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Synthesis and Characterization of Cds and Cdse Quantum Dots by UV-VIS Spectroscopy

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Abstract
The results of the experimental investigations of the synthesis and characterization of Cds and CdSe quantum dots is presented. In this work cadmium sulphide (CdS) and cadmium selenide(CdSe) quantum dots are synthesized successfully by adopting the hot injection /solvo thermal chemical synthesis method using oct-decane as a non-coordinating high boiling point organic solvent in place of trioctyphosphine (Top) which posed environmental hazard. A sudden injection of room temperature sulphur and selenium solution into the hot cadmium solution produce seed crystals which grow quickly and they are monodispersed. Samples are withdrawn from the hot solution and quench at room temperature to produce a series of increasing quantum dots size. Subsequent characterization studies were carried out on the synthesized Cds and CdSe QDs using Uv-vis spectroscopy machine and irradiation with uv-Light. The absorption spectra exhibit a strong blue –shift with decreasing size of QDs size, which is attributed to the quantum size effect (QSE). The sizes and band gaps of the Cds and CdSe were calculated, from the outcome of the calculation, it was deduced that the band gap energies varies from larger value to smaller values due to depletion of the band gap as a result of increased temperature. The results of this research are likely to be useful toward the understanding formation mechanism of CdS and CdSe .

Keywords: Semiconductors, solvothermal, synthesis, crystals, quantum dots, band gap.

INTRODUCTION

In recent years, the emerging field of nanotechnology have spurred up enormous interest in the synthesis of nanosized materials. Nanostructures are crystalline particles with diameters defined within the range typically from 1 to 10nm. These particles possess properties that can be tuned by varying their size and shape. Neeleshwa, S. et. al., (2005) and Xia, Y. et. al., (2003).

Nanosized materials have received intense growing interest as a result of their fascinating peculiar and unique properties and their various technological application superior to their bulk counterparts. Alivisatos, P. et al., (1998). Nanocrystals are effective visual aid to demonstrate quantum mechanics, since their transition energies can be explained as a particle in a box, where a delocalized electron is the particle and the crystal is the box. Schulz, W.G. (2000) has suggested that nanotechnology is an exciting emerging field that involves the manipulation of the atom and molecules at the nanoscale.

In the nanometer size regime many of the physical properties of the semiconductor particles changes with respect to the bulk material typically among these modified behaviour are melting points and boiling points, specific heat capacities and energies which are to a first approximation proportional to the reciprocal value of their radii that is:

$$E_g \; \alpha \; \frac{1}{d} \; ------------[1.1]$$

where E_g is the band gap and d is the nanocrystals radius.

Nanomaterials can exist in three-dimensional (3-D) colloids, two dimensional (2-D) quantum well, one dimensional (1-D) wires and even zero dimension (0-D) quantum dots. In this thesis, the nanomaterial of interest is the zero dimensional nanoparticle termed quantum dot.

A quantum dot is very small crystal of semiconductor materials whose excitons undergoes quantum conferment in three spatial dimensions and thus composed of about a hundred to a few thousand atoms. Quantum dots has diameter approximately between two to ten nanometer, which put them in a special size range that retains some properties of bulk materials as well as some properties of individual atoms and molecules that constitute them. Joshua, J. (2011) and Palinginis, P. (2004).

In the quantum dot, there is the possibility of changing the semiconductor band gap – that is energy difference between the electron filled valence band and the empty conduction band by varying the particle size during fabrication process. An electron can thus be excited from the filled valence band to the empty conduction band by an absorption of photon (hF) with an appropriate energy ($hF \geq Eg$) the band gap, consequently leaving behind a space called a hole (h^+) within the neighbourhood of the valence band. Feeling each other's charge, the electron and the newly formed particles do not move independently from each other because of the coulomb attraction.

$$F = \frac{K(e^- - h^-)}{r^2} \text{ - - - - - - - - - - - - - - } (1.2)$$

The formed e^-–h^+ bound pair is called an exciton and has its lowest energy state slightly below the lower edge of the conductor band. At the same time its periodic wave function permeate a large region (several lattice spacing), i.e. the exciton radius is larger since the effective masses of charge carriers are small and the dielectric constant is high as in:

$$a_b = E_r\left(\frac{M_o}{\mu}\right)\frac{K(e^- - h^-)}{r^2}a_b \text{ - - - - - - - - - - - - - } (1.3)$$

where: a_b is the hydrogen Bohr radius

μ is the reduced mass, E_r – dielectric constant

M_o – mass of electron

The excitons in the quantum dots are confined to a distance smaller than the Bohr exciton radius, 5.4nm in bulk CdSe and 3nm in bulk Cds. Mao, H. et. al., (2005) and Norris, D.J. et. al., (1994). Since the excitons are confined, only specific wavelengths corresponding to the exciton can "fit" inside the box and still satisfy the boundary conditions. Thus the available energies of the exciton are discrete. By changing the size of the quantum dot, the size of the box changes and energies that "fit" shift up and down. To fit into the dot structure, the charge carriers have to assume higher kinetic energy leading to an increased band gap and quantization of the energy levels to discrete values. This phenomenon is commonly called quantum confinement effect in quantum physics. With decreasing particle size, the energetic structure of the semiconductors changes from a band-like one to discrete levels. Hence quantum dot absorption features correspond to transitions between discrete three dimensional particles in a box states of the electron and the hole, both confined to the same nanometer size box. The strong confinement of the excited electrons and holes leads to dramatically optical and electronic properties compared to the bulk semiconductors These discrete transitions are reminiscent of atomic spectra and have resulted in quantum dots also being called artificial atom, Silbey, P. et. al., (2005) and Delerue, C. and Lannoo, M. (2004).

Many studies have been directed on III-V and II-VI semiconductor quantum dots (QDs) element of the periodic table throughout the world. For II-VI QDs, Cds and CdSe QDs prepared by chemical methods are the most popular due to their high luminescence quantum yield, wide fluorescent emission spectral ranging from blue to red (Hine, et. al., 2001), narrow band gap and variety of optoelectronic conversion properties compares to bulk CdSe, Cds (Zhu, J.J. et. al., 2000). Up to now, numerous methods have been reported for the preparation of Cds and CdSe nanoparticles. They include the following:

Molecular beam epitaxy which is very expensive. (Zhang, B.P. et al., 1997), Metal organic vapor chemical deposition (Liao, M.c. et. al., 1997), Solvothermal (Deng, Z.X., et. al., 2002) and Hydrothermal Method (Peng, Q. et. al., 2002). Most of the techniques employed trioctylphosphine (Top) based system in which the reagent are ejected into a hot coordinating solvent at elevated temperature (200^0-400^0 c).

Little information was obtained regarding the formation mechanism of Cds and CdSe using this techniques. Furthermore, the cost of large scale synthesis is very high (Top) solvent. In addition (Top) is hazardous, unstable and environmentally unfriendly. Here, high quality Cds and CdSe were prepared using Oleic acid and paraffin liquid, i.e. octadecane instead of the usual Tri-octyl phosphine oxide which is very expensive, dangerous, unstable and environmentally unfriendly.

The method adopted for synthesis of the nanoparticle is the solvothermal process because it is easier, cheap and safe. Moreover, the experimental conditions to control the size of the CdSe and Cds nanoparticles and the optical properties were investigated in details. The structures and properties of these synthesized nanoparticles were characterized by using Uv-Vis absorption spectrometer.

Synthesis and characterization were carried out in advance physics laboratories at Sheda Science and Technology Complex (Shestco), Abuja. We identified a synthesis protocol to create the aforementioned nanoparticle in colloidal suspension and examined their light emitting characteristics using UV-illuminator. Boatman, E.G. et. al., (2005) and Bowers II, M. et. al., (2005).

SYNTHESIS OF CADMIUM SULPHIDE QUANTUM DOT (CDS)

Preparation Procedure

Cds QDs were prepared using Cadmium Oleate and elemental powdered sulphur as precursors. 0.7grams of Cadmium Oleate was dissolved in 50mls of Octa-decane and the mixture were loaded into a three-neck round bottom flask clamped into the electrothermal heating mantle on the hot place. A thermometer was inserted through one of the mouth and a pressure regulator through the other mouth. The solution was heated to 160^0C and stirred until the Cadmium Oleate was completely dissolved and a light yellow homogeneous solution was obtained.

Simultaneously, the sulphur precursor was formed by dissolving 0.3grams of powder sulphur (in 5mls of toluene) and 1ml of the resulting solution was introduced into 25mils of Octa-decane and heated until the material dissolves and the toluene evaporate away from the solution. The toluene was a vehicle through which the insoluble sulphur was introduced into the hot mixture of the Cadmium Oleate and the 50mls of Octa-decane.

Thereafter, the resulting solution of sulphur and Octa-decane were chilled and then 2.5mls is taken up in a 5ml syringe and was swiftly of rapidly injected into the hot solution of Cadmium Oleate contained in the three mouth round bottom flask placed inside the hole in the heating mantle on the hot plate.

The setup was flushed up with Nitrogen to eliminate oxygen that normally contaminates the quantum dot. The product formed were extracted from the flask by mouth drilling through rubber inserted into a pipette an appropriate quantity of nucleated quantum dot and then spilled into six sample tube collected at a semi-regular time interval between 3secs and 10mins. The image below shows a series of six samples of Cds quantum dots prepared using the synthesis described in Boatman et. al. (2005), and thoroughly documented by Lisenky, G. (2008).

Plate. 1: Experimental setup for the preparation of the quantum dots.

Plate 2: Samples of Cds Quantum Dots

Cadmium Oleate Solution + Sulphur solution $\rightarrow$ Cds (nanoparticle) + byproduct.

SYNTHESIS OF CADMIUM SELENIDE QUANTUM DOT

The following materials were used in the synthesis of CdSe quantum dots. Octa-decane (90% ODE), Oleic Acid (OA, 90%) and Selenium Powder (Selenium Dioxide). All liquid chemicals and vessels were purged or degassed with N_2 at an approximate pressure of 200ton prior to and during reactions to prevent oxidation, and the vessels were sealed with rubber septa.

Heating was achieved using a heating mantle connected to a power source in the fume cupboard. Temperatures were measured and regulated between 200 – 220^{0}C using a thermocouple digitalize temperature controller of the same model quoted in the instrumentation.

The CdSe synthesis process proceeded as follows:

1. Cadmium Oleate solution was prepared by dissolving 0.7gram of Cadmium Oleate in 25mls of Octa-decane at approximately 200 – 220^{0}C in 10ml three neck round bottom flask with stirring, heated by a heating mantle controlled by a variac. Following this 0.3gram of selenium dioxide were dissolved in 10ml of ethane doic and heated until particle dissolves. The resulting mixture of this preparation were emptied into 25ml of Octa-decane and was carefully heated to 220^{0}C in 250ml beaker. The mixture (solution) was then allowed to cool to room temperature. 5ml of the solution was taken up with syringe and swiftly and vigorously injected into the hot cadmium solution and the reaction time was monitored. When the desired reaction time had reached, the injection of the solution lower the temperature of the Cadmium Oleate solution to 200^{0}C as determined by the digitalized temperature controller attached to the setup.
2. The CdSe quantum dot sample formed were withdrawn from the hot reaction at semi-regular time intervals between 4seconds and 8minutes using 25ml pipette. A total of three samples of CdSe quantum dot were obtained within the stated time frame before granules started growing in the flask.

The synthesis activities in the two days were performed in a fume cupboard because of the toxic fumes emanating from the synthesizing vessel or flask. The image below shows a series of four samples of CdSe quantum dots prepared using the synthesis procedure described in Boatman, et. al., (2005) and Yan, Y.L. et. al. (2003).

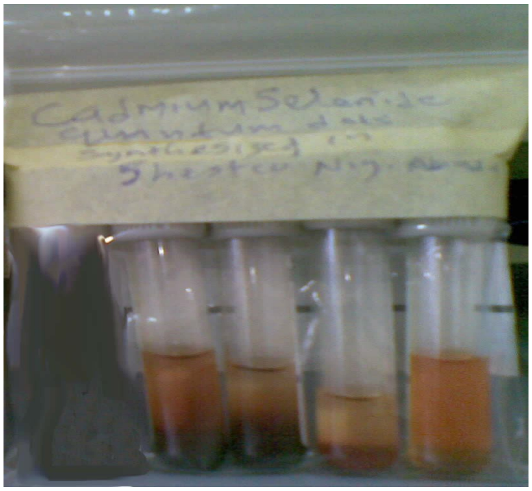


Plate 3: Samples of CdSe Quantum Dots

CHARACTERIZATION

Subsequent characterization of the fabricated nanocrystals was carried out in the Advanced Physics Laboratories (Shestco), Abuja using UV-Avac spectrometer. Therefore Absorbance of the sample was measured on an Ava Spec 2048 UV-Spectrophotometer.

In a dual beam spectrometer, the absorbance is measured in comparison to a reference sample, which is generally a cuvette filled with the same solvent as the sample is suspended in fig. 3.4. In this study, octadecane was used as the reference solvent.

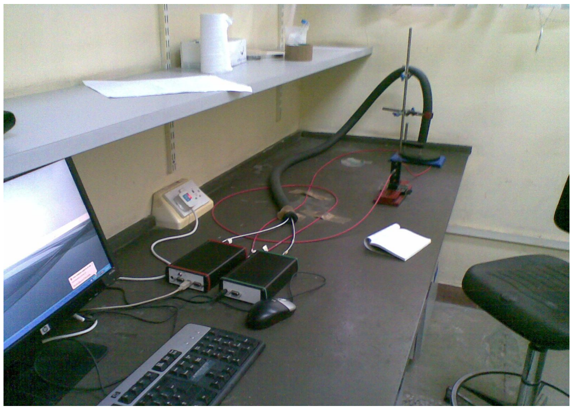


Plate 4: Dual beam spectrophotometer of the UV-Avac Spec.

Empirical formula was used to evaluate the radii of each nanoparticle. In addition, their respective band gap energy was computerized using known literature reviewed constant and formular. Wavelength were extrapolated from the absorbance peak of each nanoparticle and substituted into the formula to generate the various dot size and energy. However, samples were kept in a cool and safe place for future experiment.

Following this, each nanoparticles were illuminated with an ambient light and subsequent glowing was observed from each quantum dot, which ascertained that the samples were quantum dot.

RESULTS AND DISCUSSIONS

Consequently, the samples were administered for further optical investigation to obtain the diameter and the ban gap energies of the nanocrystals. The wavelengths of each nanoparticles were extrapolated from the peak absorbance amplitude and substituted into the band gap and the particles size formula to obtained the band gap energies and the size of the Cds and CdSe Qds respectively. The UV-vis spectra of the Cds and CdSe are presented below.

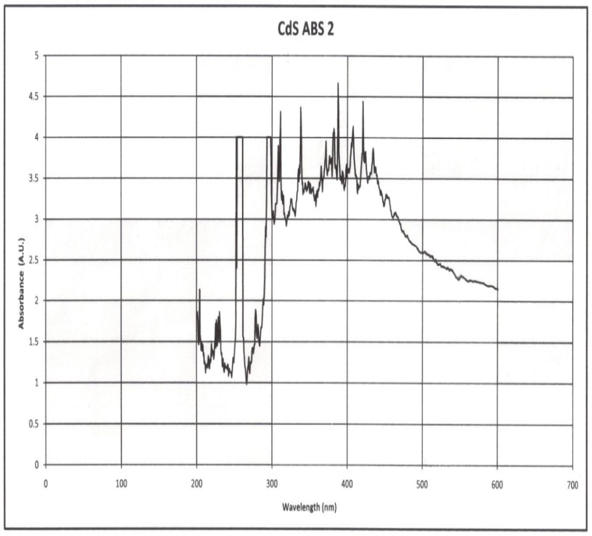


Fig. 1: UV Absorption Spectra for Cds 1 Quantum dots with absorbance peak and wavelength.

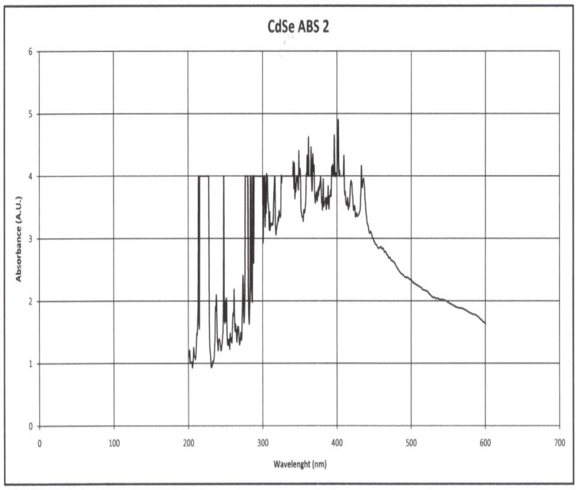


Fig. 2: UV Absorption Spectra for Cds 2 Quantum dots with absorbance peak and wavelength.

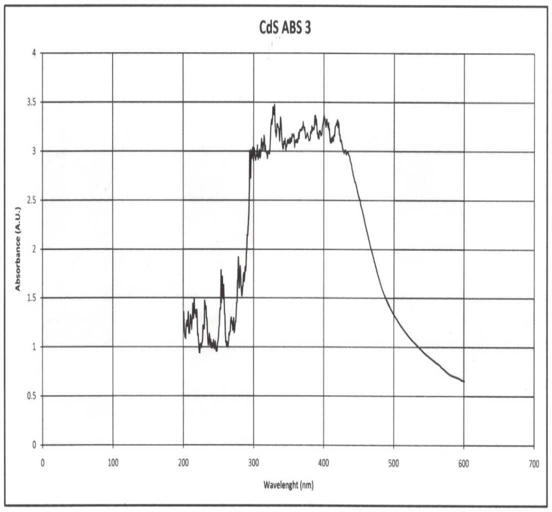


Fig. 3: UV Absorption Spectra for Cds 3 Quantum dots with absorbance peak and wavelength.

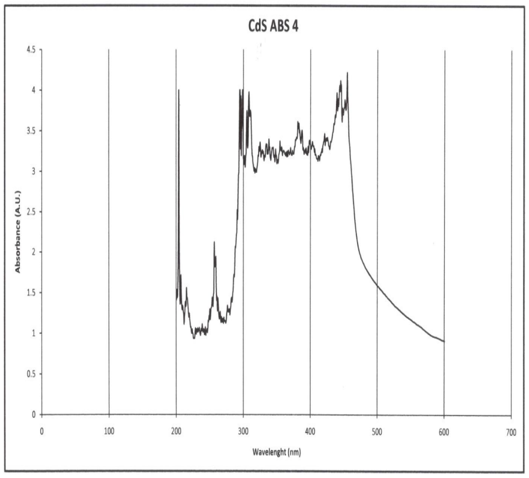


Fig. 4: UV Absorption Spectra for Cds 4 Quantum dots with absorbance peak and wavelength.

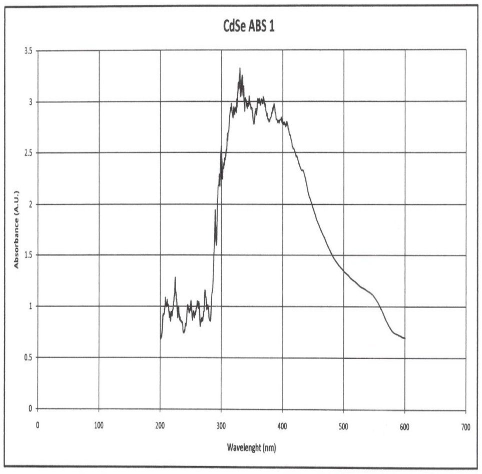


Fig. 5:UV Absorption Spectra for CdSe 1 Quantum dots with absorbance peak and wavelength

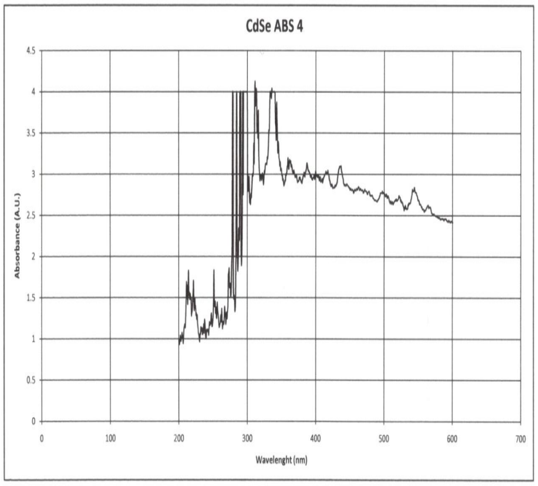


Fig. 6: UV Absorption Spectra for CdSe 2 Quantum dots with absorbance peak and wavelength

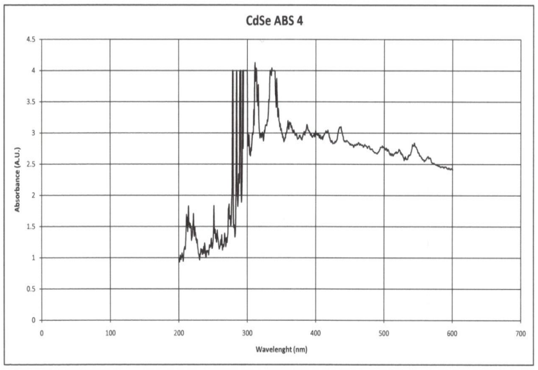


Fig. 7: UV Absorption Spectra for CdSe 3 Quantum dots with absorbance peak and wavelength

Table 1: Extrapolated wavelength of each quantum dots at various absorbance peak

Name of Nanoparticle	**Wavelength at absorption peak (nm)**
Cds_1	416.00
Cds_2	432.00
Cds_3	436.00
Cds_4	452.00
$CdSe_1$	545.00
$CdSe_2$	548.00
$CdSe_3$	563.00

Thus, using the relation:

$$E_g = \frac{hc}{\lambda}$$

where E_g is band gap of the nanoparticles.
From the excitonic absorption peak, C speed of light in space (3 x 10^8m/s), λ wavelength of the nanoparticle at various absorption peak.

The band gap of each nanoparticle as a function of wavelength as shown in table V below.

Table 2: Calculated Band-Gap

Names of Nanoparticle	Wavelength (nm)	Bandgap (eV)
Cds_1	416.00	2.988
Cds_2	432.00	2.900
Cds_3	436.00	2.850
Cds_4	452.00	2.750
$CdSe_1$	545.00	2.280
$CdSe_2$	548.00	2.270
$CdSe_3$	563.00	2.210

Concurrently, the nanoparticle diameter (size) was calculated using the relation.

$$R = \sqrt{\frac{2\pi^2\hbar^2 E_g^b}{\left(\frac{1}{M_e^*}+\frac{1}{M_h^*}\right)\left(E_g^{n^2}-E_g^{b^2}\right)M_o}}$$

where:
R = quantum dot radius
(2 R is the diameter and hence, indicates particle size)
E_g^b = bulk band gap for Cds and CdSe
E_g^n = the band gap calculated from the excitonic absorption wavelength of Cds and CdSe in table.
M_e^* = the effective mass of the electron.
M_h^* = the effective mass of hole, in kg.
For Cds M_e^* has a value of 0.19, M_h^* is 0.80
For CdSe, M_e^* is 0.13, M_h^* is 0.45
(Boatman; E.M., et al., (2005), and Peng, X. (2002)

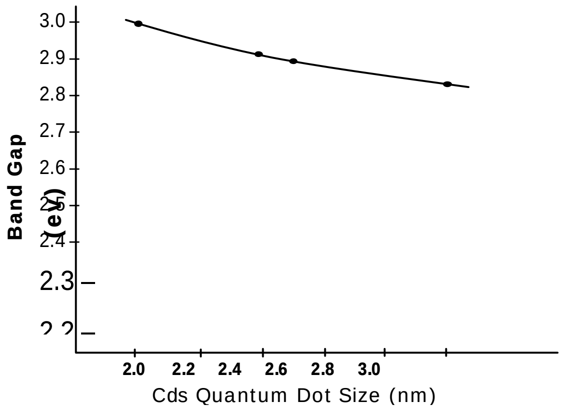
The computed nanoparticle sizes are presented in table (3) below.

Table 3: Calculated Band Gap and QDT diameter for Cds, CdSe.

Names of Nanoparticle	Band Gap (eV)	Diameter (nm)
Cds_1	2.988	2.00
Cds_2	2.880	2.40
Cds_3	2.850	2.50
Cds_4	2.750	3.00
$CdSe_1$	2.281	4.20
$CdSe_2$	2.268	4.40
$CdSe_3$	2.208	4.60

From the result of table (3), a graph of band gap was plotted against size of the nanoparticles as shown in Fig. 8 and 9.

Fig. 8: Band gap correlated against QDTs size. Band gap increasing as the dot size decreases



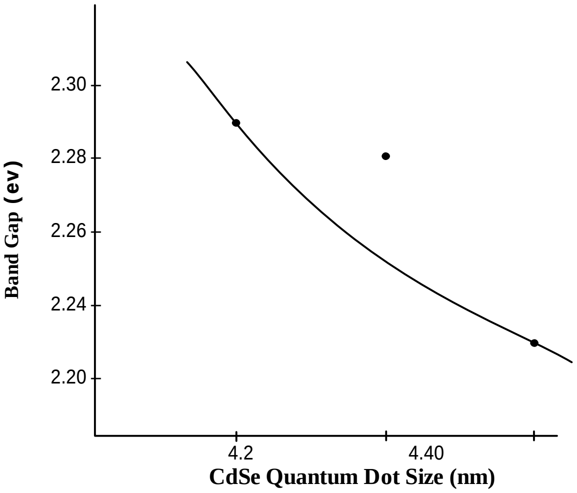


Fig. 9: Band gap correlated against QDTs size. Band gap increasing as the dot size decreases.

The colloidal suspensions of Cds and CdSe quantum dots of the increasing size from left to right are shown in Plate 5.

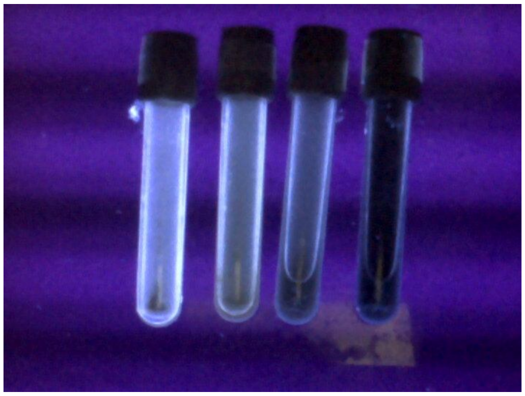


Plate 5: Colloidal suspensions of the quantum dots illuminations with UV-light

The samples were illuminated with UV-light and there was an observed fluorescent from the sample as seen with the naked eyes following irradiation with the UV-light (Evan, R., et. al., 2011). The colour of the sample viewed varied from blue-yellow to orange-red. These changes in colour are consistent with observation noted by Tadd, K., et al., (2002) and Elizabeth, M.B., George, C.L., (2005) are attributed to the increasing size of the quantum dots.

DISCUSSION OF THE UV-SPECTRAL

Generally, the electronic state is an important property that can be explained in terms of valence and conductivity bands and a gap between these bands. The UV absorbance spectral presented in the figures above reveal that as the size of the nanocrystals shrink, the maximum peak shifted to a shorter wavelength leading to corresponding increase in the confinement energies because the valence band is move downward and conduction band is pushed upward thus widening the band gap of the semiconductor nanocrystals.

The net effect is that the band gap increases. This results to a blue-shift of the (band-band) excitation energy of the semiconductor. The value of the band gaps of the various synthesized nanoparticles were quite large when compared to typical band gap in bulk Cds and CdSe. This rapid increase in band gap and shift in the electron transition to higher energies with decreasing dot size is due to enhancement in surface/volume ratio and accompanied increase in oscillation strength of the nanocrystal induced by the quantum size effect (QSE). Ashcroft, N.W. AND Mermin, (1976).

Another interesting feature of the results presented show that the band gap E_g usually decreased with an increasing temperature and a much steeper temperature dependence with decreasing particle size is observed. This explains why the band gap reduces with an increasing dot size as the temperature increase. Khaet Skii, A.V. et. al., (2000).

An immediate optical feature of the quantum dots synthesize is their colour. Although the quantum dots were of the same material but their different sizes results to emission of light of different colours. The larger the QDT size, the redder (lower its fluorescence spectrum). Conversely, smaller (QDTs) emit bluer (higher energy) light.

The colouration is directly related to the energy levels of the quantum dot. Quantitatively speaking, the band gap energy determined the energy (and hence colour) of the fluorescence light which is inversely proportional to the size of the quantum dot. The material properties changes dramatically because the quantum size effect (QSe) arises from the confinement of the electrons and holes in the material. The increased surface area/volume ratio and accompanied increase in oscillator strength as a result of the downsizing the bulk Cds/CdSe to nanometer range is responsible for the unprecedented increase in the band gap of the synthesized nanoparticle over their bulk counterpart. Lee, S.W. et. al., (2002).

CONCLUSION

In conclusion, this work has demonstrated the synthesis procedure in the hot injection/solvothermal method. Nanoparticle with varying band gaps and diameter emerge in the process. The nano-particle fluorescence when exposed to UV-light. The colouration of the nanoparticle is directly linked to the band gap. The colour of the emitted light depends on the size of the quantum dots, the larger the QDT size, the redder the light. As the dot shrinks in size, the emitted light becomes shorter in wavelength, thus moving toward the blue. A rainbow of colour can thus be emitted from a single material simply by changing the quantum dot size. With all these different colours, it is now possible to make light-emitting diode (Leds), biological labeling, bio-sensing and other technological application from Cds and CdSe quantum dots

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