

## CdTe/ZnS Quantum Dot Using Molecular Single-Source Precursors

Shohei Tanaguchi and Mark Green

### Supporting Information

#### Concentration of QDs

Concentrations of prepared QDs samples were calculated using the method presented by Yu *et al.*<sup>1</sup> The formulae are based on the experimental observation that the extinction coefficient per mole of high quality CdE (E = S, Se, Te) QDs was found to be dependent on nanocrystals size; the theory can be further extended to determine the concentration of the nanocrystals sample by a combination of the Lambert–Beer law and absorption profiles.

Systematic characterisation of mono-dispersed CdE QDs using both mass spectrometry and optical spectroscopy suggested the relationship between an excitonic peak ( $\lambda$ ) and a diameter (D) as:

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - 194.84 \quad (11)$$

The equation is only applicable to CdTe QDs. For other QDs, see the literature.<sup>A1</sup> Extinction coefficient,  $\epsilon$ , of the CdTe QDs can be obtained from an empirical function of the nanocrystals size as follows.

$$\epsilon = 10043(D)^{2.12} \quad (12)$$

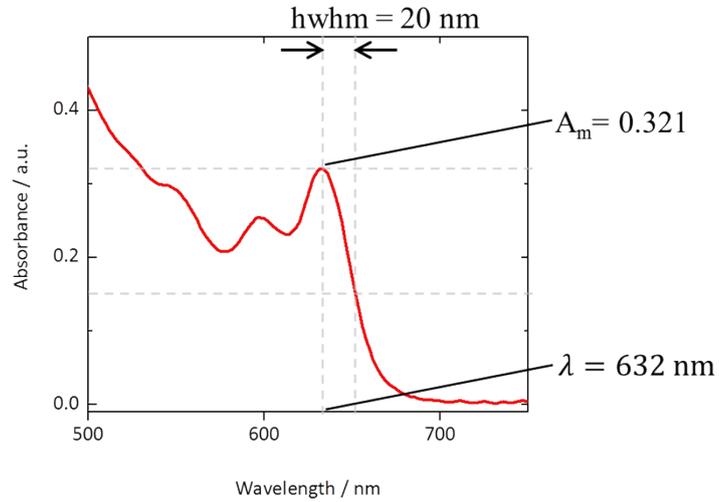
From the Lambert-Beer law, the concentration of the CdTe QDs (C) is acquired.

$$C = A_{cal}/\epsilon \cdot L \quad (13)$$

$L$  is the path length of the cuvette, and  $A_{cal}$  is a calibrated absorbance (where mono-dispersity of the sample was taken in to account). The  $A_{cal}$  can be calculated by the equation below.

$$A_{cal} = A_m \cdot (hwhm)/K \quad (14)$$

$A_m$  is the measured absorbance at the first excitonic peak and  $K$  is an average hwhm (half width at half maximum) on the long wavelength side. In the case of CdTe QDs,  $K = 18$  nm. Figure 1 explains an example of the concentration determination process.



$$\lambda = 632 \text{ nm} \Leftrightarrow D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - 194.84 = 4.02 \text{ (nm)}$$

$$\epsilon = 10043(D)^{2.12} = 10043(3.01)^{2.12} = 1.92 \cdot 10^5 \text{ (cm}^{-1}\text{M}^{-1}\text{)}$$

$$A_{cal} = A_m \cdot (\text{hwhm})/K = 0.321 \cdot 20 / 18 = 0.357$$

$$C = A_{cal}/\epsilon \cdot L = 0.357 / 1.04 \cdot 10^5 \cdot 1 = 1.84 \text{ (}\mu\text{M)}$$

Figure 1. Typical absorption spectrum of CdTe QDs (4.02 nm diameter) and the calculation process for particles concentration based on spectral data.

### Calculation of the Amount of Shell Sources for One Monolayer

In the synthesis of core/shell QDs using the successive ionic layer adsorption and reaction method, it is essential that the shell source added does not exceed the amount required to form just one layer; if excess shell precursors was present in solution, undesired nucleation occurred, which decreased the quality of the resulting core/shell QDs. Crystallographic parameters, as well as some basic physical properties, were taken into account in order to determine the amount of shell precursors to be added. First step was to calculate the shell thickness for one layer of shell material. In the case of ZnS, where two possible crystal structures are expected, we took an average thickness from two structures for further processing.<sup>2</sup> Figure 2 shows crystal structures of wurtzite (hexagonal) and zinc blende (cubic) ZnS. From the wurtzite structure, the monolayer thickness ( $d$ ) was assumed to be half of the c-lattice parameter ( $c$ ):

$$d = c/2 = 0.626/2 = 0.313 \text{ (nm)} \quad (15)$$

Also, the shell thickness is thought to be equivalent to the height of a tetrahedron highlighted in Figure B-1. In the zinc blende structure, shell thickness ( $d'$ ) was obtained based on the height of a tetrahedron:

$$d' = a/\sqrt{3} = 0.542/\sqrt{3} = 0.313 \text{ (nm)} \quad (16)$$

Where  $a$  is the lattice parameter of zinc blende ZnS. Therefore, the average shell thickness of one monolayer was 0.313 nm.

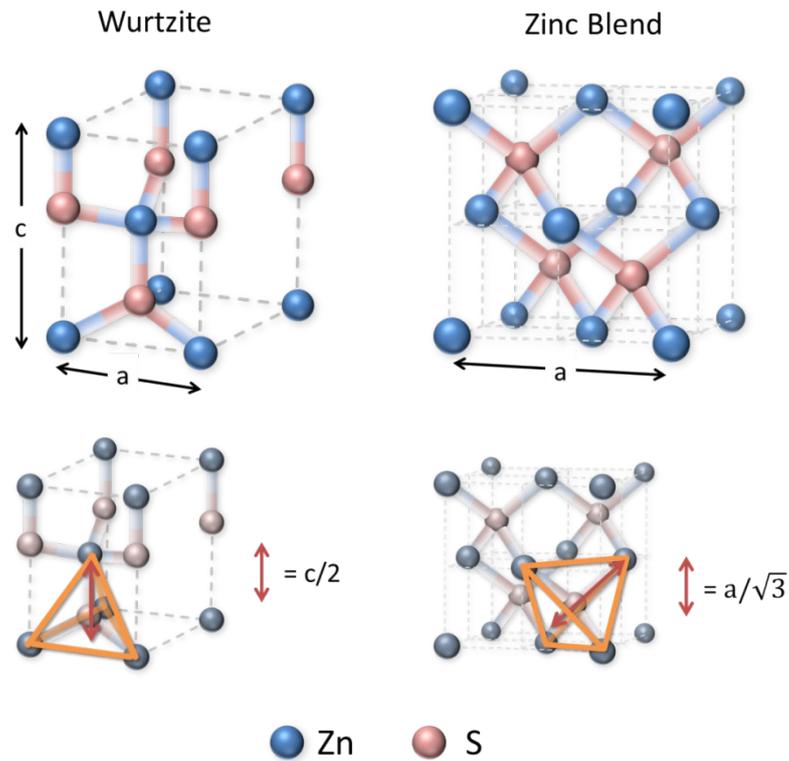


Figure 2. Schematics of wurtzite and zinc blende ZnS crystals. The tetrahedron units consisting of four zinc atoms are highlighted in orange lines.

Figure 3 shows the schematics of CdTe/ZnS QDs. For the simplicity, it is hypothesised that a particle is completely spherical and a shell forms concentrically.

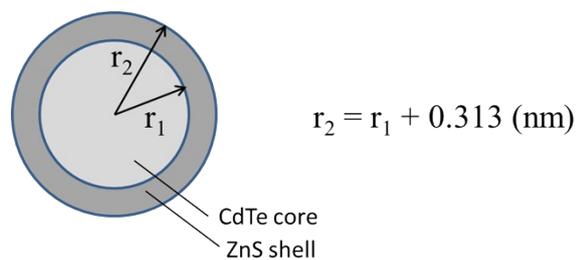


Figure 3. Simplified structure of a CdTe particle with a monolayer of ZnS shell.

When a core diameter is 4.0 nm ( $r_1 = 2.0$  nm), the volume of a layer of ZnS shell can be calculated as follows.

(Volume of CdTe,  $V_1$ )

$$V_1 = \frac{4}{3}\pi \cdot r_1^3 = \frac{4}{3}\pi \cdot (2.0 \times 10^{-9})^3 = 33.49 \times 10^{-27} (m^3) \quad (17)$$

(Volume of CdTe+ZnS,  $V_2$ )

$$V_2 = \frac{4}{3}\pi \cdot r_2^3 = \frac{4}{3}\pi \cdot ((2.0 + 0.313) \times 10^{-9})^3 = 51.81 \times 10^{-27} (m^3) \quad (18)$$

Therefore, the volume of ZnS shell is  $V_{ZnS} = V_2 - V_1 = 18.32 \times 10^{-27} m^3$ . The molar amount of ZnS precursor ( $X$ ) per CdTe core particle is described as follows:

$$\begin{aligned} X &= \frac{V_{ZnS} \cdot D}{M_w} = 18.32 \times 10^{-27} \cdot 4.10 \times 10^{-6} / 97.474 \\ &= 7.71 \times 10^{-22} (mol \text{ per a particle}) \end{aligned} \quad (19)$$

where  $D$  is the density of ZnS ( $4.10 \times 10^{-6} g/m^3$ ), and  $M_w$  is the molecular weight on ZnS (97.474 g/mol).<sup>3</sup> Finally, the overall amount of ZnS precursors for the CdTe solution can be calculated by the obtained  $X$  value.

$$[ZnS] = X \cdot C_{CdTe} \cdot V_{solution} \cdot N_A \quad (20)$$

$C_{CdTe}$  is the concentration of CdTe QDs solution calculated from equation (12),  $V_{solution}$  is the volume of the CdTe solution, and  $N_A$  is the Avogadro constant ( $6.02 \times 10^{23} mol^{-1}$ ).<sup>4</sup> When we use 10 mL of the solution having the absorption spectrum as shown in Figure A-1, the equation (20) is substituted as follows.

$$\begin{aligned} [ZnS] &= 7.71 \times 10^{-22} \cdot 1.84 \times 10^{-6} \cdot \frac{10}{1000} \cdot 6.02 \times 10^{23} \\ &= 8.5 \times 10^{-6} (mol) \end{aligned}$$

For the second shell deposition, the volume of the second layer of ZnS shell can be obtained by a re-calculation of equation (17) and (18) with new radii. Then, the new values of  $X$  and  $[ZnS]$  can be calculated in the same manner using equation (19) and (20).

## References

- 1 Yu, W. W.; Qu, L. H.; Guo, W. Z.; Peng, X. G., *Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals*. Chem. Mater. **2003**, 15 (14), p. 2854-2860.
- 2 Chen, D. A.; Zhao, F.; Qi, H.; Rutherford, M.; Peng, X. G., *Bright and Stable Purple/Blue Emitting CdS/ZnS Core/Shell Nanocrystals Grown by Thermal Cycling Using a Single-Source Precursor*. Chem. Mater. **2010**, 22 (4), p. 1437-1444.

- 3 National\_Center\_for\_Biotechnology\_Information *Pubchem*. <http://pubchem.ncbi.nlm.nih.gov/>  
**2012**. February.
- 4 National\_Institute\_of\_Standards\_and\_Technology *Fundamental Physical Constants*.  
<http://physics.nist.gov/cgi-bin/cuu/Value?na> **2012**. February.