra of the samples. We then recorded the intensity of the absorbance band around 355 nm (λ_{exc}) and the integrated fluorescence band intensity (fluorescence spectrum area), to plot integrated fluorescence intensity vs absorbance for this standard. We conducted the same procedure for the QDs samples, also using aliquots of 0.02, 0.03, 0.04, 0.05, 0.06, 0.07 and 0.08 mL. Using the absorption (intensity of the absorption band at 355 nm) and the emission (integrated fluorescence band intensity) spectral data of these samples, we constructed a graph of integrated fluorescence vs. absorbance. Rhodamine 101 displays absorption (~575 nm) and emission (~598 nm) bands in the same regions as CdTe nanocrystals, making it a useful standard.

Using the intensity of the absorption band at 355 nm and the integrated fluorescence intensity of rhodamine 101 and CdTe/CdS QDs with three CdS monolayers, we obtained the relationship between integrated fluorescence and absorbance, as illustrated in Figure S3.

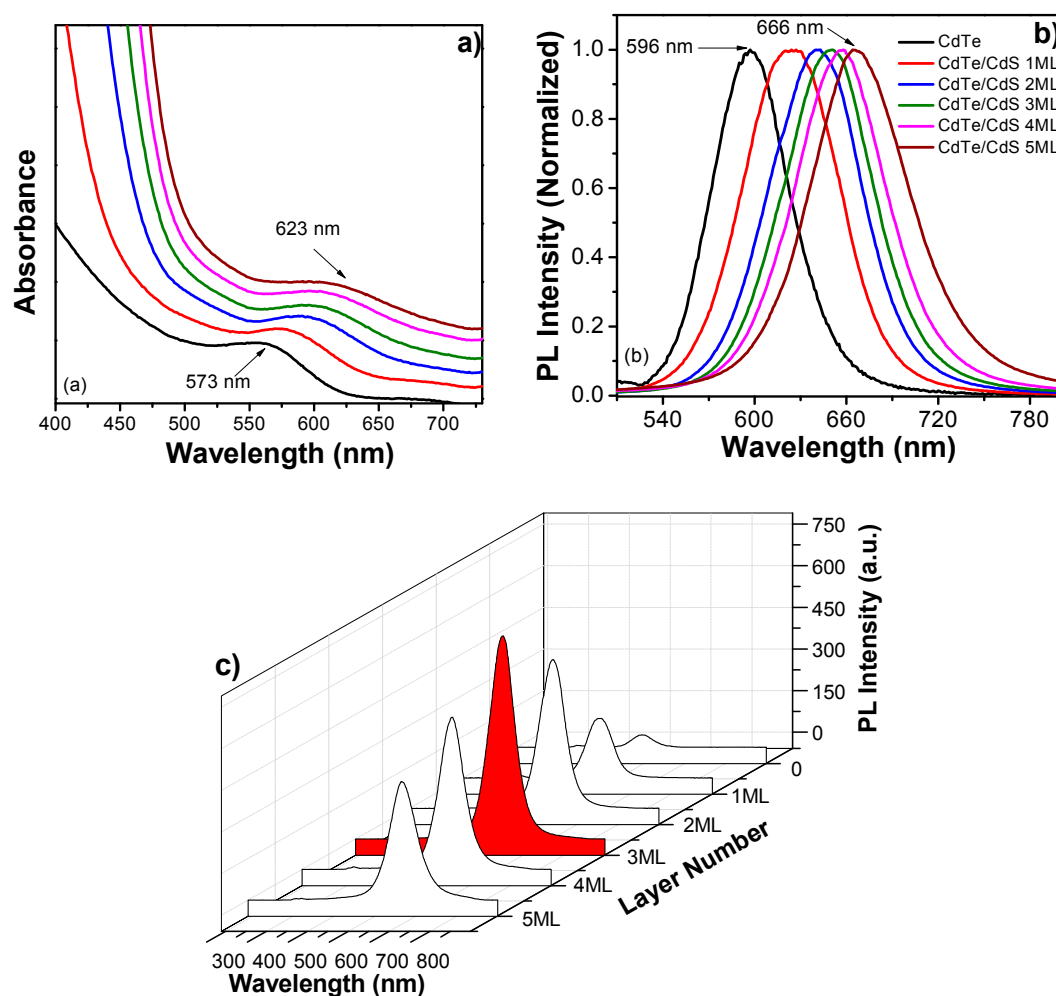


Figure S3. UV-vis absorption (a) and PL (b) and (c) spectra of CdTe/CdS QDs prepared with 1 to 5 monolayers of CdS, and CdTe nanocrystals—3.45 nm.

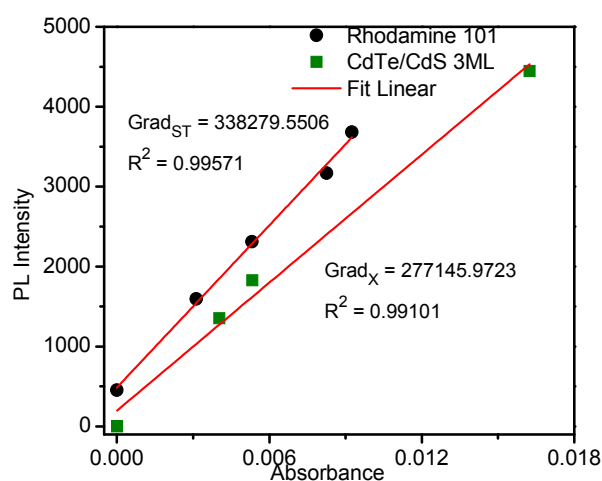


Figure S4. Relationship between absorbance and integrated fluorescence intensity for rhodamine 101 (standard) and CdTe/CdS QDs with three CdS layers.

Using the gradients obtained for the curves presented in Figure S3, we used Equation (7) and obtained QY (ϕ_f) equal to 81.92%. The subscripts X and ST represent the test sample and the standard, respectively; Grad corresponds to the slope of the straight line obtained by plotting integrated fluorescence intensity vs. absorbance; and η is the solvent refractive index. For the QDs,

we obtained ϕ_f by excluding the refraction index, because we used water ($\eta=1.0$) as solvent to prepare the rhodamine and the QDs stock solutions.

$$\phi_X = \phi_{ST} \left(\frac{Grad_X}{Grad_{ST}} \right) \left(\frac{\eta_X^2}{\eta_{ST}^2} \right) \quad (7)$$

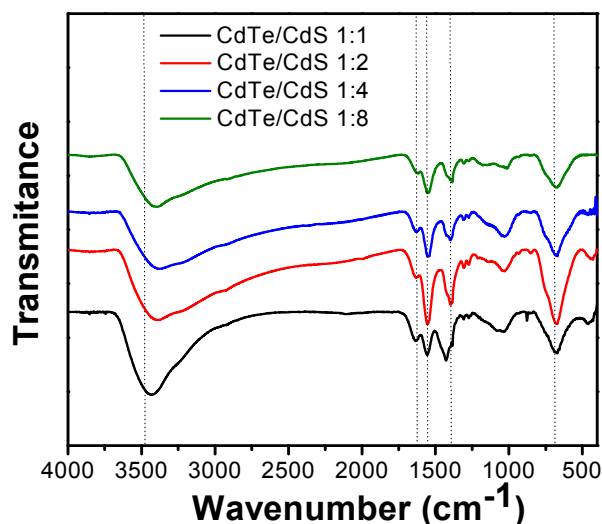


Figure S5. FTIR spectra of the CdTe/CdS core/shell growth with a Cd²⁺:thiourea (S²⁻) molar ratio of 1:1, 1:2, 1:4 and 1:8.

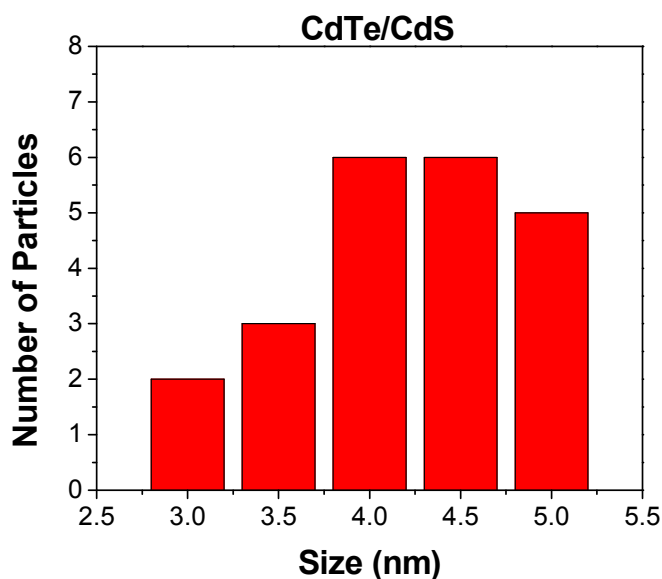


Figure S6. Histogram of the particle size distribution of CdTe/CdS 1:2 obtained.

3. Procedure for Ligand Exchange

The CdTe nanocrystals and CdTe/CdS QDs precipitates obtained by both methods were submitted to ligand exchange. The short-chain MPA was replaced with the long-chain ligand 1-dodecanol (DDT), so that the initially water-soluble QDs would be soluble in organic medium. To achieve phase transfer, the QDs were first dissolved in 1 mL of ultrapure water and then added to 1 mL of DDT and 3 mL of acetone. The latter solvent helped to diminish the water/DDT interface surface tension. The final mixture was vigorously stirred and heated to the acetone boiling temperature. In this way, the QDs present in the aqueous phase were rapidly transferred to the organic phase, as detected by the change in the color and PL of the latter phase. After transfer, the

organic phase containing the QDs was separated and diluted with toluene 1:1 *v/v*. Finally, the QDs in the organic phase were successively washed with methanol, to remove remaining impurities.

References

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