

Quantum Dots: Synthesis, Properties, and Simulation

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Abstract

Quantum Dots, a new class of nanoparticles comprised of semiconductors, are changing modern technology. The photoluminescence that these quantum dots exhibit at ambient temperature makes them extremely beneficial in digital technologies. In this work, we carry forward the prior research in this area and explore and investigate the quantum dot properties in an effort to establish a quantifiable relationship between quantum dot size and light emission wavelength. The work includes the physical understanding behind the nature of quantum dots, method for the synthesis of quantum dots, simulation using Brus equation, and spectra of light absorbed and emitted.

Keywords: quantum physics; chemical synthesis; quantum dots; quantum confinement; energy bands

1 Introduction

Quantum physics has gained popularity in electronics and research in recent years. And in other instances, the hypothesis of quantum physics is being tested using modern technologies. Quantum dots are one example of how the theory has been applied to the field of technology. A quantum dot is a nanoscopic particle, which shows the effect of photoluminescence. They are made of a single material, such as zinc, cadmium, or selenium. They are also referred to as nanocrystals. It emits different wavelengths of light depending on its size when exposed to external excitation. Due to this property, it is used in lasers, light-emitting diodes, solar cells, QLED TVs. They are also employed in the creation of quantum computers and in biological imaging.

Quantum dots are unique in physics because they're the only nanoscopic particle that has a size where quantum mechanical effects can be observed. These quantum dots emit photons and electrons, even at room temperature. The emitted light is of a specific color, depending on the size of the quantum dot.

Quantum confinement is a phenomenon that creates quantum dots. The spatial confinement of particles in one or more dimensions is referred to as quantum confinement. The confinement in the case of quantum dots is in three dimensions. The potential energy barrier produced by the material around a quantum dot is what holds electrons there. Due to the potential energy barrier, the electrons are trapped inside the quantum dot.

The energy band gap is the difference between the energy of the valence band and of the conduction band. The energy band gap of a quantum dot is inversely proportional to the size of the quantum dot. Thus if provided with a certain energy, the electrons in the quantum dots will be excited to the conduction band. Hence on deexcitation they emit light. Therefore we can say there is a direct relation of wavelength of light emitted and the size of the quantum dots.

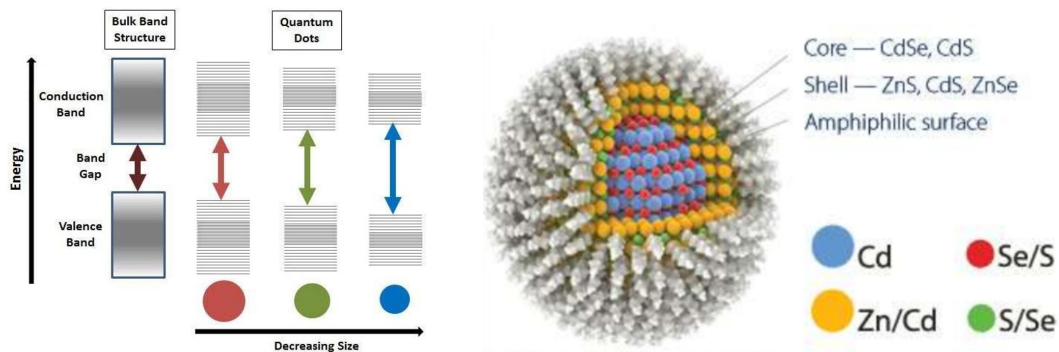


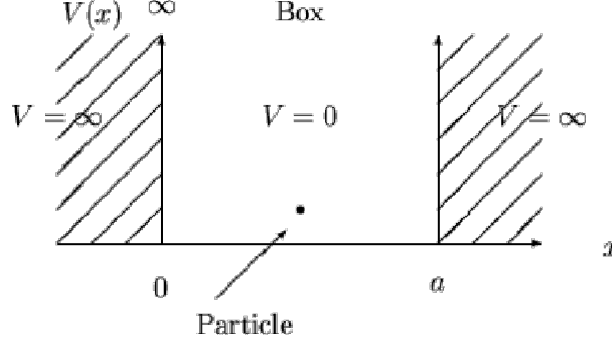
Figure 1: Quantum dot and qualitative relationship between size of Quantum Dots and Band Gap

2 Theory Formulation

Quantum dots are semiconductor nanoparticles of size in the range of 3- 9 nm. Charge carriers in the bulk semiconductor material (many times larger than 10 nm) can have a variety of energies. These energies can be considered continuous because they are so close together. Thus, the band gap refers to a specific range of prohibited energy. The vast majority of carriers naturally occupy the valence band, the energy range below the band gap. Some of them occupy the conduction band for them above the band gap.

When they get more energy from the outside, such as heat, radiation, potential, etc., they can jump to the conduction band and leave a hole in the valence band. The term "exciton" refers to this electron-hole pair.

This width of the band gap is thus dependent on the composition of the material and its chemical properties.



Now, as we know the Particle in a 1D box scenario, the Wave function is given by:

$$\psi_n(x) = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi}{l}x\right)$$

Where, x = position of the particle a = length of the box

If we were to derive the energy of the particle by solving Schrodinger's equation, we arrive at the energy being:

$$E_n = \frac{n^2 h^2}{8mL^2}$$

Thus, we say that the particle's energy is quantized and thus is allowed to have only certain allowed energy levels.

Now, if we were to extend this idea of particles in a 1D box, we can think of Quantum dots as particles in a 3D sphere.

Where in a particle in a 1D box, the potential outside the well was considered to be infinite, here we can assume that outside the sphere (semiconductor nanocrystal), the potential is also infinite. And here, this particle could be an electron or a hole. And this phenomenon is quantum confinement. To explain quantum confinement in a few words:

Quantum confinement is the phenomenon that occurs when the size of the material or compound happens to be of the same magnitude as the de Broglie wavelength of the electron wave function. And when the materials are this small, their electronic and optical properties deviate substantially from those of the bulk materials.

Thus the confinement energy in the quantum dot in its ground state can be given as which is very analogous to the energy as that of a particle in a 1D box.

$$E_c = \frac{\pi^2 h^2}{2d^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right)$$

We can see the similarities between 1 and 2, $2L = d$ (diameter) $m =$ harmonic mean of m_e^* and m_h^* s.t. $1/m = 1/m_e^* + 1/m_h^*$

Here, d is the diameter of the nanocrystal. m_e^* and m_h^* are the effective masses of electrons and holes.¹

Thus, the derivation of the confinement energy of the quantum dot is similar to the derivation of the confinement energy of that of the particle in a 1D box. So instead of us solving Schrodinger's equation in one-dimensional space, if we were to solve it for three-dimensional space and consider the particle to be inside a sphere (where the potential inside would be 0 and outside the sphere infinite).

$$V_{conf.}(r) = \begin{cases} 0, & r \leq a \\ \infty, & \text{otherwise} \end{cases} \quad (1)$$

Where, R = radius of the confining potential a = radius of the nanocrystal

¹These values are determined experimentally, and they differ from each other depending on the structure of the semiconductor. E.g., the effective mass of both might be different in bulk state CdS than in CdS as quantum dots.

We could go over the derivation of the confinement energy, but it is better explained in this article: [Confinement energy of quantum dots and the Brus equation²](#)

Thus, one of the direct implications of quantum confinement is the existence of quantum dots.

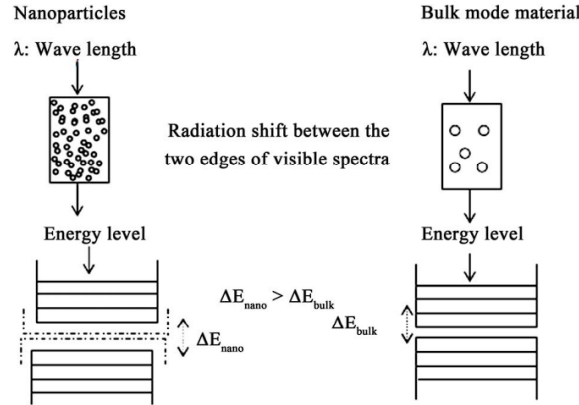


Figure 1. Quantum confinement is responsible for the increase of energy difference between energy states and bandgap [8].

We can see here that the band gap ΔE_{nano} is more significant than ΔE_{bulk} ; this is due to the reduction in dimensions of the QD, which increases the confinement energy in the dot. Thus, we can vary the size of the quantum dots by changing the chemical composition, reaction parameters, etc., which would then change the width of the band gap in quantum dots. This would result in varying optical properties of these compounds.



Hence, now we are ready to look at the Brus Equation. Brus was the first to give the relationship between band gap energy and the size of semiconductor nanoparticles based on “effective mass approximation” (EMA).

$$E_{g(qd)} = E_{bulk} + \frac{h^2}{8R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.786e^2}{4\pi\epsilon_o\epsilon_r R^2}$$

where, $E_{g(qd)}$ = band gap energy of quantum dot; E_{bulk} = band gap energy of bulk semiconductor R = radius of quantum dot; m_e^* = effective mass of excited electron; m_h^* = effective mass of excited hole; h = Planck's constant.

The first term E_{bulk} represents the band gap energy in bulk materials, which depends on the material itself. [CdSe 1.74 eV, CdS 2.42eV.] The second term is the additional energy due to quantum confinement, as we derived earlier. The third term occurs due to the coulombic interaction between the excitons. It is often neglected due to the high dielectric constant of the material in semiconductors.

Thus, we can use this equation to describe the emission energy of quantum dot :

$$\Delta E(r) = E_{gap} + \frac{h^2}{8r^2} (1/m_e^* + 1/m_h^*)$$

This is what we have tried to do in the simulations mentioned in the following sections.

²Harry, S. T., Adekanmbi, M. A. (2020). Confinement energy of quantum dots and the Brus equation. International Journal of Research -GRANTHAALAYAH, 8(11), 318–323. <https://doi.org/10.29121/granthaalayah.v8.i11.2020.2451>

3 Synthesizing a stable colloidal solution of CdS using EDTA in the lab

In the first meeting with Professor Khatua, sir provided us with documentation on the “Flash” Synthesis of CdSe/CdS Core-Shell Quantum Dots. It contained two experimental methods: ”Synthesis of the Wurtzite CdSe QDs” and “Flash Synthesis of the CdSe/CdS Dot-in-Dot QDs.” We studied both methods in-depth and listed all the chemicals required.

We consulted our teaching assistant and decided we would use a technique similar to the first one. As most of the chemicals needed in the experiment were not in the lab yet, we couldn’t experiment then. We utilized that session to understand the theoretical concepts of Particle in a 1-D box from sir and performed calculations related to that experiment.

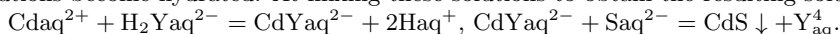
We were stuck because we needed the chemicals required by the method mentioned above. Finally, Pranit sir suggested an experimental method of preparing a stable colloidal solution of CdS using EDTA because all the chemicals needed by this method were present in the lab. We went through a research paper on this method and experimented by strictly following sir’s instructions on the concentration of chemicals required and the procedure of weighing and mixing the chemicals. We summarized the research paper as follows:

- Long ago, techniques for creating semiconductor nanocrystals were devised. Organometallic synthesis, which produces monodisperse nanocrystals with a high fluorescence yield, is currently one of the most often utilized techniques. However, the trialkylphosphine-coated nanocrystals can only form stable sols in organic solvents (chloroform, toluene, heptane, etc.). Their application in biological contexts necessitates altering surface characteristics, producing hydrophilic groups on the surface. A summary of the several studies published on the techniques for transferring nanocrystals into the aqueous phase is given. The synthesis procedure is made more difficult by the different technical processes needed for the solubilization of nanocrystals. Chemical deposition is a technique that enables the direct creation of semiconductor nanoparticles in an aqueous solution. However, this approach failed to produce stable colloidal solutions, or isolated, non-agglomerated nanoparticles. This study experimentally showed that disodium ethylenediaminetetraacetate might be used to create a stable aqueous colloidal solution of cadmium sulfide CdS in a single step (EDTA).
- Three materials were used to create a colloidal solution of cadmium sulfide by chemical condensation: sodium sulfide (Na₂S), cadmium chloride (CdAc₂), and EDTA disodium salt (C₁₀H₁₄N₂O₈Na₂) (Na₂H₂Y). The first stage included getting solutions of strong electrolytes because all three chemicals are readily soluble in water. All the ions in electrolyte solutions get hydrated due to the phenomenon called hydration, which is the interaction of ions with surrounding water molecules. As a result, water molecules, hydrated sodium ions, and hydrated sulfide ions make up a sodium sulfide solution: H₂O, Na⁺ aq, and S²⁻ aq. Water molecules, hydrated cadmium ions, and hydrated chloride ions make up a solution of cadmium chloride (H₂O, Cd²⁺ aq, Ac⁻ aq). The third solution, the solution of disodium EDTA, is composed of water molecules, hydrated sodium ions, and doubly charged ion ethylenediaminetetraacetic acid: H₂O, Na⁻ aq, H₂Y²⁻ aq.

After studying the theory and understanding how the reactions would occur, we started experimenting in the lab, which ran for 6 hours. We took three volumetric flasks because we were advised to test on three sets of concentrations, out of which, in 1 set, all solutions had the same concentration and were taken in strictly stoichiometric amounts. We prepared three solutions of Sodium Sulfide, Cadmium Acetate, and Ethylenediamine Tetraacetic acid by taking appropriate grams of them according to their molar weights in three volumetric flasks and filled them up to 10 ml. We took three reaction containers to experiment with three sets of concentrations:

1. CdAc₂: 1 mM, Na₂S: 1mM, EDTA: 1mM
2. CdAc₂: 1mM, Na₂S: 1mM, EDTA: 2mM
3. CdAc₂: 0.5mM, Na₂S: 1mM, EDTA: 1mM

Since all three substances are readily soluble in water, the obtained solutions are strong electrolytes. As a result of hydration, i.e., the interaction of ions with surrounding water molecules, all the ions in electrolyte solutions become hydrated. At mixing these solutions to obtain the resulting solution, two reactions occur:



After mixing the solutions when the reactions were going on, we kept the volumetric flask on the magnetic stirrer for one hour for observation. As in the first set, all solutions had the same concentration and were taken in strictly stoichiometric amounts. The total molecular equation of the formation of the CdS colloidal solution can be written as: $\text{CdAc}_2 + \text{Na}_2\text{S} = \text{CdS} \downarrow + 2\text{NaAc}$

The process of ”sticking,” or coagulation, is seen in this system with the dispersed phase particles when two solutions—cadmium chloride and sodium sulfide—are mixed in stoichiometric proportions in accordance with the reaction. Protective double ionic layers and adsorption-solvate layers should be established on the surface of solid particles to prevent coagulation or to give the colloidal solution aggregative stability and sedimentation stability. These layers produce electrostatic repulsion and stop the particles from adhering.

When the final reaction is carried out, hydrated ions Na⁺, H⁺, Y⁴⁻, and Ac⁻ are present in the solution where the CdS crystals are created. The ions of Cd²⁺ aq and S²⁻ aq are not present in the solution since solutions of

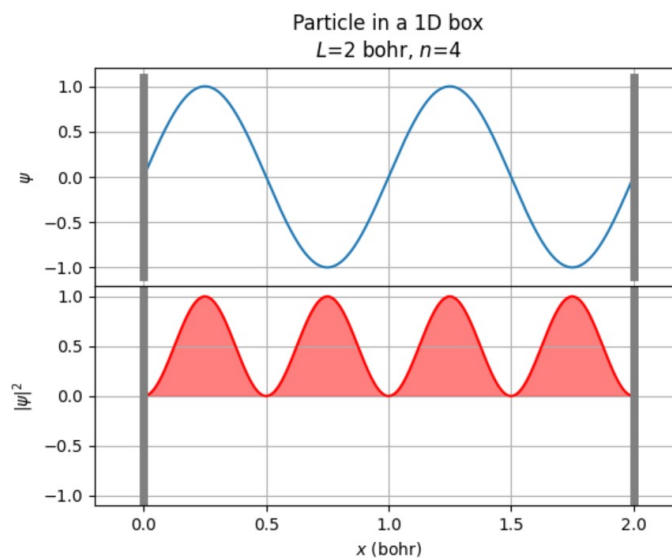
CdAc2 and Na2S were taken in stoichiometric amounts. These ions are adsorbed on the crystal following the traditional adsorption rule, together with the ions necessary to complete the formation of the crystal lattice of the solid phase and compounds that are difficult to dissolve. These ions are not present in the solution being addressed. The resultant colloidal solution was stable despite this.

4 Simulations and Code

4.1 Particle in 1D

We wrote the code to simulate the wave equation and probability density function for the particle in a 1D scenario using python. The following snapshot represents the condition when $n=9$ (called quantum number).

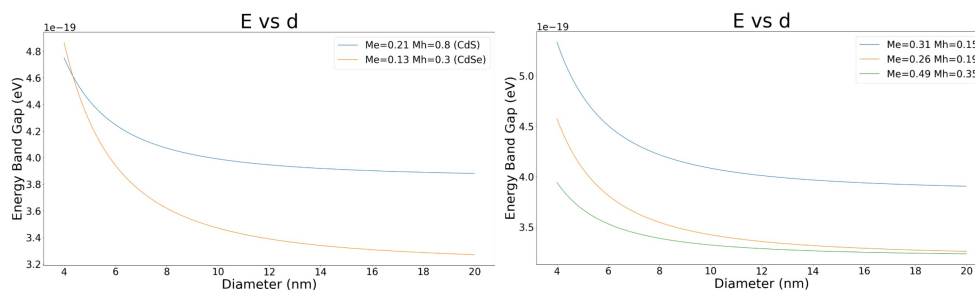
$$\psi_n(x) = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi}{l}x\right)$$



4.2 Brus Equation

We performed two simulations using Brus Equation. Since effective mass of electrons and holes are different in different case (depends on the material composition). After doing research we found widely used values of effective mass of electrons and holes for CdSe and CdS which we then used in the code for simulating Brus equation and getting the final corresponding result. We also took three more values of M_e and M_h to further see how the band gap varies. The corresponding graphs obtained in these case are:

$$\Delta E(r) = E_{bulk} + \frac{h^2}{8r^2} (1/m_e^* + 1/m_h^*)$$



5 Mistakes after synthesis of CdS

After successfully synthesizing three sets of colloidal CdS solutions, we had our mid-semester examination, followed by a break. Our mistake was that we did not perform any confirmatory tests of quantum dots. We left the three solutions unattended for more than two weeks. When we returned, we started with the confirmatory tests by

illuminating the solutions with UV rays, but we could not find any color emitted by any of the solutions. None of the solutions contained quantum dots. As we stored the CdS quantum dots for a long time during the exams and the break, the particles agglomerated, which increased the surface defects and led to defect emission.

We learned from our mistakes and started the second synthesis. We retook three sets of concentrations, but this time we changed the volume ratio this time. We halved the volumes of every chemical except EDTA. The reason for this is that EDTA is a capping agent.¹ Capping agents are stabilizers that inhibit the over-growth of nanoparticles and prevent their aggregation in the colloidal synthesis of CdS. The capping ligands stabilize the interface between nanoparticles and their preparation medium. The capping on the surface of nanoparticles is responsible for specific structural characteristics. These stabilizing substances are crucial in changing biological processes and environmental viewpoints. Such altering physicochemical and biological features are caused by the steric effects of capping agents deposited on the surface of nanoparticles.

We successfully synthesized quantum dots in two out of three experiment sets in the 2nd iteration. After synthesizing, we performed several tests on the same day of synthesis and collected datasets to use during the simulation to confirm the formation of quantum dots. Following are some of the tests and techniques we used and their corresponding results that we obtained:

1. **Sonication:** After synthesizing three samples of colloidal CdS, we sonicated the samples by putting them in an Ultrasonic bath. Sonication is used to loosen the particles adhering to surfaces. It is mentioned in Sample Preparation of Pharmaceutical Dosage Forms, “sonicators, also referred to as ultrasonic extraction, can be considered both particle size reduction techniques and an agitation technique. Due of its ability to disperse, mix and dissolve samples, it is widely used in the sample preparation of dosage forms.” An ultrasonic bath employed as a sonicator can achieve rapid sample preparation while avoiding chemical degradation of the Active Pharmaceutical Ingredient (API) due to excessive heat.



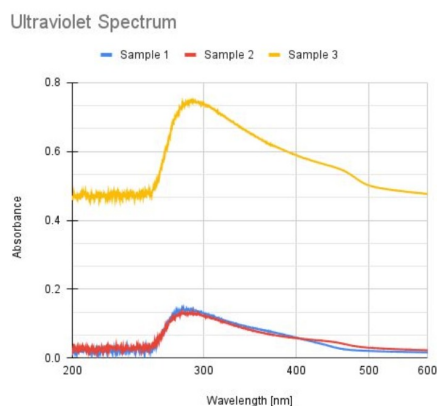
2. **UV:** After sonication we illuminate the three samples by UV light to see the colors of quantum dots. When quantum dots are illuminated by UV light an electron in quantum dots can be excited to a state of higher energy which results in bright colors. After emitting UV light, two samples showed pink and greenish color, and one sample did not show any color. We confirmed that only those two samples contained quantum dots.



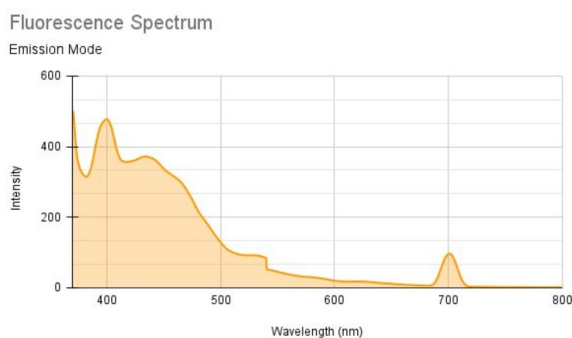
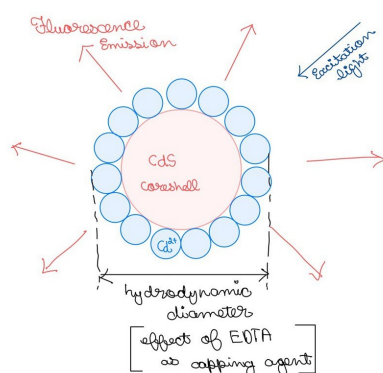
3. **Spectrophotometer:** We used a spectrophotometer on all samples to plot the graph between wavelength and Absorbance (Intensity). The spectrophotometer is a device that calculates how much light a substance absorbs. The spectrophotometer measures the light intensity of a sample by passing a light beam through

¹Javed, R., Zia, M., Naz, S. et al. Role of capping agents in the application of nanoparticles in biomedicine and environmental remediation: recent trends and future prospects. J Nanobiotechnol 18, 172 (2020). <https://doi.org/10.1186/s12951-020-00704-4>

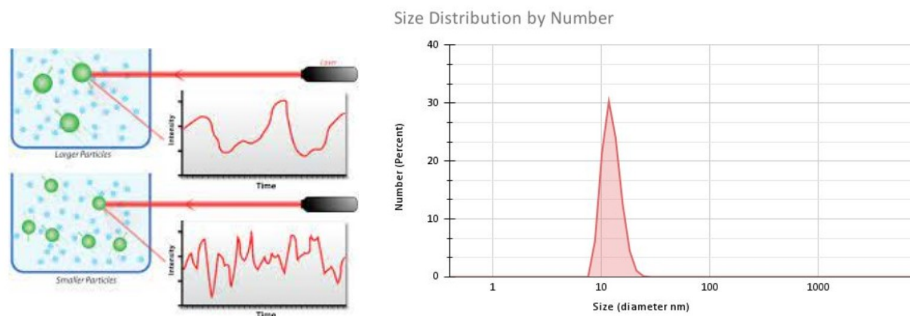
it. These tools are used to measure color and to check color correctness throughout the production process. The higher the absorbance, the less light is being transmitted, resulting in a higher output reading.



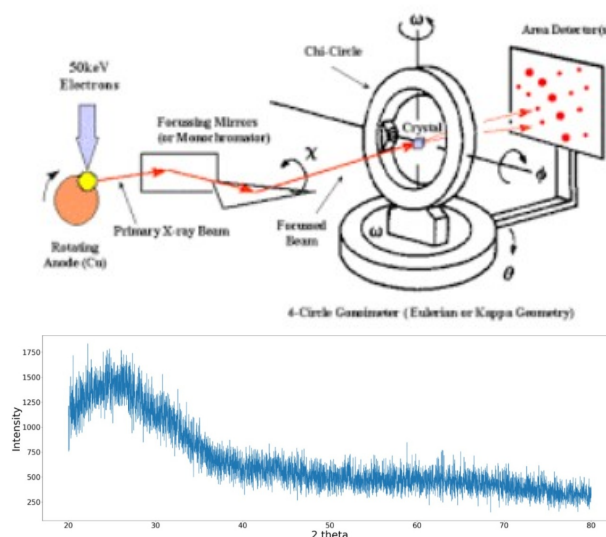
4. **Spectrofluorometer:** We also plotted Intensity vs Wavelength using Spectrofluorometer. Spectrofluorometer is an instrument that accurately measures fluorescence from a sample. The key difference between spectrophotometer and spectrofluorometer is that spectrophotometer involves the absorption measurement whereas spectrofluorometer involves the transition of polyatomic fluorescent molecules from their higher energy level to a ground state by lowering their energy level through the emission of photons. Spectrofluorometer is an instrument which helps us to measure the fluorescence of a sample based on its specific excitation or emission wavelengths. To carry out this test, we need a light source, an excitation monochromator, a sample cuvette, an emission monochromator, and a detector. The light source sends out light to the sample through the excitation monochromator which transmits the excitation wavelength corresponding to the nanoparticle while blocking the others. After excitation, the nanoparticle emits an emission light with a wavelength normally greater than that of the excitation wavelength which passes through the emission monochromator placed at a right angle to the excitation light. This minimizes the scatter and isolates the emission wavelength before it reaches the detector. Finally, the detector measures the emitted wavelength, and displays the fluorescence spectrum of the nanoparticle.



5. **Dynamic Light Scattering:** Our goal was to find the size of the Quantum dots. We achieve that through DLS by measuring the random changes in the intensity of light scattered from a suspension or solution (Brownian Motion). The DLS technique measures the hydrodynamic diameter of QDs. the hydrodynamic diameter is the diameter of a hypothetical hard sphere that diffuses with the same speed as the particle being measured. The hydrodynamic diameter of the best sample is around 10 nm which is greater than the actual diameter. Dynamic Light Scattering is a precise measurement technique for characterizing quantum dots sizes in the sample. This is based on Brownian motion of the nanoparticles in the sample. It states that the smaller nanoparticles move faster in a sample whereas the bigger ones move slower. The light scattered by particles contains information on the diffusion speed and thus on the size distribution. Therefore, we determine the size of the quantum dots by measuring the random changes in the intensity of light scattered from the sample. This technique exactly measures the hydrodynamic diameter of the quantum dots which is a hypothetical sphere that diffuses with the same speed as the QD being measured.



6. **X-Ray Diffraction:** Finally, we analyzed nature of the materials using XRD patterns by looking at the peaks appearing in the XRD pattern. XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material. Amorphous material gives a broad humped peak while crystalline material gives a sharp peak. X-ray diffraction (XRD) is a technique to analyze the nature of the quantum dots by analyzing the type of peaks in the generated XRD pattern. The X-rays scattered from the X-ray tube are reflected through the sample and onto the detector. The scattered X-rays constructively interfere with each other. This interference can be looked at using the Bragg-Brentano (para-focusing) Law to determine various characteristics of the materials. The detector records the intensity of the sample at each angle θ . Therefore, the XRD pattern generated will be the intensity of the scattered X-rays at each angle 2θ . If the XRD pattern generated has a broad humped peak, then the QD is amorphous in nature whereas if it has a sharp peak, then it is crystalline in nature.



Although, we were still not satisfied because we got only two samples that contained quantum dots out of which the diameter of one sample was around 64 nm according to DLS which is clearly not acceptable. We planned that we will have at least five samples of quantum dots having different diameters. Hence we carried out the third synthesis of quantum dots with four samples, and this time we halved the volume of Na₂S, and tripled the volume of EDTA. Unfortunately, we could not find quantum dots in any of the samples again due to few errors in the calculations and synthesis. That's why with two successful samples out of ten, we moved on towards the simulation and theory.

6 Questions asked in the Presentation

1. What is the principle underlying in the DLS machine?

Answer: In the DLS experiment, the monochromatic incident light is typically provided by a laser and impinges upon a solution containing tiny particles moving in Brownian motion. The incident light will subsequently be scattered in all directions with varying wavelengths and intensities as a function of time by particles whose sizes are sufficiently small compared to the wavelength of the incident light through the Rayleigh scattering process. Since the size distribution of the particles under study and the light scattering pattern exhibit strong correlations, it is possible to analytically analyse the spectral properties of the scattered light to obtain size-related information about the sample.

2. How do you interpret peaks in XRD graphs?

Answer: Peak intensity tells about the position of atoms within a lattice structure. and peak width tells about the crystalline size and lattice strain. Generally, peak width or broadening increases with the decrease in crystalline size. Amorphous material gives a broad humped peak while crystalline material gives a sharp peak.

3. We talked about effective masses of electrons and holes in Brus equation. So it is usually a fraction multiplied to the mass of electron. How is the multiplier determined?

Answer: The effective masses of electrons and holes are a function of their concentration in the material and ultimately of composition and structure of the semiconductor. Thus, the effective mass of electron will be different as quantum dots to that found in bulk semiconductor.

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