Synthesis and Characterization of ZnS capped CdSe Quantum Dots

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Introduction

Quantum dots are nanocrystalline semiconductors which exhibit absorbance and emission in the UV/VIS region of the electromagnetic spectrum depending on crystal radii.[1] The emission and the absorbance spectrum of a quantum dot is easily tuned by size and composition.[2] Tuning of this emission and absorbance has paved the way for electrochemical devices utilizing quantum dots.[3]

Figure 1 shows the synthesized CdSe quantum dots under short wave UV radiation (left) and the capped ZnS – CdSe Quantum Dots (right)

Experimental

Synthesis of CdSe Quantum Dots [2]

Selenium powder (99mg, 1.25 mmol) was added to 5.5 mL of trioctylphosphine. Powder dissolved at room temperature. Cadmium Acetate (53 mg, 0.19 mmol) was added to oleic acid (0.6 mL) and octadecene (5.5 mL). Growth solution was then prepared using 10 mL of octadecene. The growth solution was heated to 165 ^{o}C.

The cadmium solution was heated to 130 ^{o}C. 1 mL of the cadmium solution and 1 mL of the selenium solution was injected into the heated growth solution under vigorous stirring. The CdSe clusters form immediately, and 1 mL of the solution was drawn first at every 30 seconds for the first 1.5 minutes. 1 mL was extracted every minute until there was no solution remaining. **Figure 1** shows the first 7 solutions extracted from the mixture under UV light.

Capping of CdSe quantum dots with ZnS

NaS_2 (15 mg, 0.26 mmol) was added to oleic acid (1 mL) and trioctylphosphine (2mL). Solution was heated to 130 ^{o}C to aid in the dissolution of the zinc sulfide. $Zn(NO_3)_2$ (0.59 mg, 0.26 mmol) was added to oleic acid (1 mL) and trioctylphosphine (2 mL). The tenth extraction was split into two 0.5 mL portions. One of the portions was heated to 130 ^{o}C along with both the zinc and sulfide solutions. After temperature was equilibrated 1 mL of each solution was added to the tenth extraction.

A 0.25 ml aliquot was extracted every five minutes after 30 seconds. **Figure 1** shows these aliquots under UV light.

Results and Discussion

As the time increased from initial injection of quantum dots growth solution, the absorbance bands red shifted. This is visualized in **Figure 1** and **Figure 2**.

Excitation of a quantum dot occurs when a photon generates an electron-hole pair that are bound with a columbic potential.[4] When the Bohr excitation radius of the electron is larger than the size of the dot, quantum confinement effects begin to become significant.

The electron in the quantum dot can then be treated as a particle confined to a sphere. This effect causes the lowest energy level of the electron in the quantum dot to be localized over the entire dot as a spherical field. The Hamiltonian operator of the electron can then be calculated for each discrete energy level just like the two particle hydrogen atom system.

Solving this system gives the simplified equation below for the estimating energy of excitation for the quantum dot.[5]

$$E_{QD} = E_{Bulk\ Semiconductor} + \frac{\hbar^2 \pi^2}{2\mu r^2}$$

As the radius of the dot increases, the energy of excitation and thus the energy of emission decreases.

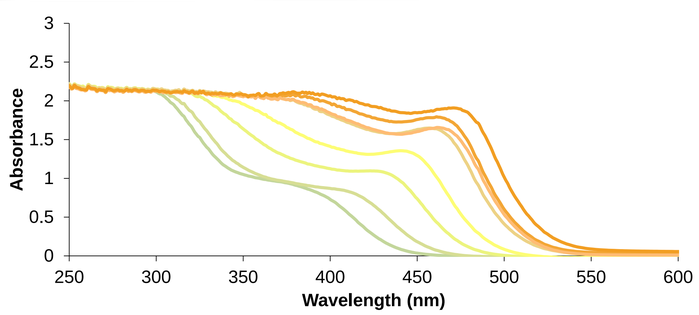

Figure 2 shows the synthesized CdSe quantum dots absorbance spectra. Early aliquots (green-yellow) absorbed at higher energy than later aliquots (yellow-orange).

The ZnS shell has a larger band gap than the CdSe and thus the capped dots absorb at higher frequency. This can be visualized in **Figure 1** and **Figure 3.** The ZnS shell absorbs and then re-emits light to then excite the CdSe core. The ZnS shell has also been reported to increase emission intensity – however this was not observed.[6]

As the reaction time increases the solution begins to emit white light as visible in **Figure 1.** This was most likely due to the formation of byproducts, (CdS, ZnS, and ZnSe quantum dots).

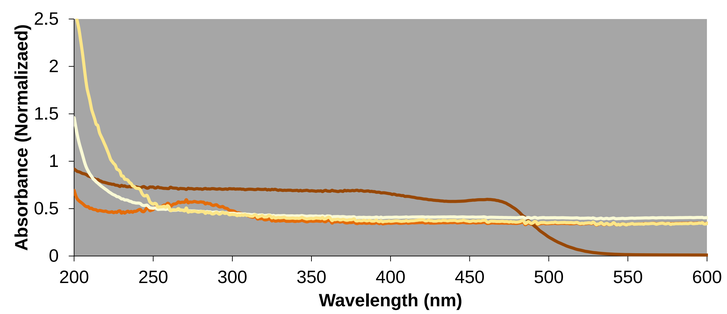

Figure 3 shows the measured UV-VIS spectra of the ZnS-CdSe quantum dots. Darker colors were extracted earlier.

Quantum Dot Growth Cycle

$Cd(OAc)_2$ + Se (s) —(Oleic Acid, TOP; 130 ^{o}C, Stir, 15 s – 10 min)→ CdSe Quantum Dots

CdSe Quantum Dots —($Zn(NO_3)_2$, NaS_2; Oleic Acid, TOP, 100 ^{o}C, 5 – 20 min)→ ZnS – CdSe Quantum Dots

Figure 4 shows a conceptual image of a typical core shell ZnS-CdSe quantum dot. The gray is the CdSe, the brown is the ZnS and the shadows covering the exterior are TOP and oleic acid ligands that solvate the microcrystal.[1]

Future Work

Continuing work would include synthesis of CdSe quantum dots followed by a purification using a centrifuge and micrometer syringe. This would remove excess starting material. The quantum dots would then be redispersed in solvent and capped. This would eliminate the problem with the formation of secondary products that can be visualized in **Figure 1** and **Figure 3**.

Citations

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