The influence of temperature and size on the absorption coefficient of CdSe quantum dots

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Abstract. Because of Cadmium selenide quantum dots (CdSe quantum dots) has a tuning energy gap in the visible light range, therefore; it is provided a simple theoretical model for the absorption coefficient of CdSe quantum dots, where the absorption coefficient determines the extent to which the light of a material can penetrate a specific wavelength before it is absorbed. CdSe quantum dots have an energy gap can be controlled through two effects: the temperature and the dot size of them. It is found that; there is an absorption threshold for each directed wavelength, where CdSe quantum dots begin to absorb the visible spectrum at a size of 1.4 nm at room temperature for a directed wavelength 300 nm. It has been observed that; when the wavelength is increasing its absorption threshold is increased. For wavelengths (400, 500, 600) nm, the absorption thresholds for each quantum sizes are (1.8, 2.2, 3.2)nm respectively. On the other hand, a rising of the temperature led to reduces the absorption coefficient value , that at 400 K for all quantum sizes, the absorption coefficient increases >2000cm⁻¹ (According to the directed wavelength) than it is at 0 K. CdSe quantum dots can be considered as one of the most promising materials because it has a tuning gap for the visible wavelengths for different applications, such as light-emitting diodes in different colors of the visible spectrum. It is found that ;there is a good agreement between our theoretical calculations and experimental results.

Keywords: CdSe quantum dots, Tuning Energy Gap, Absorption Coefficient, Absorption Threshold

1. Introduction

Recently, CdSe quantum dots have been an intensely researched compound due to their size and shape-dependent properties arising from the quantum confinement regime [1,2]. This regime depends on the spherical particle-in-a-box model that predicts strong quantum confinement, besides it has a tuning energy gap [3].

One of the most important photometric techniques in solids is the light absorption scale, the absorption coefficient, which can determine the depth at which light of a specific wavelength penetrates a material. The wavelengths that include the visible and the infrared are the most important wavelengths for applications. The absorption coefficient depends on the properties of the CdSe and the energy of the incident photon, whether it is greater, less, or equal to the energy gap [4]. Taking into consideration, the atomic structure and density of states of the conduction band and valence, and the type of energy
gap, whether direct or indirect [5]. Researchers have studied the absorption coefficient due to its importance, Jinjun Sun and Ewa M Goldysthey are analysis the linear absorption coefficient that due to interband transition in CdSe quantum dotstheoretically [6]. C.A. Leatherdale et al use models of light scattering from light-absorbing small particles in CdSe quantum dots [7]. Ehud Shaviv et al. used a method to obtain-CdSe QRs concentrations are based on a comparison of the absorption far above the transition of the bandgap [8]. Other researchers as W. W. Yuetal, A. Striolo etal, O. Schmelzelatal and C. A. Leatherdale etal have studied the determination of the molar absorption coefficients of CdSe QD experimentally [9–12].

The characteristics of CdSe are highly sensitive with respect to various growth processes as well as ambient conditions [13]. Due to the importance of the absorption coefficient for its apparent effect on the optical properties, in addition to some optical constants, therefore, in this paper, we present a theoretical model of CdSe quantum dots that study the effect of temperature and the quantum dot size on the absorption coefficient.

2. Theoretical Model

The absorption rate of light is proportional to the intensity of the flux of photons of different wavelengths. When light passes through material, the flux of photons gradually decreases, so that the material absorbs some of the photons. Thus, the number of photons that will reach a given point in a CdSe quantum dots depends on both the wavelength of the photon and the distance from the surface. Tauc relation is using to calculate the absorption spectra due to the optical transition energy, it is expressed as [14, 15]:

\[
\alpha (h\nu) = B (h\nu - E_g)^\gamma 
\]

where \( B \) is a proportionality constant, \( \alpha \) is the absorption coefficient, \( h\nu \) is the energy of the photon, \( E_g \) is the optical band gap and \( \gamma \) is an indication of the type of electronic transitions, where \( \gamma = 1/2 \) for direct transition and \( \gamma = 2 \) for indirect transition.

It is known that CdSe has a direct energy gap and is characterized by direct and allowed electronic transition, therefore; Eq. (1) becomes:

\[
\alpha (h\nu) = \frac{B}{h\nu} (h\nu - E_g)^\frac{1}{2} 
\]

It is important to be mentioned that; the proportionality constant can be calculated from the formula [16]:

\[
B = e^2 \left( \frac{2 \ast m_e^* \ast m_h^*}{m_e^* + m_h^*} \right)^\frac{3}{2} \frac{n \ast c \ast h^2 \ast m_e^*}{e^2} 
\]

where \( e \) is the electron charge, \( n \) is the refractive index is Planck’s constant, \( m_e^* \) is the effective mass of electron and \( m_h^* \) is the effective mass of the hole [16].

Since we have two influences that affect the absorption coefficient in our study, the first is the temperature, so the energy gap will be calculated as a function of temperature [4]:

\[
E_g(T) = E_{g0} - \alpha \ast T^2 \beta + T 
\]

Where \( \alpha, \beta \) are coefficients fitted with experimental data for each material which equal to \((3.3 \times 10^{-4} \text{ eV.K}^{-1}, 83 \text{ K})\) respectively, \( E_{g0} \) is the energy gap at 0K which equals 1.834eV [4].

In terms of the change in the electron’s effective mass as a function of temperature, it can be formulated with the following relationship [17]:

\[
m_e^*(T) = m_{e300} \ast \frac{E_{g300}}{E_g(T)} 
\]
While the effective mass of hole as a function of temperature is expressed by [17]:

\[ m_h^*(T) = m_{h300}^* \frac{E_{g300}}{E_g(T)} \] ………… ……… (6)

where \( E_{g300} \), \( m_{e300}^* \) and \( m_{h300}^* \) are the energy gap, the effective electron mass, and the effective hole mass at room temperature, respectively [17].

The other influencing factor is the size that due to the quantum confinement of an atom in three dimensions appears with characteristic electronic and optical properties [17].

In this study, we will use the Burs equation [18],

\[ E_{gQD} = E_g(Bulk) + \frac{\hbar^2}{8r^2} \left( \frac{1}{m_e^*(T)} + \frac{1}{m_h^*(T)} \right) \] ………… ……… (7)

where \( E_{gQD} \) is the energy gap of quantum dot, \( E_g(Bulk) \) is the bulk energy gap, \( r \) is the quantum dots’ size.

To study the effects on the quantum dots of CdSe, we substituted equation (4) with the term \( E_g(Bulk) \), and substituted equations (5) and (6) (which represent the change in the effective mass of the electron and the hole respectively as a function of temperature) in equation (7) to get an equation describing the energy gap of CdSe quantum dots as a function of temperature which denoted by \( E_{gQD}(T) \):

\[ E_{gQD}(T) = E_g(T)(Bulk) + \frac{\hbar^2}{8r^2} \left( \frac{1}{m_e^*(T)} + \frac{1}{m_h^*(T)} \right) \] ………… ……… (8)

To obtain the absorption coefficient of CdSe quantum dots as a function of energy and temperature, we substitute the Eq. (8) in Eq. (2).

\[ \alpha(h\nu, T) = \frac{B}{h\nu} \left( h\nu - E_{gQD}(T) \right)^{\frac{1}{2}} \] ………… ……… (9)

3. Results and Discussion

The occurrence of the absorption process inside the materials is described or measured by the absorption coefficient, so the absorption coefficient of CdSe Quantum Dots (eq. (9)) has been studied from; two effects the temperature, and the quantum size of dots. It can be noticed that in Figure (1) the energy gap of bulk CdSe was its highest value at 0 K., It is beginning to decreasing sharply with rising temperatures, which its highest value at 400K. The reason for this behavior is the increase in the energy of electrons due to interaction between the thermal phonons and the electrons. This lead, in fact, to an increase in the vibration inside the atom where the lengths of the atomic bonds increase, which makes them weaker with the ability to break them is easier to release the electron, which facilitates the transfer of a high-energy electron from the valence band to the conduction band and as a result of the multiple electron transitions, the energy gap decreases [19, 20].
Figure 1. The energy gap of bulk CdSe decreases with increasing temperature

Figure (2) indicates the change in the energy gap due to the decrease in the quantum dot size, it is noted that; the energy gap value changes lightly when the quantum size decreases from 10 nm to 4 nm. This means that these sizes in this range are close to the behavior of the bulk. But when the size is smaller than a size 4 nm, the energy gap begins to increase very significantly until it reaches the highest values at 1 nm. In fact, that is due to the effect of quantum confinement that shifts the energy state to higher (lowest) levels at the conduction band (valence band), which increases the size of the energy gap [21,18].

Figure 2. The energy gap of CdSe quantum dots as a function of quantum size dots

Figure (3) shows the absorption coefficient as a function of wavelengths (300nm-730nm) at room temperature. Must attract attention to two important points, the first is that; the different ranges of the
absorption coefficient are due to the different energy gaps of the quantum size of CdSe. It is noted that as the size is larger, it takes a greater range than before, where the size of 1.4 nm takes the range of ultraviolet spectrum only, while the size of 10 nm includes the range of ultraviolet, visible, and some of infrared spectrum. The other point is the energy gap which is inversely proportional to the quantum dot size of the CdSe [22, 23]. It can be seen from the figure that; the response of the quantum sizes as a function of wavelengths begins at 1.4 nm, while sizes of 1nm to 1.2nm, with a very large energy gap, do not absorb the energies of this range of wavelengths at room temperature. Where the wavelength 300nm has the highest energy is 4.141 eV, therefore; the electrons cannot cross the optical energy gap and exciting [24]. Whereas at the quantum dot size of 1.4nm, electrons able to absorb this range (λ=300 nm) of wavelengths at room temperature because it has an energy gap of about 3.571 eV. For this reason, it will allow more energy to be absorbed when the optical gap is smaller. Now, it is appropriate to explain the mechanism that causes the absorption coefficient to decrease according to the relationship $E = \frac{hc}{\lambda}$. where the ability of the incident light energy to excite electrons from the top of the valence band to the bottom of the conduction band decreases because it does not have an energy equal to or greater than the size of the optical energy gap to excite it [25]. It can be said that; the range of quantum sizes that have been relied upon in this research from 10 nm to 1.4 nm. In this range, the absorption coefficient gradually decreases as the quantum dot becomes smaller [24, 26]. This leads us to believe that the possibility of CdSe quantum dots in tuning colors according to the size. Where the blue shifting is observed when the size of the quantum dots decreases, while red shifting is tuning when the size be larger.

![Absorption Coefficient vs Wavelength](image)

**Figure 3.** The absorption coefficient as a function of wavelength at the different size of CdSe quantum dots between from 1.4nm (absorption threshold) to 10nm.

Figure (4) represents the absorption coefficient as a function of temperature (0-400) K by fixing specific wavelengths, where it is found that the absorption coefficient increases with rising temperature [27]. This increase is evident after the temperature of 100 K at the wavelengths between 300nm to 600nm except the threshold size at the wavelength from 500nm to 600nm where the increase begins with values greater than 100 K and at 700nm after 300K With an increase in temperature, the energy gap get smaller from its usual size as a result of the vibration of the electrons with the increase in their energies, which makes them able to leave their sites and move inside the band, or if its energy
is sufficient, it can move from the valence band to the conduction band. Therefore, with increasing the contribution of the transition processes, the optical absorption coefficient increases.

Noticing Figure (4), there are several important points, the first is that; the absorption coefficient, in general, decreases as the wavelength of the electromagnetic spectrum increases. The other point, the threshold size increases with an increase in wavelength, for example, we find that the size threshold at \( \lambda = 300 \text{nm} \) is 1.4 nm while for \( \lambda = 600 \text{nm} \) is 3.6nm. This is because the energy of the specified wavelength is less than the value of the energy gap so that the electron transitions only respond at a size in which the energy gap corresponds to the energy of a photon of wavelength directed to it. However, the sizes of the quantum dots will be determined for each wavelength, the reason could be due to that; the energy gap be smaller and the susceptibility of incident wavelengths to the excitation of electrons [28, 29]

As a result of what was mentioned above, which is that some of the threshold sizes are unable to absorb the wavelength falling on them except at a specific temperature, as is the case at \( \lambda = 500 \text{nm} \), so that the threshold appears only at a temperature of 200 K and the same is the case of \( \lambda=600\text{nm} \). As for 700 nm, the 6 nm minimum appeared at a temperature of 300K, as mentioned earlier, resulting from a decrease in the size of the energy gap with higher temperatures.

Figure 4. The absorption coefficient increasing with temperature at different wavelength, a(300nm), b(400nm), c(500nm), d(600nm).
Figure (5) shows the absorption coefficient as a function of the size of the quantum dots. In this figure, for all wavelengths, the absorption coefficient decreases with the size of quantum dot be smaller. But, for each wavelength there is a specific size that suffers a curvature then sharp descent in the absorption coefficient. For the wavelength of 300 nm, the absorption coefficient begins to decrease sharply at the size of 3 nm, while the wavelength of 400 nm, it begins at the size of 4 nm. The other wavelengths follow the same behavior according to the energy compatibility of the energy gap of the quantum dots. This behavior is attributed to the number of electronic transitions, which is almost constant at large sizes, then the transitions begin to decrease until they disappear. In fact, this confirms the existence of an absorption threshold for each specific wavelength. On the other hand, it can be found that small quantum sizes do not react at high temperature which is due to the large energy gap arising from the quantum confinement, as compared to large quantum sizes, which show a direct reaction at high temperatures due to the small energy gap that they have.

**Figure 5.** The absorption coefficient as a function of quantum dot size at different wavelength. a (300nm), b (400nm), c (500nm), d (600nm).

The most of experimental results review the optical absorption coefficient in the form \((\alpha h \nu)^2\). So, it is showed our calculations in the same format in Figure (6c), which gives a suitable match for both Fig.(6a) [27] which represents experimental results, and Fig. (6b) [30] which acts as theoretical models.
Figure 6. Absorption Coefficient of CdSe quantum dots. a. experimental results [27], b. theoretical models [30], c. our calculations

4. Conclusion

For CdSe quantum dots, not all sizes are capable of absorbing electromagnetic radiation, where the absorption threshold begins in quantum dot size 1.4 nm at room temperature. Thus, CdSe quantum dots can be tuned to absorb different wavelengths according to the quantum dot sizes until they reach 10 nm which can be absorbing all wavelengths in the range of the visible spectrum. Therefore, CdSe quantum dots can be considered as one of the most promising materials for tuning energy gap applications, such as light-emitting diodes in different colors of the visible spectrum. On the other hand, each wavelength has an absorption threshold in which the energy of photon of wavelength corresponds to the energy gap of the size of the CdSe quantum dots. Also, for each specific wavelength, the absorption coefficient remains relatively constant for all quantum sizes until it reaches a size in which the energy gap does not match to the energy of the specified wavelength, where the absorption coefficient value drops sharply until it vanishes this is an indication of the end of electronic transitions in the material. All calculations were done by using software MathCAD 15.
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6. References

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