Synthesis of White Cadmium-Selenium Quantum Dots

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Approval Page

Project Title: Synthesis of White Cadmium-Selenium Quantum Dots

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Abstract:

A process was developed for the synthesis of cadmium-selenium quantum dots that fluoresce at multiple wavelengths, giving a white color to the solution. The process involved making a selenium pre-cursor, then a cadmium precursor, then injecting the selenium precursor into the cadmium precursor and extracting a sample. Once the a repeatable process for synthesizing white quantum dots was developed, the absorption and fluorescence was measured and recorded over a period of two weeks. In the development of the process, the key variables were the temperature of the cadmium precursor and the time between injecting the selenium precursor and extracting the sample. Extracting the quantum dots within the first second of injection and using a temperature of 220 ±6 °C repeatedly yielded the desired white quantum dots. The white dots exhibited three main fluorescence peaks: at 430-450 nm, 560-580 nm and 610-620 nm. The sample dots showed absorbance from 250 nm to 310 nm. Over time as the quantum dots remained in solution, the peaks shifted to higher wavelengths by 18.5 nm over two weeks, and the intensity decreased by 46%. The shift was caused by growth of the quantum dots over time, but did not significantly affect the visible white color of the dots. The testing showed white quantum dots could be made using a repeatable process with potential applications in white light LED technology.

Keywords:

Materials, semiconductors, quantum dots, cadmium, selenium, LED

1. Introduction & Background

The objective of the project was to optimize a process for synthesizing and characterizing white-fluorescing cadmium-selenium (CdSe) quantum dots. Measures for success were developing a repeatable process to produce white quantum dots, analyzing the absorption and fluorescence of the white quantum dots, and determining the stability of the quantum dots in solution. White quantum dots could potentially be used in LED applications for lighting.

1.1. Lighting:

Improving lighting technology is an important part of reducing energy use around the world. According to the U.S. Energy Information Administration, up to 18% of energy in residences is used by lighting, where incandescent bulbs are still the most common light used.[1] Figure 1 below shows the energy consumed in the life-cycle of different light sources. Incandescent bulbs are inefficient, have a short lifetime, and are fragile. LEDs use less energy, last longer, and are solid-state.

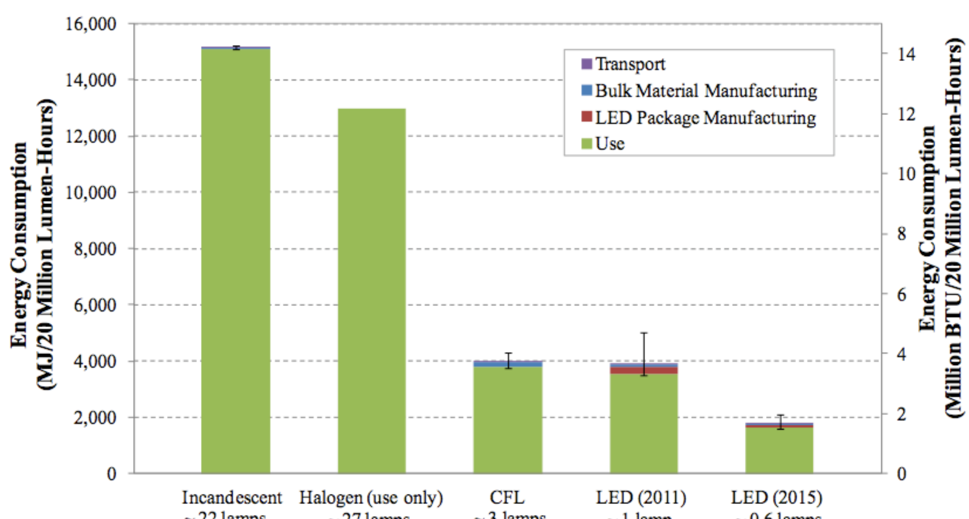

Figure 1. Comparison of life-cycle energy of light sources.[2]

A major drawback to LEDs as replacements for incandescent bulbs is the spectrum of light LEDs emit. Current LEDs use a blue LED with a yellow phosphor coating that fluoresces over the rest of the visible spectrum to create white light. Figure 2 shows the distribution and relative intensity of the light emitted by a conventional LED.

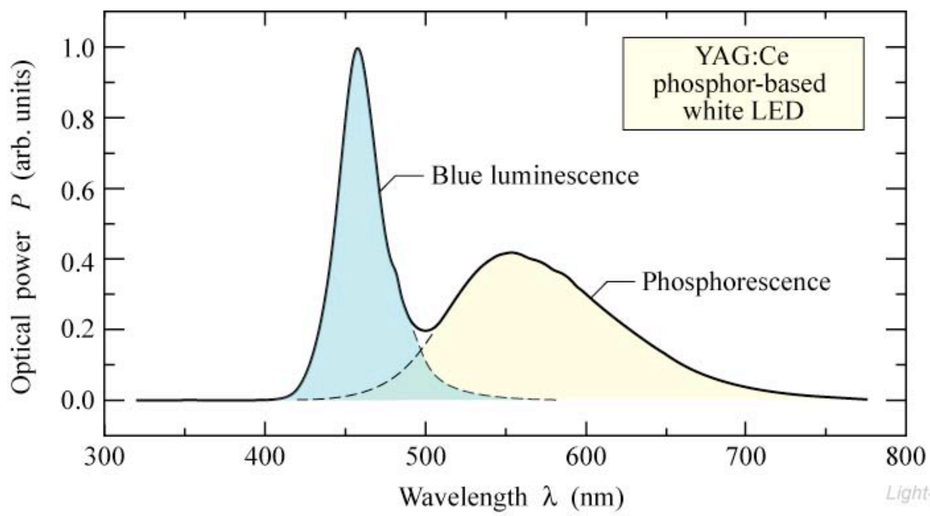

Figure 2. The emission spectrum of a conventional white LED.[3]

The blue peak from the LED has a significantly greater intensity, so it gives the white light a bluish tint. This distribution of light is harsh and unnatural to human eyes. Using quantum dots to distribute light more evenly over the visible spectrum could lead to more widespread use of LED lighting.

1.2. Quantum Dots:

Cadmium selenium quantum dots are nanoparticles, between 1 and 10 nm in diameter, that exhibit a relationship between particle size and electronic properties. This relationship is caused by quantum confinement, which happens when the diameter of the quantum dot becomes smaller than the Exciton Bohr

Radius. As particles get smaller and nearer to the size of the Exciton Bohr Radius, energy bands go from continuous to discrete energy levels. Figure 3 shows the difference between energy bands in bulk semiconductors, quantum dots, and individual molecules.

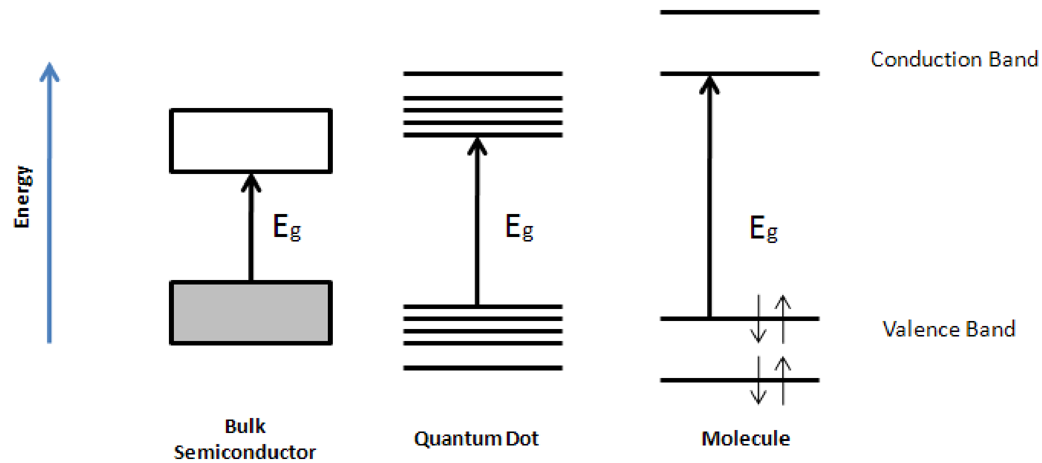

Figure 3. Energy band diagrams of bulk semiconductors, quantum dots, and individual molecules.[4]

When a quantum dot is excited by a photon, if the photon has enough energy, a valence electron is excited to the conduction band, then released back to the valence band with lower energy photons, dictated by the size of the particle. Figure 4 illustrates the relationship between particle size and resulting photon energy. To get white quantum dots, a distribution of different size quantum dots, emitting a wide range of photons is required.

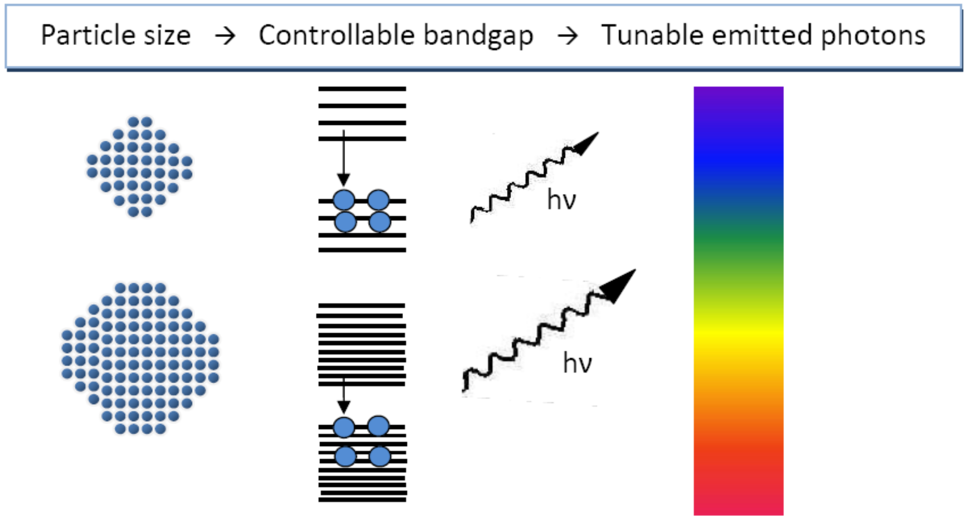

Figure 4. Relationship between particle size, band gap, and photon energy.[5]

1.3. Broader Impacts:

In the synthesis of quantum dots, environmental and health and safety constraints must be carefully considered because of the use of cadmium oxide and selenium powder. This must be considered in the manufacture, use, and disposal of quantum dot LED lights.

1.3.1. Health and Safety:

The synthesis process used cadmium oxide (CdO) powder, which is classified as extremely hazardous if ingested according to it's material safety data sheet.[6] It is carcinogenic, and can be deadly in the case of severe over-exposure. It is very hazardous when inhaled, and causes irritation when it contacts the skin or eyes. It is important to use gloves and goggles at all times while handling the CdO powder and the solutions it is used in. Selenium powder can also be hazardous in large quantities, so similar precautions are used. All experiments were conducted behind a fume hood, and gloves and goggles were worn.

1.3.2. Environmental:

Because of the toxicity of the chemicals used, all waste products were carefully disposed of. All liquid waste was collected in a large, labeled jug which was stored under the fume hood when not in use. The dry waste was collected in a covered bin labeled as dry hazardous waste. The waste was disposed of according to the procedures outlined by Cal Poly Environmental Health and Safety.[7]

2. Experimental Procedures

A process to synthesize quantum dots was developed at through a number of senior projects and masters theses, most recently updated in Josh Angell's thesis. Figure 5 below from Josh's thesis shows a simple flow chart of the steps required to synthesize quantum dots. Laura Sparks synthesized a

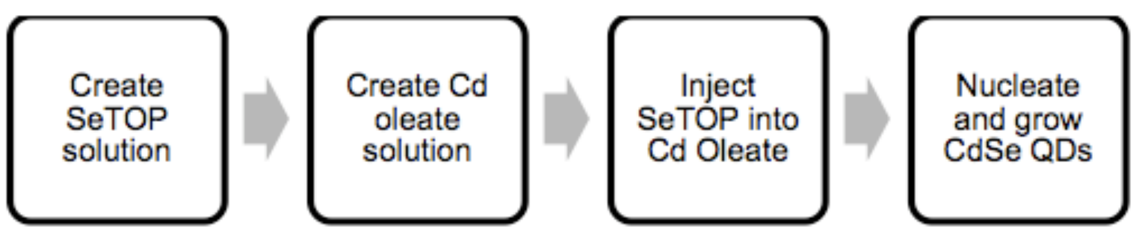

Figure 5. Process flow diagram for quantum dot synthesis.[8]

batch of white quantum dots using a slight alteration to the procedure from Josh's thesis. She immediately extracted the quantum dots after injecting the selenium precursor into the heated cadmium precursor instead of waiting for the reaction

to take place, which resulted in a sample that fluoresced bright white under UV light.

2.1. Time and Temperature Experiments:

The procedure developed in Josh's thesis outlines the temperature the cadmium precursor should be heated to when the selenium precursor is injected, but it doesn't specify the times and temperatures used in previous steps. The temperature when the ODE goes into the silicone bath, the time between adding the ODE and the oleic acid, and the temperature when the oleic acid is added are not specified. Each of these variables was monitored during synthesis to see if there was an effect on the ability to synthesize quantum dots.

Extracting the dots within 1 second was the known step for yielding white quantum dots. This required inserting the injection needle and the extraction needle at the same time, then while plunging the injection needle of SeTOP solution with one hand, immediately beginning to extract the quantum dot solution with the other hand. Different trials were attempted with quenching some resulting quantum dots in acetone and letting some air-cool.

2.2. Characterization:

After synthesis, the quantum dots were transferred into a glass cuvette which was placed in the LED apparatus shown below in Figure 6. The apparatus was connected to an OceanOptics spectrometer. The characterization was repeated over a period of weeks to determine the stability of the quantum dots in solution.

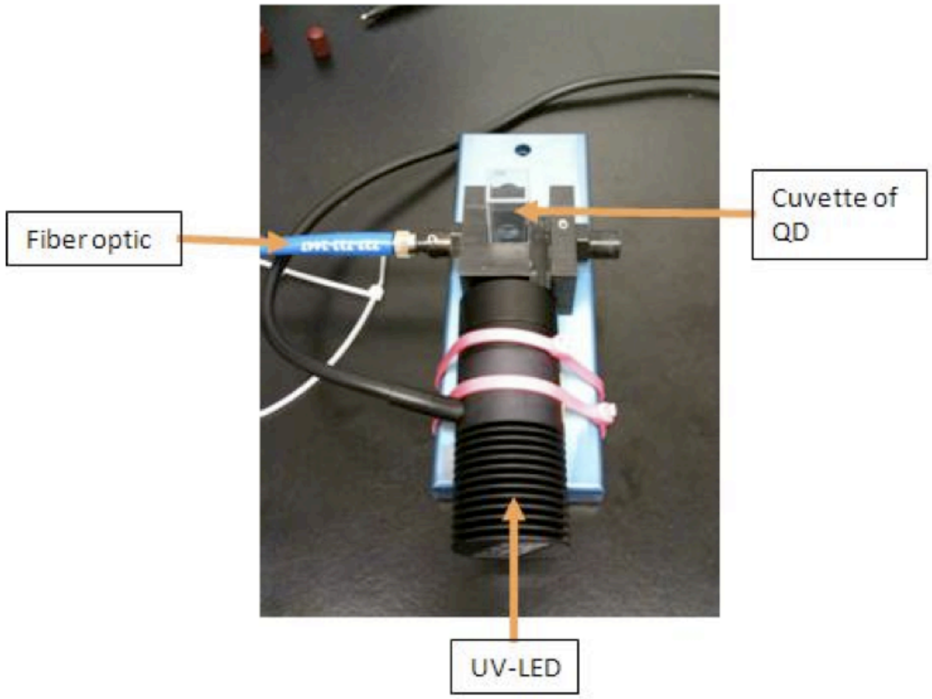

Figure 6. UV-LED apparatus connected to OceanOptics Spectrometer.[4]

2.2.1. Fluorescence:

Using OceanOptics' SpectraSuite software for analysis, fluorescence peaks were measured for each of the quantum dot samples.

2.2.2. Absorbance:

The UV apparatus from Figure 6 was replaced with a similar apparatus connected to a halogen-quartz lamp with fiber optic cables. It shined through the cuvette and into the fiber optic cable connecting to the spectrometer. SpectraSuite was used to calculate the absorbance.

2.2.3. Color:

Color measurements were taken using the color measurement utility in SpectraSuite. The measurements showed a 1931 CIE color chart with the color

of the fluorescing quantum dots plotted on the chart. It also provided x and y values that could be compared to other samples quantitatively.

3. Results and Analysis

Extracting the quantum dots within 1 second of injecting the SeTOP precursor to the Cd-oleate precursor resulted in quantum dots that fluoresced white under UV light. The fluorescence was measured with an OceanOptics spectrometer and SpectraSuite software to analyze the fluorescence. The quantum dots exhibited peaks at 3 wavelengths in the visible spectrum, one at 430-450 nm (blue/violet), one at 560-580 nm (green/yellow), and one at 610-620 nm (orange/red). The key adjustments to the procedure were the temperature of the Cd precursor when the Se precursor was injected, and the time between injection of the Se precursor and extraction of the quantum dots. It was difficult to consistently inject the Se precursor into the Cd precursor at a set temperature because the oil bath and therefore the reaction flask temperatures fluctuated unpredictably. White quantum dots were able to be synthesized when the temperature at injection was 220 ±6 °C. The extraction of the quantum dots was the most important step in the modified process to yield white quantum dots. Extracting the quantum dots in less than 1 second successfully resulted in white quantum dots. Figure 7 below shows the updated process flow diagram for the synthesis of white quantum dots.

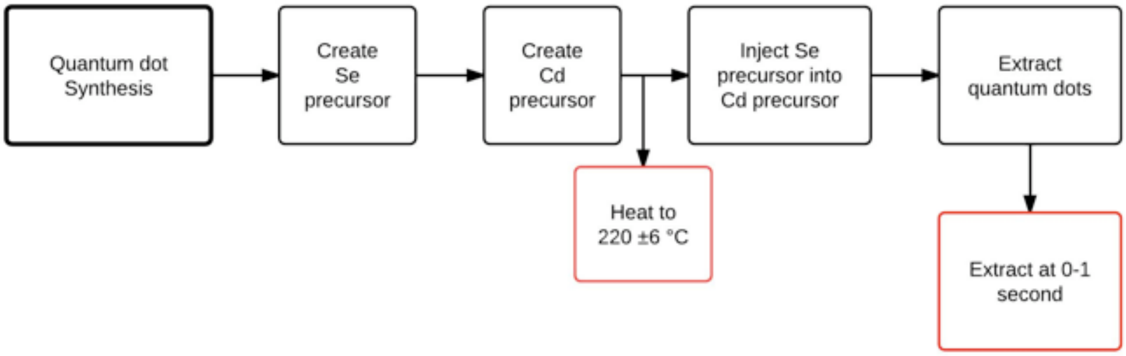

Figure 7. Updated process flow diagram for yielding white quantum dots.

If the needles were fumbled with or if the extraction needle failed to reach the surface of the solution before pulling up on the plunger, it was too late to get the white quantum dots. Figure 8 shows side-by-side examples of quantum dots extracted from the same synthesis. The second sample was extracted as quickly as possible after the first sample. It took about 5 seconds to deposit the first sample in the vial, then reinsert the needle and extract a second sample. This noticeable changed the fluorescence of the sample from white to orange.

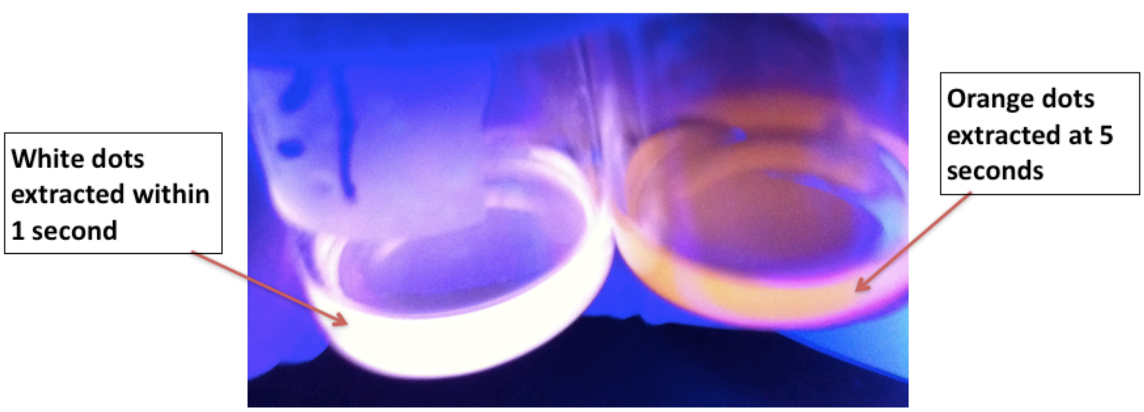

Figure 8. Comparison of quantum dots extracted at 1 and 5 seconds.

3.1. Fluorescence:

The white quantum dot samples had peaks at three wavelengths. Figure 9 below shows the distribution of light over the visible spectrum. It has a more balanced distribution than the emission spectrum from the phosphor LED in Figure 2. The background of the fluorescence spectrum is superimposed with the colors of the visible light spectrum to show the color of each of the peaks. The peaks are not exactly at red, green, and blue wavelengths, but they are close enough to result in white light.

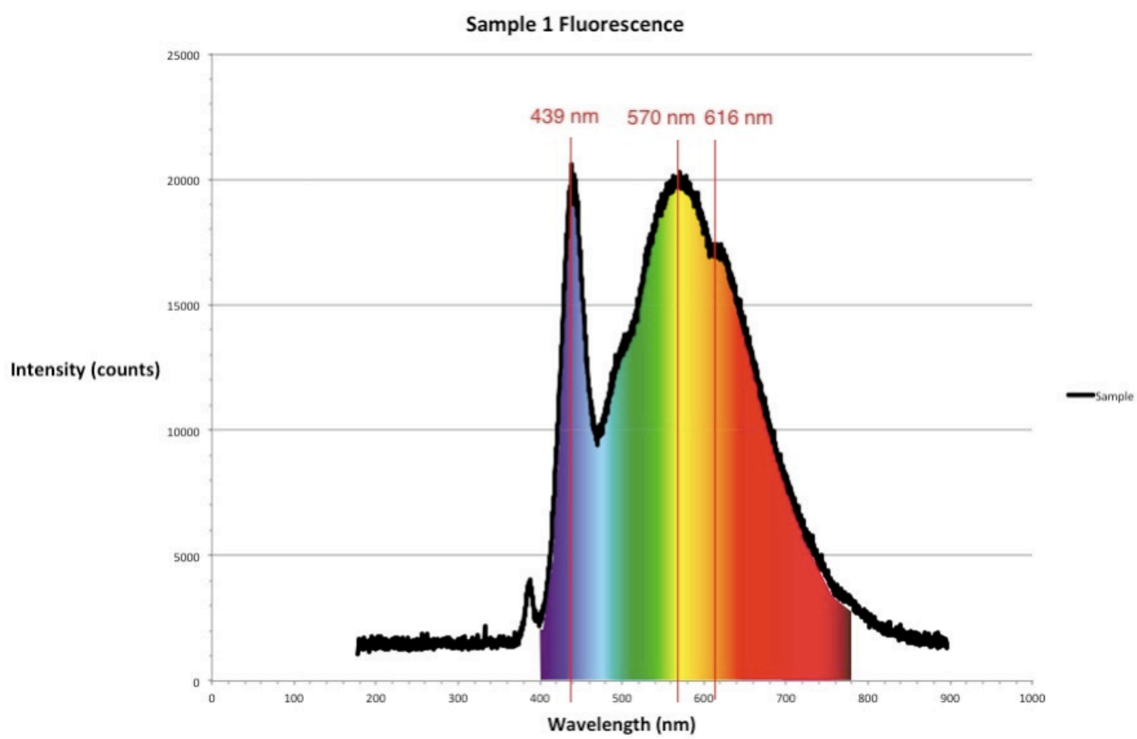

Figure 9. The emission spectrum of a sample of white quantum dots.

3.2. Absorbance:

The absorbance plot in Figure 10 shows that light is absorbed by the quantum dots only in the ultraviolet region of the spectrum.

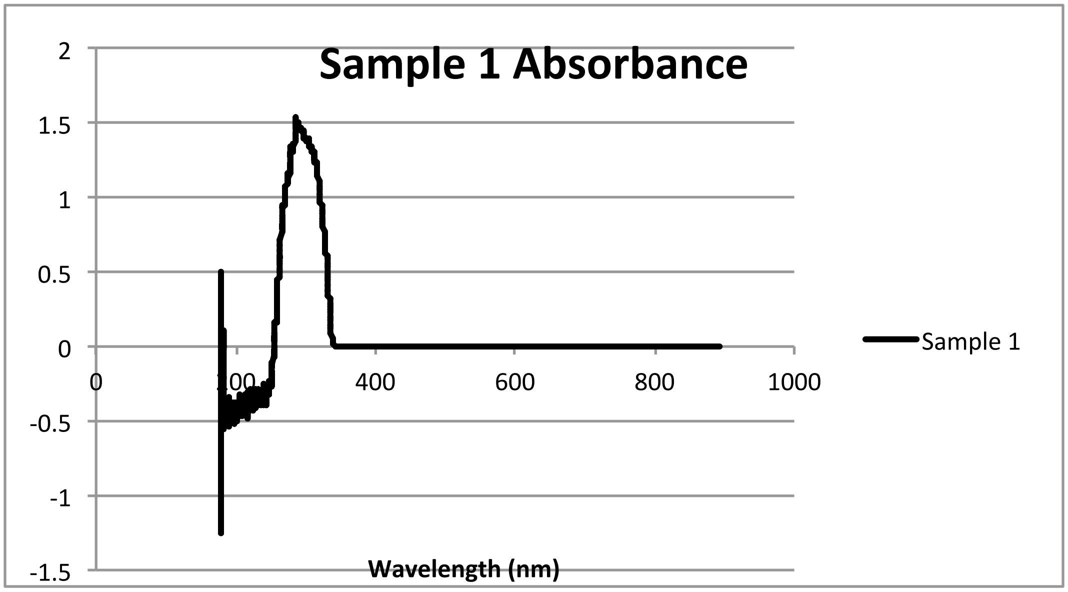

Figure 10. The absorbance of a white quantum dots.[4]

3.3. Color:

The color measurement utility in SpectraSuite confirmed that quantum dots that appeared white to the human eye were indeed white according to numerical data and using an international reference standard. Figure 11 shows 5 samples plotted on the 1931 CIE color chart twice each; once on the first day of synthesis and one after 14 or 60 days. All 10 measured color values remained within the white region of the CIE color chart.

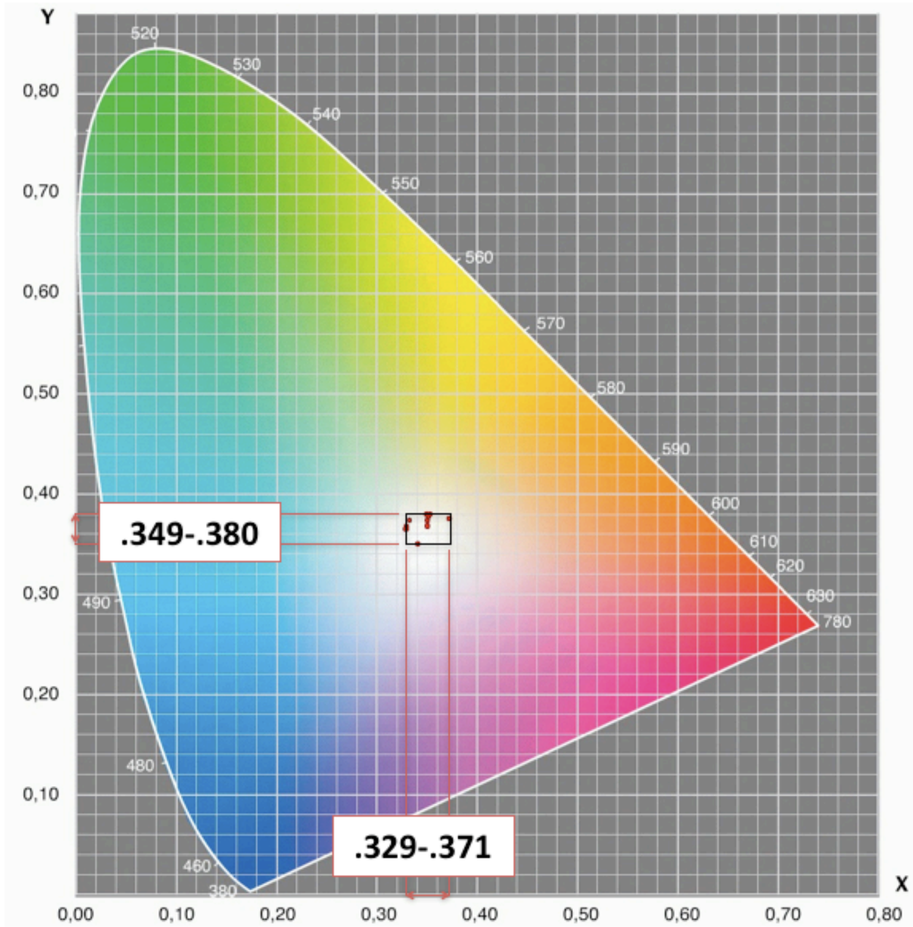

Figure 11. 5 samples of white quantum dots on the 1931 CIE color chart.

3.4. Stability:

Fluorescence, absorbance and color measurements were taken on each sample over varying periods of time. The earliest samples were measured repeatedly for 60 days. Later samples were measured for 14 days. Over 14 days, the peaks shifted to higher wavelengths by an average of 8.2 nm and decreased in intensity by an average of 31 %. Figure 12 shows the shift in wavelength and decrease in intensity of one sample over 60 days. Overall, after 60 days the samples

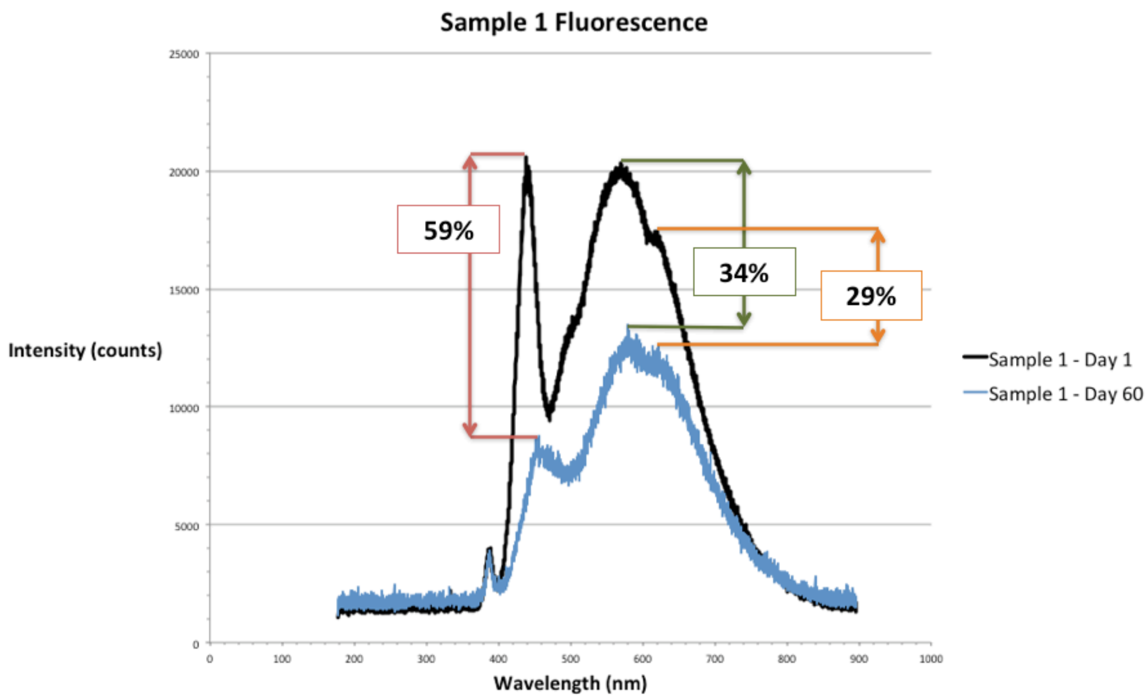

Figure 12. Decrease in intensity over 60 days.

averaged a wavelength shift of 18.5 nm and an intensity decrease of 46 %. The shift in wavelength was not significant enough to change the white color. The decrease in intensity was likely due to a precipitate that formed in the bottom of the sample vials over time.

4. Conclusions

1. Extracting quantum dots in 0-1 seconds at 220 ±6 °C will yield white quantum dots with 3 main peaks: at 430-450 nm, 560-580 nm and 610-620 nm.

2. Over 60 days, the peaks shift to higher wavelengths by an average of 18.5 nm.

3. Over 60 days, the intensity of the fluorescence will decrease by an average of 46%.

4. Over 60 days the quantum dots maintain their white color.

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