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Quantum Yield Enhancement of Cd/Se Colloidal Quantum Dots by Variation of Surface Ligands

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14. ABSTRACT

Colloidal cadmium/selenium (Cd/Se) quantum dots (QDs) were synthesized with two different sets of ligands. The first used simple components, octadecene (ODE), which serves both as a solvent and a ligand, and oleic acid, which also serves as a ligand. The second used more complex ligands, octadecylphosphonic acid, and oleyamine. Transient samples have been collected during the course of each synthesis. Then the particle diameter and quantum yield (QY) of the samples were calculated from transmission and emission data obtained with UV/VIS spectrometer and flourometer. Calibration data for QY measurements were obtained with reference to the literature data on the QY of a known standard, rhodamine 6G (Rh6G). These measurements helped elucidate the effect surface ligands have on the QY of semiconductor colloidal QDs.

15. SUBJECT TERMS

Cd/Se, colloidal dots

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Acknowledgments

Student Biography

David Gudeman will be receiving his Bachelors of Science from the University of California, Los Angeles (UCLA) in 2013. His major will be chemistry with specializations in physical chemistry and computational chemistry, as well as a math minor. He originally participated in research on super-hard materials but now has found an interest in colloidal quantum dots (QDs), and he hopes to further his studies after graduating from UCLA.

1. Background

Colloidal quantum dots (QDs) are a relatively new area of research in nanotechnology/nanoscience. Their wide-absorption spectra and narrow-, but tunable, emission spectra have many important applications for emerging technologies. Some applications important to the Army are solar cells (*1*), focal-plane arrays (*2*), and low-energy displays (*3*). The main obstacle encountered presently is how to suppress non-radiative mechanisms of relaxation, because decreasing the occurrence of these mechanisms will increase the quantum yield (QY) of QDs and allow for some novel applications. It is thought that imperfections on the surface of the crystal cause non-radiative relaxation (*4*). Appropriate ligands used in the experiments pacify these imperfections, leading to an increase in quantum yield.

2. Experiments/Calculations

Both syntheses followed a simple procedure. The precursors for cadmium (Cd) and selenium (Se) are prepared first, and then one is injected into the other. The experimental setup used in these experiments is shown in figure 1.
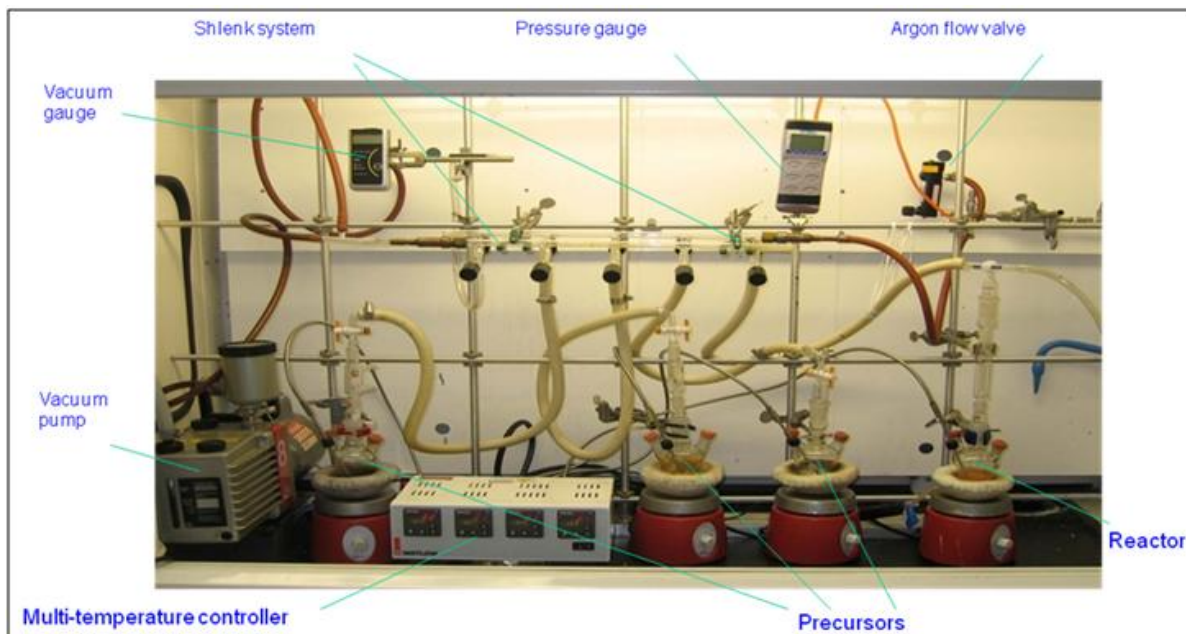

Figure 1. Experimental setup.

In synthesis 1, the Se precursor was prepared by taking 120 mg of Se powder and mixing it with 10-ml octadecene (ODE) and 0.4-ml tributyl phosphine. The mixture was outgassed at room

temperature for 30 min, and then the temperature was brought to 100 °C and outgassed for another 30 min. To prepare the Cd precursor 26 mg of cadmium oxide (CdO) powder was mixed with 1.2 ml of oleic acid (OA) and 9.0 ml ODE. The mixture was outgassed for 30 min at room temperature, then the flow of argon (Ar) was started, and the temperature was raised to about 200 °C and kept there until the CdO dissolved forming a clear solution. The temperature was reduced to 100 °C, and the solution was outgassed for 30 min to remove water formed during the reaction. After that the flow of Ar was started on both solutions, and their temperatures were raised to 250 °C. Once both solutions were ready 1.34 ml Se precursor was injected into the Cd precursor. The solution reacted for 20 min, while samples were taken at the intervals of 0, 0.5, 1, 1.5, 3, 4, 6, 8, 10, 12, 15, and 20 min. The reaction proceeded at 250 °C.

In synthesis 2, the selenium precursor was prepared by mixing 420 mg Se with 5.25 ml of trioctyl phosphine and outgassing the mixture at room temperature for 15 min. The temperature was raised to 80 °C and kept at that temperature until the Se dissolved. It was cooled to room temperature, and then 5.25 ml of oleyamine and 1.2 g of octadecylphosphonic acid were added to the reactor. The mixture was outgassed under vacuum at room temperature for 15 min. The temperature was raised to 80 °C until the solution became clear. To prepare the Cd precursor 384 mg of CdO was mixed with 6 ml of OA and outgassed under vacuum at room temperature for 15 min. Then under Ar the temperature was raised to 200 °C until the CdO dissolved. After which it was cooled to 100 °C and injected with 9 ml of ODE. The mixture was outgassed under vacuum for 1 h. Then both solutions were placed under Ar and raised to 200 °C. Twelve milliliters of Se precursor was then injected into the Cd precursor. The solution was left to react for 15 min, and samples were taken at the intervals of 0.5, 1, 1.5, 2, 3, 4, 6, 8, 10, 12, and 15 min. The reaction proceeded at 200 °C.

The purification process for both syntheses was the same except for the final solvent. Fifty milliliters of ethanol was added to the final reaction mixture and sonicated to separate the QDs from residual reactants. It was centrifuged until the organic solvent settled at the bottom. Then the supernatant was disposed of, hexane was added to the pellet, and the suspension was centrifuged again. This took some of the remaining impurities out of the solution. The supernatant was stored in a container for long-term storage, and the pellet was disposed of. For the first synthesis the supernatant was stored in hexane; the second was stored in toluene.

The peak absorption was measured with a UV-VIS spectrometer for both sets of solutions, and then the empirically derived formula reported in the literature (5) was used to calculate the diameter (in nm) of the nanoparticles:

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + (41.57) \quad (1)$$

where λ is the position of the first (at the longest wavelength) absorption peak of the QD solution.

The formula used for the calculation of QY is given in equation 2, which was also obtained from the literature (*6*):

$$QY_x = (QY_r)(OD_r/OD_x)(I_r/I_x)(n_x/n_r)^2(A_x/A_r) \qquad (2)$$

where OD is the optical density of the sample, I is the intensity of the incident light, n is the index of refraction, and A is the integral intensity of fluorescence. The indices x and r refer to the sample and the reference fluorophor (in our case it is rhodamine 6G [Rh6G] dissolved in ethanol), respectively. Optical density was obtained from transmission T, equation 3:

$$OD = \log(1/T) \qquad (3)$$

Incident light of $\lambda = 480$ nm was used for both the reference and the samples, thus the intensity of the light was the same for all measurements, and equation 2 gets reduced to

$$QY_x = (QY_r)(OD_r/OD_x)(n_x/n_r)^2(A_x/A_r) = (QY_r)(n_x/n_r)^2(OD_r/A_r)(A_x/OD_x) \qquad (4)$$

The QY of Rh6G in ethanol excited by a source of 480 nm is 95% (*7*), the indices of refraction for Rh6G (ethanol) and the samples (hexane) are 1.36168 and 1.3749 (*8*), respectively.

In order to determine the value of (OD_r/A_r) measurements of absorption and emission for different concentrations of Rh6G were made. The slope of the graph OD_r versus A_r, shown in figure 2, was found to be 1.579×10^{-7} and was used for calculations of Qys of our samples:

$$QY_x = (95)(1.579 \times 10^{-7})(1.3749/1.3617)^2(A_x/OD_x) = (1.530 \times 10^{-5})(A_x/OD_x)\ [\%] \qquad (5)$$
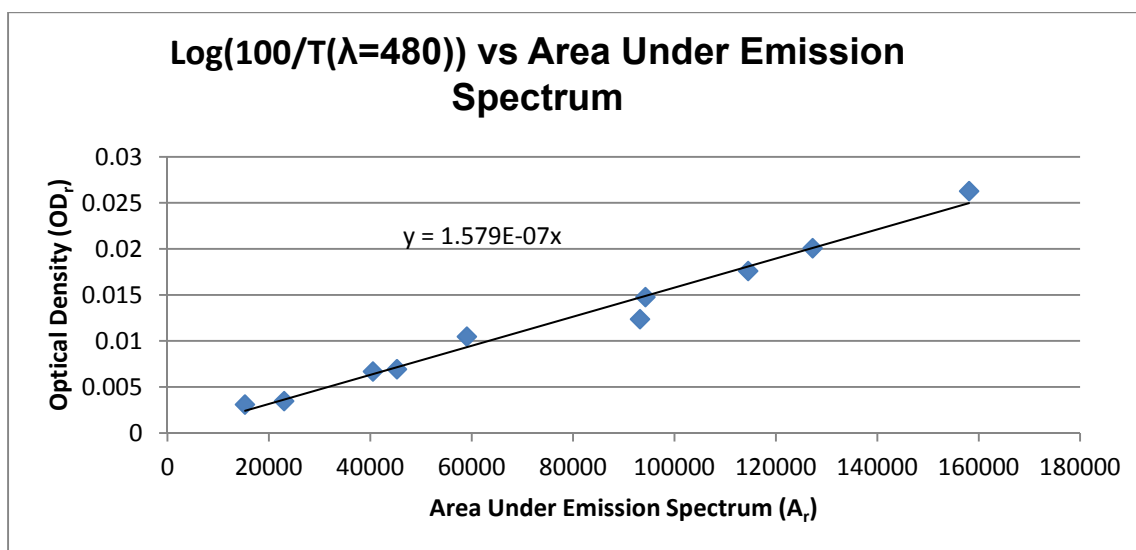

Figure 2. QY of the final products of the syntheses.

3. Results and Discussion

Development of the particle size with time during syntheses is shown in figure 3.
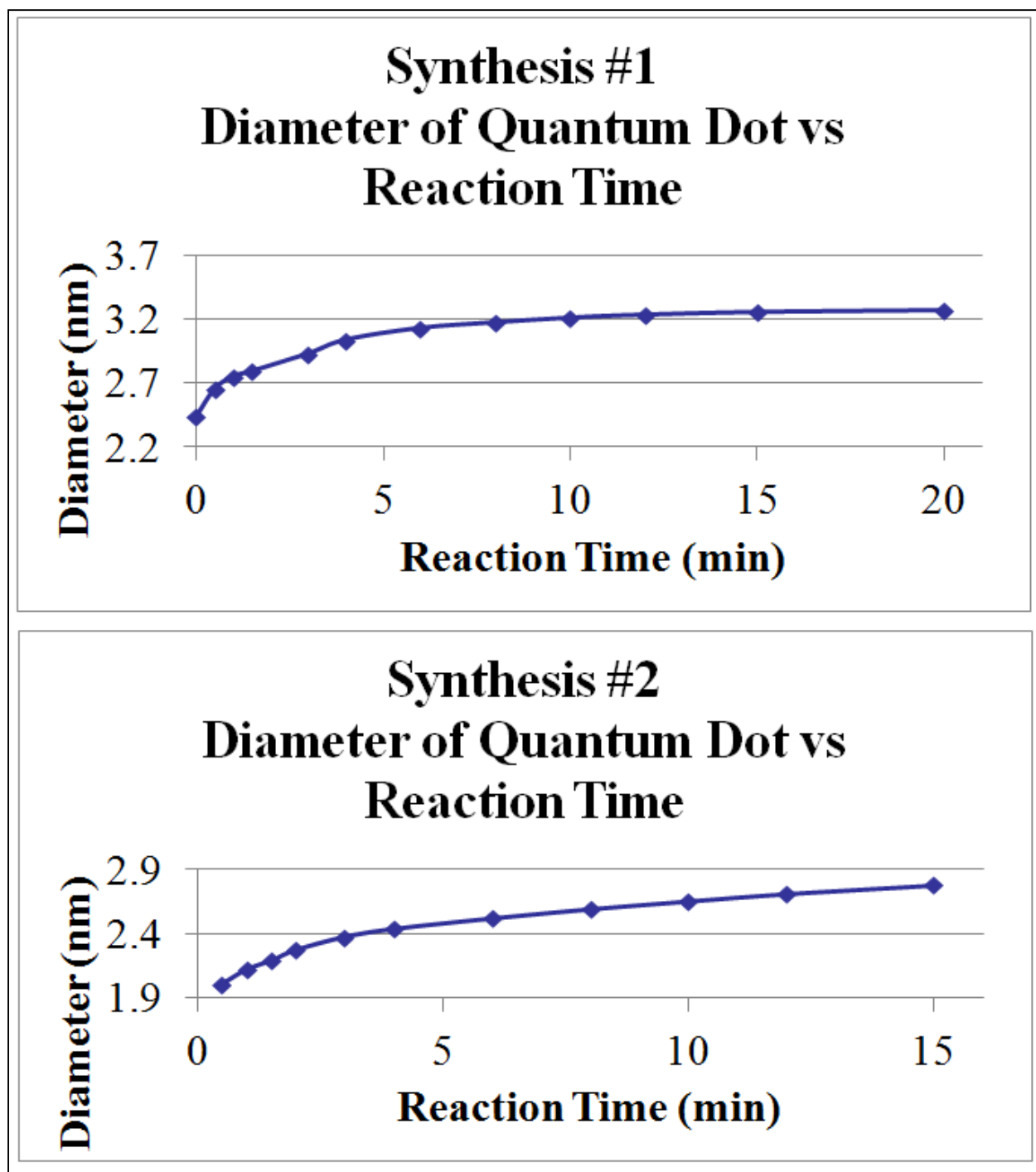

Figure 3. Development of the grains with time during the syntheses.

As can be seen both syntheses follow a logarithmic-like curve, with synthesis 1 showing the growth of larger grains. The fact that the curves do not start and stop at the same diameter is apparently the result of different reaction kinetics due to changed growth conditions (particularly different ligands). The change in the grain diameter with time is reflected in the changing color of the light emitted by the QDs, as illustrated in figure 4.

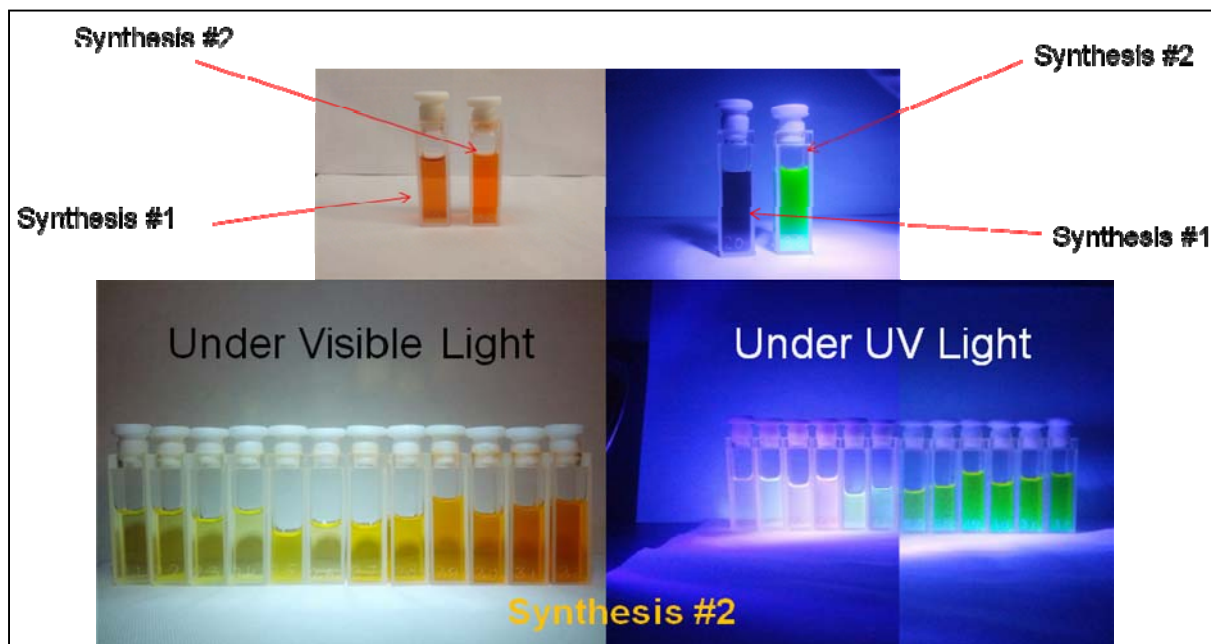Figure 4. Change of the color of the samples during the course of syntheses.

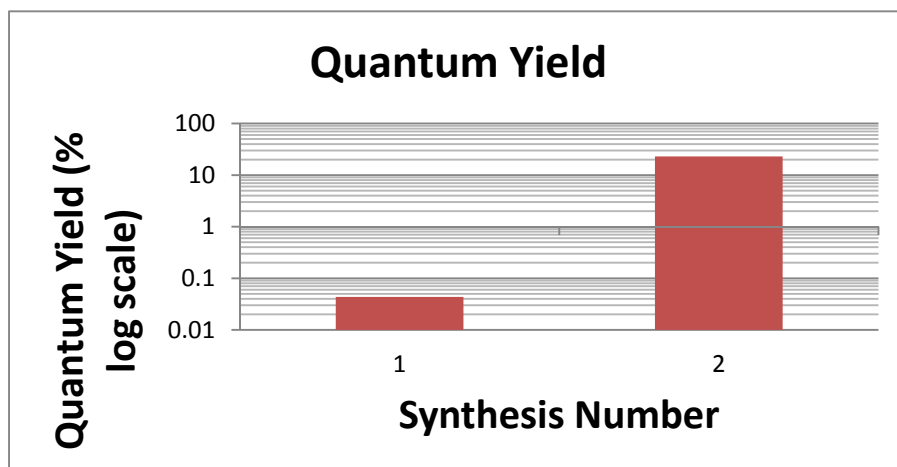The quantum yields of the QDs in the final product solutions are illustrated in figure 5.

Figure 5. QY of the final products of the syntheses.

As can be seen in figure 5 the intensity of fluorescence of QDs synthesized in process 1 is about 3 orders of magnitude lower than that from process 2; however, for full disclosure it should be

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noted that there were two days between synthesis and measurement for process 1 and atmospheric oxygen might have quenched the florescent abilities of the QDs. Based on other experiments done in the laboratory it can be assumed, however, that such a factor could not be responsible for the extremely low QY of the samples from synthesis 1.

In addition to measurements of QY of the final products, such measurements were also made for the aliquots taken during synthesis 2 (figure 6) (due to extremely weak fluorescence from synthesis 1; measurements for samples from synthesis 1 were deemed not worth the extra effort).

Figure 6. Change in QY of the QDs during synthesis 2.

The results shown in figure 6 indicate a general increase in QY of the crystals as the growth progresses, although there is a considerable scatter of individual points. It illuminates an issue that is believed to lie in fluorescence measurement of the samples. There is a possibility that when carrying out the measurements there might have been some dirt stuck on the inside and/or outside surface of the cuvette, which interfered with the measurements.

4. Summary and Conclusions

In summary, synthesis 2 produced QDs with a much higher QY relative to that found for synthesis 1. However, this conclusion comes with some troubling results. The fluctuations in

figure 6 indicate that something in the measurement process might have been skewing the results. The fluorometer is sensitive to smudges/dirt on the cuvette. Similarly, slight smudges on the cuvette walls might have affected the absorption/transmission measurements. This might be responsible for the fluctuations in the measured QY of synthesis 2. Another aspect of the experiment, which could have done better, was time between synthesis and measurement in synthesis 1. The two days between measurement and synthesis might have introduced an error due to fluorescence quenching by atmospheric oxygen.

In order to continue this line of experiments the reason for the fluctuations in QY results would have to be probed. Also, in order to make educated choices about future experiments, the reasons why synthesis 2 produces QDs with a higher QY must be further explored. Once the reasons are known better ligands/methods can be chosen.

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List of Symbols, Abbreviations, and Acronyms

Ar   argon
Cd   cadmium
CdO   cadmium oxide
OA   oleic acid
ODE   octadecene
QD   quantum dots
QY   quantum yield
Rh6G   rhodamine 6G
Se   selenium

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