Characterization of ZnS Quantum dot (q-dot) by Ultraviolet Visible (UV-VIS) Absorption Spectrum Studies & Comparison with CuO Nanocrystal

Mamun Mohanty[1], Aurobinda Acharya[2], Bairagicharan Panda[3], Selvaraju Balamurgan[4], Subhendu Pattnaik[5], Gouri Sankar Roy[6]

[1]124/126, Satyanagar, Bhubaneswar
[2]Tata Consultancy Services, Kalingapark, Bhubaneswar, Orissa, India
[3]Dept of Physics, R.I.H.S Bhograi, Balasore
[4]Alpha College of Engineering, Thirumazhhaisai, Chennai
[5]Pathani Samanta planetarium, Bhubaneswar, Orissa (India)
[6]Govt. (Auto) College, Bhawanipatna, Orissa, India
subhendu_patnaik@yahoo.com

Abstract: Ultrasize ZnS quantum dots have been synthesized with (3-Mercatopropyl) trimethoxysilane as the capping agent by the all-aqueous procedure. The size of quantum dot by this method is in the range 4 nm to 10 nm. These quantum dots have been characterized by UV-Visible absorption spectrum. The absorption spectrum of synthesized quantum dots indicate a blue shift with decrease of size of quantum dot. Further UV-Visible absorption spectrum of quantum dot has been compared with that CuO nanocrystal.

[Mamun Mohanty, Aurobinda Acharya, Bairagicharan Panda, Selvaraju Balamurgan, Subhendu Pattnaik, Gouri Sankar Roy. **Characterization of ZnS Quantum dot (q-dot) by Ultraviolet Visible (UV-VIS) Absorption Spectrum Studies & Comparison with CuO Nanocrystal.** *Rep Opinion* 2014;6(11):84-87]. (ISSN: 1553-9873). http://www.sciencepub.net/report. 13

Keywords: Quantum dots, UV-Visible spectrum, Blue shift

1. Introduction

Recent advances in producing highly luminescent quantum dots have led to the applications of quantum dots in imaging biological samples [1, 2] but the composition toxicity is a problem. Most of the quantum dots contain toxic heavy-metal elements such as Cd, Hg, Pb etc., which make them, unfit for some practical applications. It is well known that semiconductors are characterized by a band gap of the order of an electron volt (eV), between the valence band, which is fully occupied with electrons, and the empty conduction band. Hence under some circumstances they can emit radiation of a specific wavelength when electrons are injected into the material. This is called electroluminescence [3, 4]. The same thing can also happen when electrons are promoted from the valence to the conduction band by shining light of appropriate wavelength. Under these conditions, holes will be left behind in the valence band and when the electrons and the holes recombine, radiation with energy equal to the band gap will be emitted. This phenomenon is called photoluminescence [5, 6, 7]. For either of the abovementioned phenomena to occur the semiconductor must be of 'direct band gap' type, which is a requirement arising from momentum conservation in the process of light emission. Besides, for the emission of visible light of different wavelengths the band gap must have energy appropriate to the corresponding wavelength. This, in turn, requires that it should be possible to tune the band gap of the semiconductor. The commonly used semiconductor silicon is an 'indirect band gap' material with the magnitude of the gap rather small compared to the energy of light in the visible range. Hence it is not a light emitter. In contrast Cadmium sulphide (CdS) and Cadmium selenide (CdSe) are 'wide band gap' semiconductors [8, 9]. Hence these are more appropriate for light emission provided their band gaps can be tuned for emission of a particular colour of light. CdSe fulfills this requirement when prepared in the nanoform. When CdSe nanoparticles prepared in different sizes are suspended in a liquid and white light is shone on the test tubes containing these suspensions, each test tube emits light of a different colour depending on the size of the nanoparticle suspended in it. This clearly indicates that the band gap of CdSe changes depending on the size of the nanoparticle. in fact, the smaller the size the larger is the band gap of the material. As a consequence of these even materials that are not emitters of light in their bulk form start emitting in their nanoform. This is often referred to as "band gap engineering" or "quantum size effect". Thus silicon, the base material of electronics technology, can be made to emit light in its nanoform.

One of the most favourite q-dots of biology are CdSe nanoparticles We can make CdSe quantum dots in three or four different sizes and illuminate them

with the same light when they would fluoresce in different colours. as shown in the figure-1.

Figure 1: Fluorescence in different-sized CdSe quantum-dots

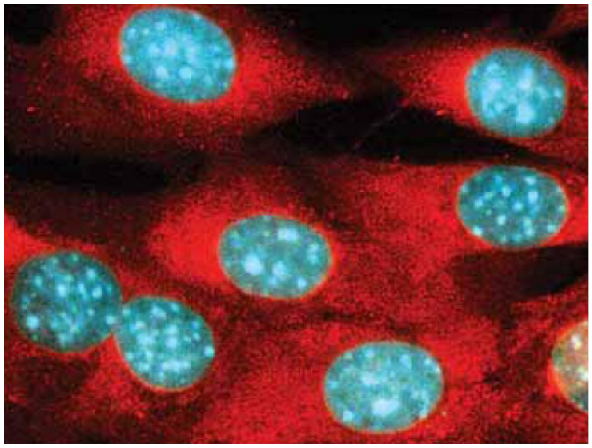

Figure 2: Quantum-dots in visualising biological processes

This property can also be used for reporting about different functioning of the cell as shown in the figure 2. But to do that they need to be made water-soluble so that they can enter the cell as inert objects. To enable them to report on different zones or regions of the cell they can be attached to different biological molecules, which in turn can then attach to the cell membranes or pass through them reporting on their activity. With this technique in mind, Scientists have succeeded in detecting cancer cells at an early stage; which is a big achievement. However, more investigation is called for before putting the use of q-dots into a common practice for any diagnostic activity, just to ascertain that their use does not cause any toxicity. One way of making these quantum dots nontoxic is to coat them with some inert material. Nonetheless, the possibilities with quantum dots in imaging, diagnostics and site-selective drug delivery into cells are exciting and extensive. There is the possibility that they will emerge as biosensors, bio-analytical agents, etc., with multifarious uses. The many faceted monitoring of cells using q-dots of varying sizes and coatings, to report on what is happening at different sites in the cell is still at a developmental stage.

Recently Evident Technologies developed a type of non heavy metal quantum dots, which are harmless in that way - ZnS quantum dots. ZnS quantum dots prepared earlier was unstable and big in size so that they get easily disintegrated and settle down. In order to achieve small size quantum dots we have synthesized ultra fine ZnS quantum dots through one-step aqueous procedure with (3-mercatopropyl) trimethoxysilane as a capping layer. The quantum dots prepared by this method are very stable and highly luminescent. After preparation of the sample we have studied UV-VIS spectrum of ZnS quantum dots with the help of Lambda 35 UV-Visible Spectrometer and compared with that of CuO nanocrystal.

2. Experimental Work

The experimental work has been done in Raman Research Institute, Banglore.

2.1 Preparation Of Zns Semiconductor Quantum Dots

ZnS quantum dots were synthesized directly with (3-Mercatopropyl) trimethoxysilane as the capping agent by the all-aqueous procedure.The prepared ZnS quantum dots are highly stable and exhibit photoluminescence. The size of the quantum dots obtained by this method was in the range between 4 to 10nm. The experimental procedure as follows 0.04 M of aqueous zinc nitrate was prepared by dissolving 1.18988 g of zinc nitrate in 100 ml deionized water, and 0.02 M of aqueous sodium sulfide was prepared by dissolving 0.5136 g of sodium sulfide in deionized water. For a sample with the MPS:Zn:S ratio of ½ : 2 :1, 0.04 mmol of MPS was dissolved in 41 ml of deionized water and stirred for 5 min with a magnetic stirrer. 2ml of the 0.04 M zinc nitrate solution was added to it in a drop wise fashion with a constant stirring for 10min.The mixture was then titrated with tetrapropylammonium hydroxide until the pH value of the reaction mixture reaches 12 followed by the rapid addition of 4 ml of 0.02 M of sodium sulfide solution. Now, the reaction mixture is left for 5 min without any disturbance to form ZnS quantum dots before adding another 2 ml of 0.04 M of zinc nitrate with constant stirring for 5 more minutes. The final suspension was clear and colourless. The obtained quantum dots suspension was quenched at 0^0 C and then stored at 4 ^{0}C, to stop further reactions.

Samples with different MPS:Zn:S ratios have been synthesized in the same manner but in varying

amount of MPS which results in formation of quantum dots of varying size. All the above reactions were carried out under temperature environment of 200 ^{0}C to 300 ^{0}C in the laboratory.

3. UV-Visible Spectrometer

We have used the Lambda 35 UV- Visible Spectrometer which is a versatile spectrometer operating in the ultraviolet and visible spectral ranges. Lambda UV-Visible spectrometer is scanning double beam spectrometer uses two light sources, a deuterium lamp for ultraviolet light and a halogen lamp for visible light as shown in the figure 3. The mirrorM1 is raised to permit radiation from the lamps to strike source mirror M2.The radiation from the source lamp is reflected from source mirror M2 through an optical filter to passes through a slit and hits a diffraction grating (monochromator) which can be rotated allowing a specific (single) wavelength to be selected. Appropriate optical filter on a filter wheel assembly located on the beam path to pre filter the radiation before it enters the monochromator. The radiation is dispersed at the monochromator to produce a spectrum. The rotational position of the grating effectively selects a segment of the spectrum, reflecting this segment through exit the slit 2 to mirror M3.This slits provide a spectral selectable band pass of 0.5,1,2 or 4nm. From the mirror M3 the radiation is reflected onto a beam splitter, which allows 50% of the radiation to pass onto the plane mirrorM4, and reflects on a filter wheel assembly located on the beam path to pre filter the radiation before it enters the monochromator. The radiation is dispersed at the monochromator to produce a spectrum. The rotational position of the grating effectively selects a segment of the spectrum, reflecting this segment through exit the slit 2 to mirror M3.This slits provide a spectral selectable band pass of 0.5,1,2 or 4nm. From the mirror M3 the radiation is reflected onto a beam splitter, which allows 50% of the radiation to pass onto the plane mirror M4, and reflects 50% of the radiation onto the plane mirror M5. Mirror M4 focuses the radiation beam to the sample cell. The beam then passes through a convex lens onto the photodiode detector. Mirror M5 focuses the radiation beam in to reference cell. The beam then passes through a convex lens onto the photodiode detector.

The advantage of double-beam operation is the better stability and allows reference to be measured and corrected in real time and fast scanning is done. The grating monochromator used here is a holographic concave grating with 1053 lines /mm in the center. Photodiodes are used as detectors. The optical path in the sample compartment is 121mm. This spectrometer can be operated in an ambient operating temperature of 15^o C to 35^o C and humidity range of 20% to 80% without condensation. The power requirements to operate this spectrometer are about 100V to 240 V AC, frequency of 50/60Hz.

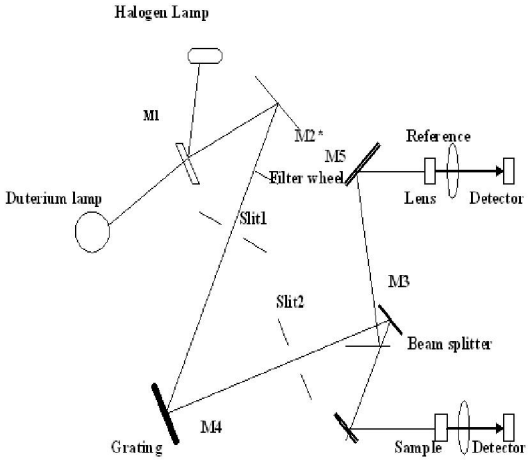

Figure 3: Block Diagram of UV-Visible Spectrometer

4. Results And Discussion

The absorption spectrum of synthesized quantum dots as shown in figure 4 shows a blue shift as the quantum dot size decreases. This is because of the fact that when geometry of surface of quantum dots changes, the band gap energy changes. In case of small size quantum dots the band gap will be energetically larger. Such a quantum dot is blue shifted reflecting the fact that electron should fall to a greater distance in terms of energy thus producing a radiation of shorter wave length. Had it been a case of larger size quantum dot they would been red shifted producing a radiation of larger wave length.

Further we have studied the Ultra-Violet absorption spectrum of CuO nanocrystal. Unlike the spectrum of ZnS quantum dots where there is a absorptance with Increase in wavelength upto 330 nm wavelength and then after remains constant, there is a wave like pattern of UV-Visible absorption spectrum in the case of CuO nanomaterial in the wave length region 500 nm – 800 nm as shown in the figure 5.This shows that the absorption band of CuO nanomaterial.

In case of CuO nanocrystal the UV-VIS spectrum (figure 5) absorption band shows a clear blue shift. This optical phenomenon indicates that these nanocrystals show quantum size effect. The absorption band of CuO nanocrystal is in the wavelength range of 300 nm to 400 nm and the hump in the broad absorption range (500 nm to 800 nm) is due to surface plasma.

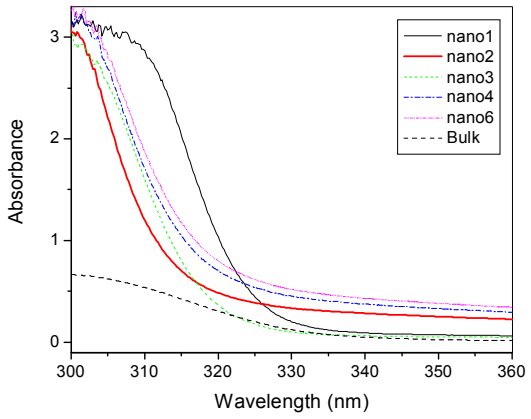

Figure 4: UV-Visible absorption spectrum of ZnS quantum dots

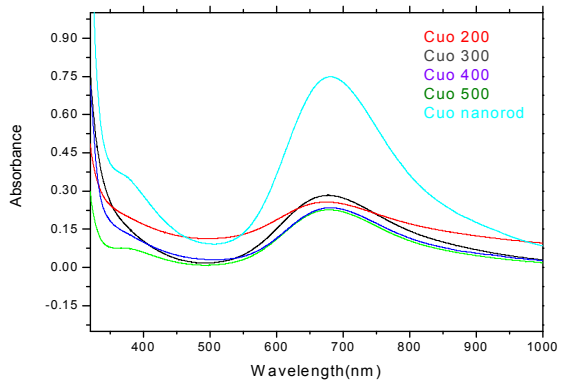

Figure 5: UV-Visible absorption spectrum of CuO nanocrystals

5. Conclusion

Thus we conclude that the absorption spectrum of synthesized quantum dots shows a blue shift with decrease of quantum dot size. Further the optical phenomenon indicates that CuO nanocrystals shows quantum size effect. The absorption band of CuO nanocrystals also shows blue shift.

References

1. S. Anandampillai, X. Zhang, P. Sharma, Gillian C. Lynch, M.A. Franchek, K.V. Larin "Quantum dot–DNA interaction: Computational issues and preliminary insights on use of quantum dots as biosensors" Computer Methods in Applied Mechanics and Engineering, Volume 197, 41-42, 2008, P. 3378-3385.
2. Bingbo Zhang, Xiaofei Liang, Lijuan Hao, Jing Cheng, Xiaoqun Gong, Xuhui Liu, Guiping Ma, Jin Chang "Quantum dots/particle-based immunofluorescence assay: Synthesis, characterization and application "Journal of Photochemistry and Photobiology B: Biology, Volume 94, 2009, P.45-50.
3. B.A. Andreev, Z.F. Krasilnik, D.I. Kryzhkov, K.E. Kudryavtsev, V.P. Kuznetsov"The features of electro-optical memory effect for 1.54 μm electroluminescence of an Er doped Si diode" Physica B: Condensed Matter, Volume 404, 23-24, 2009, P. 4597-4600.
4. R. Brüggemann, S. Olibet "Analysis of electroluminescence from silicon heterojunction solar cells " Energy Procedia, Volume 2, August 2010, P.19-26.
5. T. Abdellaoui, M. Daoudi, A. Bardaoui, R. Chtourou "Study of n+ type porous GaAs by photoluminescence spectroscopy: Effect of the etching time on the deep levels "Applied Surface Science, Volume 256, 2010, P. 5946-5951.
6. Sho Shirakata, Katsuhiko Ohkubo, Yasuyuki Ishii, Tokio Nakada "Effects of CdS buffer layers on photoluminescence properties of Cu(In,Ga)Se2 solar cells" Solar Energy Materials and Solar Cells, Volume 93, June 2009, P. 988-992.
7. R. Brunner, E. Pinčík, H. Kobayashi, M. Kučera, M. Takahashi, J. Rusnák "On photoluminescence properties of a-Si:H-based structures" Applied Surface Science, Volume 256, 2010, P.5596-5601.
8. Da-Wei Deng, Jun-Sheng Yu, Yi Pan "Water-soluble CdSe and CdSe/CdS nanocrystals: A greener synthetic route" Journal of Colloid and Interface Science, Volume 299, 2006, P.225-232.
9. Peigen Zhang, Chuanwei Cheng, Peipei Jiao, Yingying Li, Zhipeng He, Haiqian Zhang "Well improved photoswitching characteristic of CdSe nanorods via CdS nanoparticle-decoration" Materials Letters, Volume 62, 2008, P.1151-1154.