The Particle-in-a-Box Model: Analysis of CdSe Quantum Dot Nanocrystals and Linear Conjugate Dye Molecules

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KEYWORDS: quantum dots, particle-in-a-box, conjugated dye, fluorescence

ABSTRACT: The length of 1-dimensional and 3-dimensional particle-in-a-box models were determined using UV-vis and fluorescence spectroscopy. The 1-D models were the conjugate dyes trans,trans-1,4-diphenyl-1,3-butadiene and 1,6-diphenyl-1,3,5-hexatriene, and the box lengths were found to be 6.92 Å and 8.45 Å, respectively. The 3-D models were CdSe quantum dots of various sizes, and the box lengths were found to range from 58.1 to 68.9 Å from UV-vis analysis, and 52.2 to 58.5 Å from fluorescence analysis, depending the length of time of formation.

Electron movement through space is a common occurrence and is best described by the particle-in-a-box model.[1] This model is used to illustrate a particle, typically an electron, trapped between impenetrable walls (i.e. in a box). The particle moves between the walls where its potential energy is zero, but this potential energy becomes infinite at the edges of the box, causing the walls to be impenetrable (Figure 1).[1]

The particle-in-a-box model can be 1-, 2-, or 3-dimensional. In the 1-D model, the electrons are confined to moving between two walls on a line, such as a conjugated alkene, where the electrons in the p-orbitals are able to move along the alkene. In a 3-D model, the electron is free to move in the x-, y-, and z-axis directions, such as inside a spherical shape.

When the 3-D particles are made of semiconducting material, they are called quantum dots.[3] As the electrons move through the space inside a quantum dot, they create conduction inside of the semiconductor, due to the negatively charged electron pairing with positively charged holes that they vacated.[4]

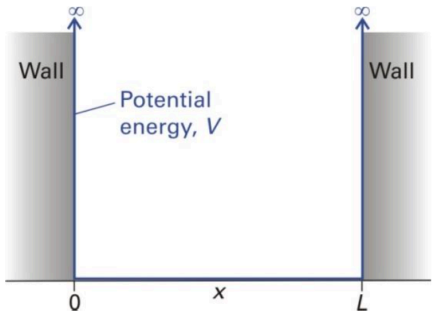

Figure 1. The 1-dimensional particle-in-a-box model, with the potential energy barriers defining the size of the box that has length *L*. Modified from Atkins, 2010.[2]

Quantum dots are nanocrystals that are so small that quantum effects are important to their character. Technological advances have made it so that the size and shape of the box, as well as the number of electrons inside the box, can be controlled.[3] Their size ranges from a few hundred to thousands of atoms.[4] The first quantum dots to be discovered were CdSe and CdS in 1932 by H. P. Rocksby but were not linked to the energy states determined by the confinement of electrons in the quantum dots until 1985.[4] Now, quantum dots are used primarily in nonlinear optics and the Q-switching of lasers,[4] but are also used in used to understand atomic and molecular systems,[5] as light emitters for fiber optic communication,[6] and as superluminescent diodes for use in fiber optic gyroscopes.[7] The field of medicinal chemistry has used quantum dots to investigate cellular processes and biological phenomena due to their ability to be used as assays and fluorescent probes, indicating binding sites.[8]

In this experiment, UV-vis spectroscopy was used to determine the box length of 1- and 3-dimensional particle-in-a-box models, and fluorescence spectroscopy was used to confirm the box length of the 3-dimensional particle-in-a-box model.

1-D Particle-in-a-Box Experiment. To model a 1-dimensional particle-in-a-box, conjugated dye solids of

trans,trans-1,4-diphenyl-1,3-butadiene (Sample A; Figure 2) and 1,6-diphenyl-1,3,5-hexatriene (Sample B; Figure 2) were made. 10 μM solutions of both conjugate dyes were made by diluting in cyclohexane and run on the spectrometer between 300 and 425 nm (Figure 3).

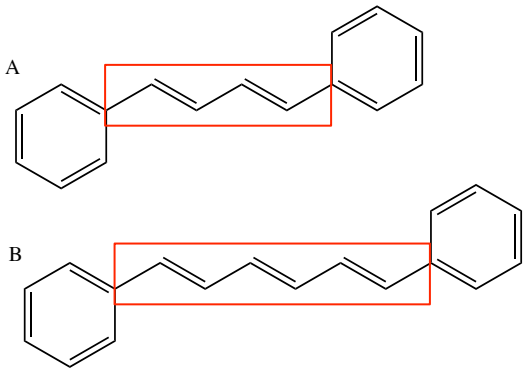

Figure 2. The molecular structures of (A) trans,trans-1,4-diphenyl-1,3-butadiene and (B) 1,6-diphenyl-1,3,5-hexatriene. The red rectangles indicate the box length in the particle-in-a-box model (though this is a 1D model), where the phenyl rings are the walls (Fig. 1).

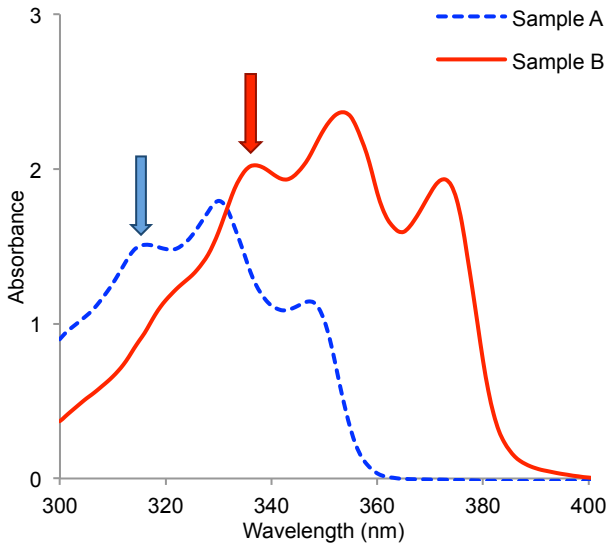

Figure 3. The UV-vis spectra of trans,trans-1,4-diphenyl-1,3-butadiene and 1,6-diphenyl-1,3,5-hexatriene. The lowest wavelength peak, noted by the arrows, for each spectra were used to determine box length.

3-D Particle-in-a-Box Experiment. A 3-D particle-in-a-box model was made with CdSe semiconductor particles. 0.0172 g CdO was massed into a round-bottomed flask. This flask was clamped to a ring stand, and situated in a thermal well on a stir plate. Stirring was started, and 0.6 mL oleic acid and 10 mL octadecene was added. A thermometer was inserted, and the solution was heated to 225°C while being stirred. At 225°C, a previously prepared Se precursor of 30 mg Se and 5 mL 1-octadecene, heated and stirred, was added to the cadmium solution. A timer was immediately started and a 1 mL sample was taken and put into a test tube in an ice bucket. Eleven samples were taken at various intervals (Table 1) while the temperatures were maintained at 225°C. The samples that reacted longer produced larger quantum dots, and thus emitted lower frequency wavelengths of light, which resulted in a color shift from yellow to red[2] (Figure 4). A UV-vis and fluorescence spectrum of each sample was taken (Figures 5 and 6).

Figure 4. The quantum dot solutions in order of the time they were taken, from left to right. There is a color change from yellow to red due to the increase in quantum dot size from the increased reaction time.

Sample	Time Sample Taken (s)
1	0.00
2	10.64
3	17.84
4	26.71
5	36.07
6	52.78
7	71.42
8	96.67
9	105.47
10	123.05
11	148.28

Table 1. The times at which each sample was taken from the flask after the Se solution was added. Samples 1 and 2 were lost due to a lab accident.

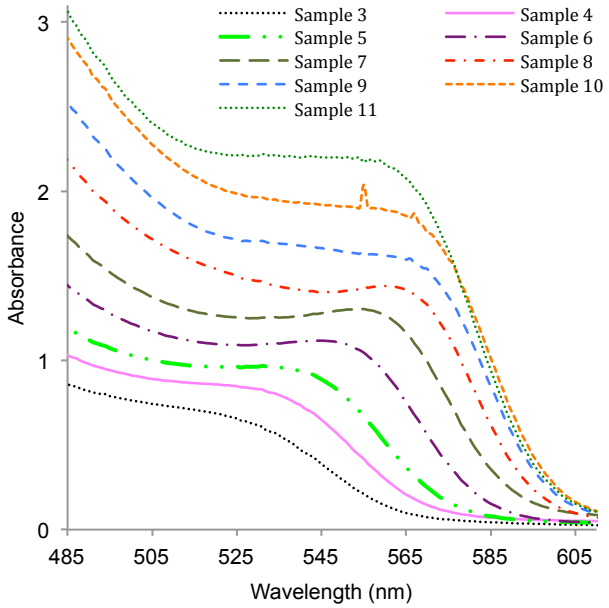

Figure 5. The UV-vis spectra of the quantum dot samples. There is a general trend of increased peak wavelength with increased quantum dot size.

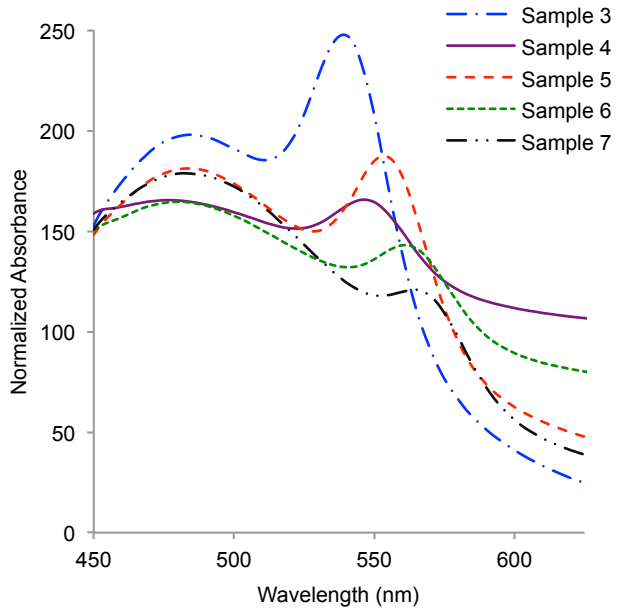

Figure 6. The fluorescence spectra of the quantum dot samples. The absorbance values have been normalized to allow for the spectra to be overlain on one graph. There is a shift in peak wavelength with increased quantum dot size. Samples 8 through 11 did not exhibit the expected peaks likely due to oleic acid scorching, and thus are not displayed in this figure.

Results. The length of a side in the particle-in-a-box model can be calculated through both UV-vis and fluorescence spectroscopy. In both, the electrons inside the box are excited, and the HOMO electrons transition to the next highest energy position. This transition absorbs energy, which produces a peak in UV-vis spectroscopy. When the electrons transition back to their ground state, they emit energy, which produces a peak in fluorescence spectroscopy.

1-D Particle-in-a-Box Results. The lengths of the boxes for the conjugated dyes were expected to differ between one another, due to the different number of carbon bonds in each. The 1,6-diphenyl-1,3,5-hexatriene would have a longer length for its box than the 1,4-diphenyl-1,3-butadiene because of the two extra bonds between the two benzene rings (Figure 2).

The shortest wavelength peak (Figure 3) was used to determine the length of the box by combining the relationship between the energy of a photon and wavelength (Eq. 1) and the energy associated with the electron transition (Eq. 2) to form a new equation (Eq. 3).

$$E = \frac{hc}{\lambda} \tag{1}$$

$$E = \frac{(n_f{}^2 - n_i{}^2)h^2}{8mL^2} \tag{2}$$

$$L = \sqrt{\frac{(n_f{}^2 - n_i{}^2)\lambda}{8mc}} \tag{3}$$

In these equations, n_i is the HOMO and n_f is LUMO in an unexcited state, h is Planck's constant, c is the speed of light, m is the mass of an electron, λ is the wavelength of the shortest wavelength peak, and L is the length between the phenyl groups.

The calculated lengths for A and B were compared to values found from Spartan Student and were within 10% and 4.5%, respectively (Table 2). Compared to experimentally derived values, A and B were within 0.43% and 15.1%, respectively (Table 2). The experimentally derived values were determined using 0.139 nm as the average length of a carbon-carbon bond in a conjugated system, and using trigonometry to determine the length of the box.[9] Variation with the theoretical versus other lengths is likely due to the assumption that the bond lengths are fixed, and do not change between samples A and B. Variation with the Spartan box length is likely due to assumptions that the program makes. These assumptions in the theoretical and Spartan calculations may not occur in the actual experimental analysis.

Sample	λ (nm)	Calculated Box Size (Å)	Spartan Box Length (Å)	Theoretical Box Length[9] (Å)
A	316	6.92	6.218	6.95
B	337	8.45	8.828	9.73

Table 1. The UV-vis data allowed for the size of the box to be calculated for both conjugated dyes. This was compared to box lengths determined by Spartan Student and literature values.

3-D Particle-in-a-Box Results. In order to calculate the radius and diameter of the box, E_g^{nano}, the energy gap in the nanoscale material, must be calculated using Equation 1, where λ is found by extrapolating from the UV-vis spectra (Figure 5) to find λ (Figure 7).

The radius of the box was determined via Equation 4.

$$r = \frac{-\left(\frac{1.8e^2}{4\pi\varepsilon\varepsilon_0}\right)\sqrt{\left(\frac{1.8e^2}{4\pi\varepsilon\varepsilon_0}\right)^2 + (E_g^{nano} - E_g^{bulk})\frac{h^2}{2m_0}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right)}}{2(E_g^{nano} - E_g^{bulk})} \quad (4)$$

In this equation, e is the charge of an electron, ε is the permittivity of CdSe (10.6), ε_0 is the permittivity of free space, m_e^* is 0.13, m_h^* is 0.45, and m_0 is the mass of a free electron. E_g^{bulk} is the energy gap for the bulk material (Eq. 1) where λ for the bulk material is 709 nm. The diameters of the boxes were found (Table 3). The size of the quantum dots were seen to increase the longer they were allowed to form.

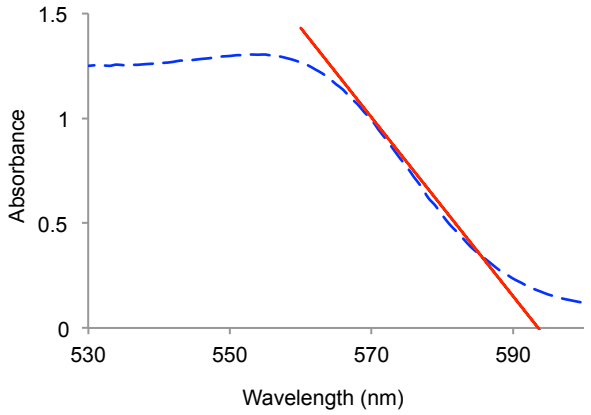

Figure 7. The value of λ for E_g^{nano} must be extrapolated from the UV-vis spectra using a linear approximation. The dashed blue line is part of the spectra from Sample 7 (Figure 5), while the solid red line is the extrapolation. E_g^{nano} is where the solid red line intersects the x-axis.

Fluorescence emission spectroscopy was performed on the samples, and spectra were taken of each (Figure 6). The spectrum from Sample 8 exhibited a much smaller peak than Samples 3-7, while Samples 9-11 did not exhibit following the trend of the other samples. This was likely due to the Cd solution heating too slowly, scorching the oleic acid. Since oleic acid stabilizes metal nanocrystals, and allows for higher purity and evenly sized quantum dots,[10] the scorching of the oleic acid would have led to less stable quantum dots. In the future, more rapid heating to 225°C might prevent this problem.

Sample	UV-vis Diameter (Å)	Fluorescence Diameter (Å)	Average Diameter (Å)
3	58.1	52.2	55.2
4	60.2	51.9	56.1
5	61.3	54.7	58.0
6	64.7	56.3	60.5
7	66.7	57.7	62.2
8	68.2	58.8	63.5
9	69.3	-	69.3
10	69.3	-	69.3
11	68.9	-	68.9

Table 3. The length of the box (i.e. the particle diameter) based on UV-vis and fluorescence calculations. The length of the box generally increased as the samples were allowed to react for longer.

The wavelength of maximum emission was used to determine E_{exiton}, the electron-hole pair (Eq. 6).

$$E_{exiton} = \frac{h^2}{8r^2}\left(\frac{1}{m_e}+\frac{1}{m_h}\right) - \frac{1.8e^2}{4\pi\varepsilon r} \quad (6)$$

where m_e and m_h are 1.18 x 10^{-31} kg and 4.10 x 10^{-31} kg, respectively. To do this, the value of $E_{transition}$ must be found (Eq 5.), which can then be used to find E_{exiton} (Eq. 7) when E_{ground} is 1.751 eV.

$$E_{exiton} = E_{transition} - E_{ground} \quad (7)$$

The particle radii were determined and compared to the radius calculated from UV-vis spectra (Table 3).

These values are similar to literature values, where the average crystal diameter of CdSe quantum dots made in the same manner is 52 Å, a value calculated by the Debye-Scherrer approach.[8]

Conclusion. The box lengths found for both the 1- and 3-dimensional particles were comparable to literature and Spartan values, indicating that not only were they prepared correctly, but that the UV-vis and fluorescence spectroscopy worked properly. However, scorching of the CdSe quantum dots led to Samples 9-11 not having peaks that showed up in fluorescence. In the UV-vis spectroscopy, these three samples did not follow the trend of increasing box length as Samples 3-8 did. In future experiments, this could be avoided by heating the Cd solution more quickly and holding at a more steady temperature during sampling.

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Author Contributions

Both authors contributed to experimental work and data analysis. The corresponding author was the sole author of this paper.

Funding Sources

This experiment was funded by Dickinson College.

ACKNOWLEDGMENT

Thank you to Sarah St. Angelo for assisting in determining a safe method for synthesizing the CdSe quantum dots, as well as for helping with the calculations.

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