Using Optical Spectroscopy to Determine Radii of Quantum Dots

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In this paper, we calculate the radii of several quantum dots using optical spectroscopy, determine the material they are made of, and find a value for Planck's constant. The energy of the light that quantum dots emit corresponds directly to the energy within the quantum dot. Using this knowledge, we can derive a relationship between a dot's size and wavelength of emitted light. By observing the wavelength, we can determine the dot's radius. With knowledge of the dots' corresponding radii and wavelengths, we derive a value for Planck's constant.

Quantum Dots are semiconducting nanoparticles with diameters on the order of $10 - 100nm$. They have often been referred to as 'artificial atoms' due to their similar quantum mechanical properties such as discrete electron energy levels and associated photon emissions [1]. The unique property that distinguishes quantum dots from other nanoparticles is that its allowed energy levels and thus, the wavelength of its emitted light, is dependent on the dot's radius. Dots with smaller radii emit bluer, higher frequency light while dots with larger radii emit redder, lower frequency light [2]. A dot of a single material can be made to have a wide variety of radii which will each emit at a specific wavelength. So, by carefully manipulating the dots' radii, one can obtain a high resolution optical spectrum. Because of their discrete energy levels similar to individual atoms, they can be thought of as a 3-dimensional analogy to the well-known quantum mechanical 1-d particle in a box.

The wavefunction and allowed energy levels of a 1-d particle in a box are given by:

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \tag{1}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \tag{2}$$

where n=1,2,3..., L is the width of the 1-d well, $\hbar$ is Planck's constant divided by 2π, and m is the mass of the particle.

Similarly for a quantum dot, we can derive a zero-point energy term for a 3-d well, or sphere, which is nearly identical to (2):

$$E_{sphere} = \frac{\hbar^2\pi^2}{2mR} \tag{3}$$

where R is the radius of the quantum dot [3]. However, to fully describe the zero-point energy for the quantum dot, we must also account for the energy of the dot's exciton and semiconductor band gap energy (E_g). An exciton is the electron and the 'hole' it leaves behind when it jumps from one state to another (see FIG. 1). Accounting for these factors gives us the quantum dot's zero-point energy which is equal to the energy of it's emitted photon:

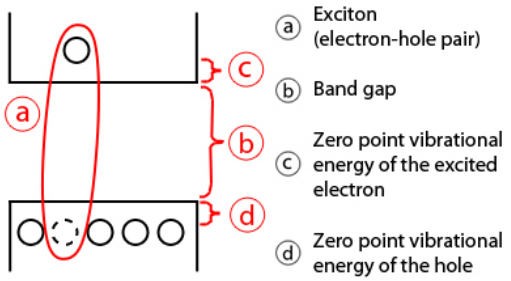

FIG. 1. An exciton is the electron-hole pair that is created when an electron moves energy states [4]

$$E_{QD} = \frac{\hbar^2\pi^2}{2m_eR} + \frac{\hbar^2\pi^2}{2m_hR} + E_g = \frac{hc}{\lambda} \tag{4}$$

Where m_e is the effective mass of the electron in the semiconductor, m_h is the effective mass of the electron's hole in the semiconductor, h is Planck's constant, c is the speed of light, and λ is the wavelength of light emitted by the quantum dot [3]. Notice that if we know the radius of the quantum dot, we can calculate the value of Planck's constant.

From this equation, we can see that the energy of the dot's emission is related to its size. The larger the radius, the larger the wavelength of light and the smaller the radius, the shorter the wavelength of light. This is due to a phenomenon called quantum confinement. According to solid-state physics, materials have certain 'bands' or energy states that electrons can occupy. These bands have different levels of freedom for the electrons to flow. 'Valence' bands are energy levels where electrons are still bound to their nucleus. If enough energy is applied to the electron, it can be excited from this bound state to a 'conduction' band where the electron is no longer bound to the nucleus and can flow freely. The energy separating the valence and conduction bands is called the material's band gap energy (E_g). In bulk materials, adjacent energy levels of multiple atoms and molecules overlap creating a 'narrow' band gap. However, as your material

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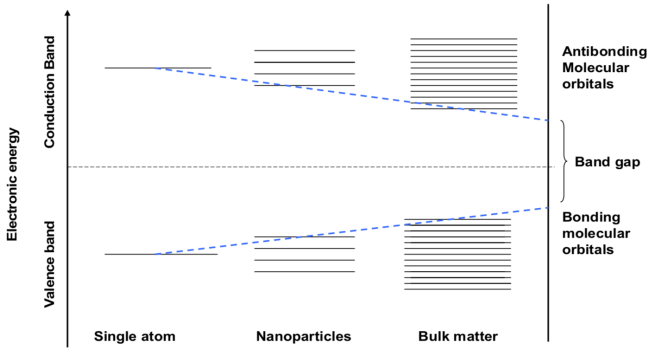


FIG. 2. Quantum confinement of band gap energy. The smaller, more confined the material is, the more discrete the material's band gap. The bigger the material, the more overlap of its various atoms and molecules' energy levels which narrows the band gap energy [5]

becomes more fine, less energy levels overlap which discretizes these levels and widens the band gap (FIG. 2). Thus, the smaller the particle, the wider the band gap which means the energy needed to excite an electron from the valence band to the excited band is larger. Because this energy is directly related to the emitted photon, the larger the band gap, the more energetic the quantum dot's light.

In this experiment, we determine the radii of various quantum dots by obtaining their spectra as well as determine the material the quantum dots are made of. We then display how one can calculate Planck's constant if the radius of a quantum dot is known.

We first obtained four CENCO-Nanosys vials each filled with quantum dots made of the same material, but different radii (FIG. 3). The material and radii of the dots were initially unknown to the authors of this paper. To excite the electrons within the quantum dots of the vials, we used a Class III $405nm$ laser pointer. To obtain the emitted spectra of the vials, we used a Red Tide USB650 Fiber Optic Spectrometer connected to a computer to display and save our results. To easily manage our experiment, we used some 3-pronged grippers to hold the vials, laser pointer, and spectrometer - this also allows for better spectrometer readings because the setup is static and not being help by a person (FIG 4). The black holder that contains the vials has openings underneath each vial which is where we decided to shine the laser pointer.

Before taking the spectra of the four vials, we calibrated our spectrometer by taking the spectrum of the Sun (FIG. 5). We compared our result with another spectrum of the sun taken with a similar spectrometer and under similar conditions to ours [6]. The Fraunhofer lines as indicated in the comparison spectrum agree well with ours. We took this agreement to indicate the spectrometer was calibrated correctly and proceeded to take the spectra of the vials.

Using the setup shown in FIG. 4, we shined the laser

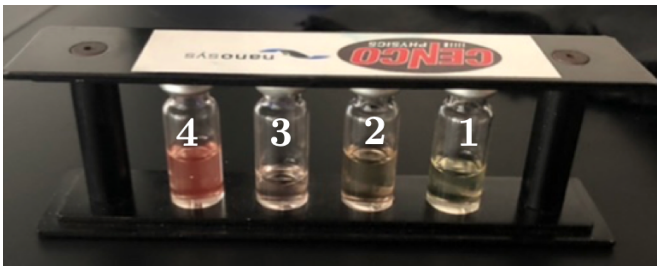


FIG. 3. Four, non-emitting, CENCO-Nanosys vials containing quantum dots made of the same material but of different radii labeled 1, 2, 3, and 4

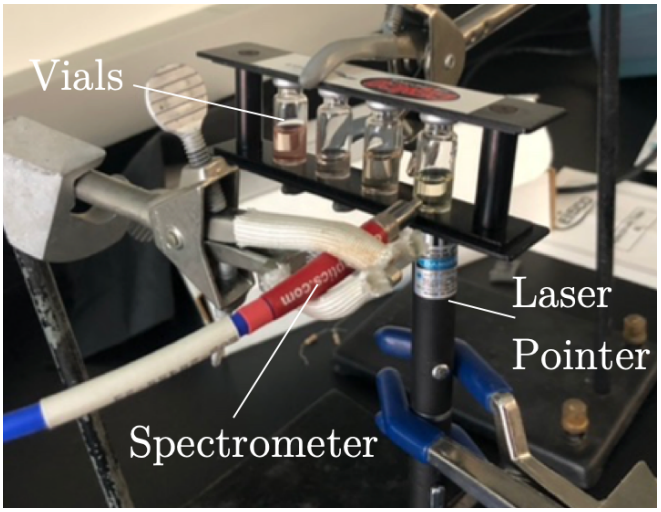


FIG. 4. Setup of experiment including vials, a $405nm$ laser pointer to excite the quantum dots, and a Red Tide optic fiber spectrometer

pointer into each vial from below and took the spectra. We display those spectra and analyze them here.

Using the peak wavelengths observed in FIG. 6, the radius of the quantum dots contained in each vial can be calculated. Rearranging equation (4) and solving for R

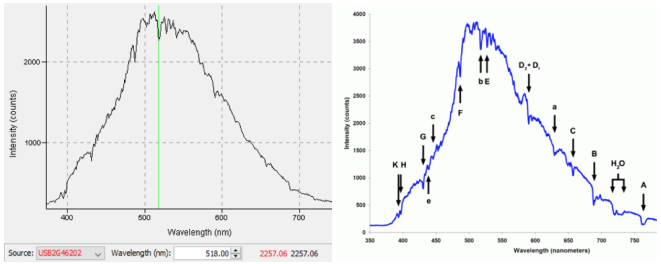
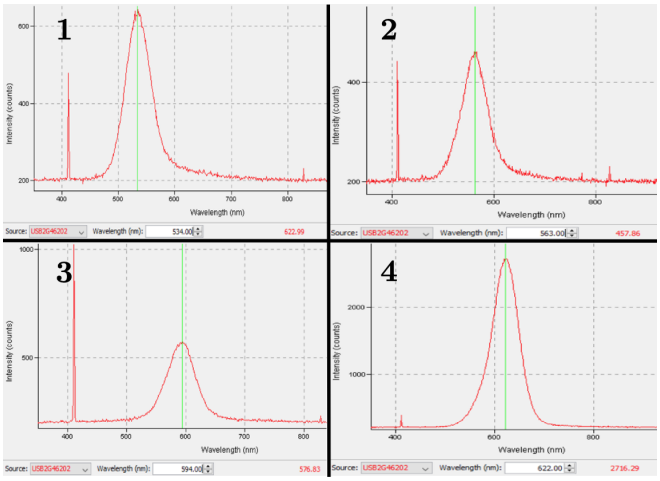


FIG. 5. To calibrate our spectrometer, we took a spectrum of the Sun (left) and compared it to a widely used spectrum indicating the Sun's Fraunhofer lines (right) [6]. In the software used to analyze our spectrum (left), we can place a green vertical line on the x-axis and the wavelength value will be displayed in the box ($518.00nm$)



Vial	Peak Wavelength	Max Intensity
1	534±24nm	622.99 counts
2	563±21nm	457.86 counts
3	594±24nm	576.83 counts
4	622±50nm	2716.29 counts

FIG. 6. Optical spectra of vials 1, 2, 3, and 4. Each vial contains quantum dots all made of the same material, but with different radii. The radius of a quantum dot determines the wavelength it will emit at. The error in the wavelengths were calculated by taking the square root of the max intensity.

Vial	Radius
1	$2.34 \pm 0.13nm$
2	$2.49 \pm 0.12nm$
3	$2.68 \pm 0.16nm$
4	$2.87 \pm 0.39nm$

TABLE I. Calculated Radii of the quantum dots in vials 1, 2, 3, and 4

gives:

$$R = \sqrt{\frac{\hbar^2\pi^2\lambda(m_e + m_h)}{2m_e m_h(hc - \lambda E_g)}} \tag{5}$$

The effective mass of the electron (m_e) is given to be $7.29{*}10^{-32}kg$, the effective mass of the electron hole (m_h) is $5.47{*}10^{-31}kg$, and the band gap (E_g) of the material is given to be $2.15 * 10^{-19}J$ [3]. The reason the mass of the electron differs from the standard $9.11{*}10^{-31}kg$ is due to potentials inside the semiconductor that effect how the electron moves - this known as the Kronig-Penney Model [7] [8].

We calculate the radii of the quantum dots in each vile to be:

We are also able to determine the material from which these quantum dots were made by getting the ratio effective electron mass and hole to the normal electron rest mass and by converting the material's band gap energy

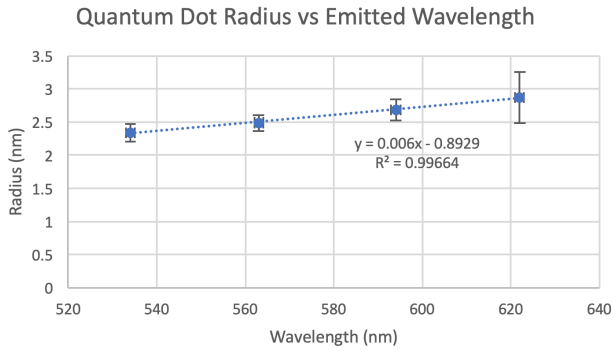


FIG. 7. Plot of Quantum dot radius vs. emitted wavelength in nm. A linear trend is apparent.

to electron-volts. This give a band gap energy of 1.34eV, $m_e/m_o = 0.08$ and $m_h/m_o = 0.6$ which indicates our quantum dots are made of Indium Phosphide (InP) [3].

Finally, we can calculate the value of Planck's constant (h) from our known wavelengths and radii (granted we had to know the value of Planck's constant to calculate the radii). Again, starting from equation (4) we can rearrange to get a quadratic equation:

$$h^2[\frac{1}{8R^2}(\frac{1}{m_e} + \frac{1}{m_h})] - h[\frac{c}{\lambda}] + E_g = 0 \tag{6}$$

Compressing $\frac{1}{8R^2}(\frac{1}{m_e} + \frac{1}{m_h})$ into the term A, we use the quadratic equation to solve for h

$$h = \frac{c}{\lambda} \pm \frac{\sqrt{\frac{c^2}{\lambda^2} - 4AE_g}}{2A} \tag{7}$$

Calculating this for each wavelength and radius of our quantum dots, we find an average value of Planck's constant $h = (6.64 \pm 0.02) * 10^{-34}\frac{m^2kg}{s}$.

In summary, quantum dots are nanoparticles that, when excited with ultraviolet light, emits photons of a specific wavelength depending on the its radius. In this paper, we obtained the spectra of 4 vials of quantum dots made of the same material but of different radii. We were able to calculate the radii of the quantum dots and determine that they were synthesized of Indium phosphide. Knowing the dots' corresponding wavelengths and radii, we were able to calculate an average value of Planck's constant.

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