Synthesis of ZnS Semiconductor Quantum Dots (QDs) with (3-Mercatopropyl) trimethoxysilane as the Capping Agent and Study their Characterization through UV-VIS Spectra and XRD.

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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 and XRD analysis. The absorption spectrum of synthesized quantum dots indicate a blue shift with decrease of size of quantum dot.
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1. Introduction

Quantum Dots (QDs) form an important class of low dimensional structures with size, shape and composition dependent physical as well as chemical properties." Photoexcitation of a bulk semiconductor results in the formation of a bound electron-hole pair, called 'exciton', through the transfer of an electron from valence band to conduction band. The freedom of charge carrier motion is completely restricted when all the three dimensions of the material are confined in nanometer length scale (for example, excitons in semiconductors when confined below the exciton Bohr radius). Such materials are termed as quantum dots (QDs) or zero-dimensional materials (0D).l2° One-dimensional (lD) semiconductor nanostructures can be obtained by confining two of the dimensions of a semiconductor material below the Bohr exciton radius and quantum rods or quantum wires are the best examples. Further, a (2D) quantum well structure is obtained by limiting quantum confinement in one of its dimensions i.e., only one dimension of the material is in nanoscale regime [1]. The extent of confinement of charge carrier motion results in the change in electronic energy levels as illustrated in Fig 1: the continuum in case of bulk semiconductor material was transformed to discrete atomic like energy levels due to quantum confinement, with a concomitant increase in the lowest energy states. A reduction in size of a material leads to an increase in the surface area per unit volume as schematically shown in Fig 1. In QDs, significant percentage of atoms are occupied at the surface. For example, a 2.1 nm size CdSe QD contains ~l4OO atoms of which 25 % lie on the surface and most of them possess dangling bonds.'2° Surface environment of semiconductor nanoparticle plays a key role in dictating its properties [2, 3]. Thus, the unique properties of QDs originate mainly from two factors; large surface to volume ratio and the spatial confinement of charge carriers, called as quantum confinement effect or quantum size effect.

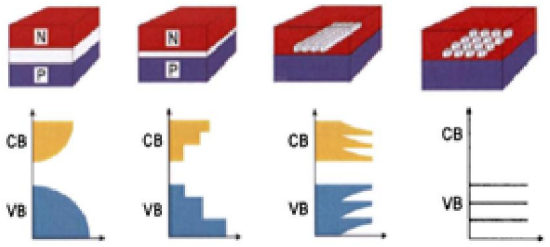

Fig 1. Schematic diagram of the density of states (DOS) in semiconductor structures; from left, bulk material, quantum well, quantum wire/rod, quantum dot array with quantum confinement in OD, 1D, 2D and 3D respectively.

1.1 Quantum Confinement Effect

The physical and chemical properties of a material are directly related to the type of the charge carrier motion as well as the space in which their motion is confined." For example, the energy levels of an electron are not quantized until it is bound to an atom, molecule or a material. Once bound, their motion becomes highly confined in a potential well and quantization sets in, resulting in quantized energy levels [4, 5]. The extent of confinement is directly related to the spatial freedom allowed for electron

movement; smaller the space in which the bound motion takes place, stronger the confinement and larger will be the energy separation between the allowed energies levels. The nuclear confinement is the strongest type of confinement as the motion of the nucleons is confined to a femtometer size scale. This is followed by electronic confinement in atoms. For example, in hydrogen atom the electron is confined to a length scale of ~50 pm. The spatial restriction in the motion of charge carriers in metals or semiconductors can be brought about by reducing the physical dimension of matter to nanometer size regime. In the case of semiconductors, a reduction in the size to nanometer length scale of ~10 nm results in the (i) splitting of energy levels of valance band and conduction band to discrete quantized atomic like energy levels and (ii) an increase in the band gap energy. This phenomenon is explained on the basis of quantum confinement effect." Both these effects are directly observable in the electronic absorption and emission spectra of direct band gap semiconductor nanoparticles.

Fig 2: Fluorescence in different-sized CdSe quantum-dots

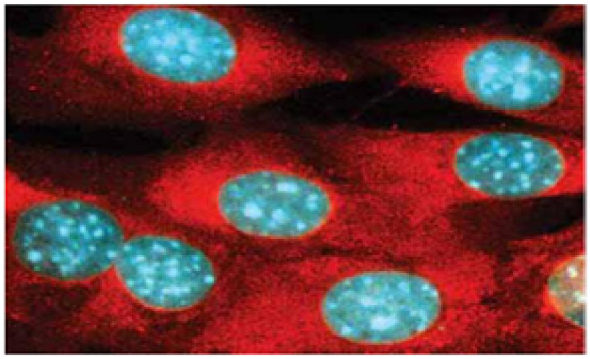

Fig 3: Quantum-dots in visualising biological Processes

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 colors. as shown in the Fig 2. This property can also be used for reporting about different functioning of the cell as shown in the Fig 3. But to do that they need to be made water soluble so that they can enter the cell as inert objects [6, 7]. 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 [8,9]. 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.

2. 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^{o}C and then stored at 4^{o}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°C to 300°C in the laboratory.

3. Result and Discussion

The absorption spectrum of synthesized quantum dots as shown in Fig 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.

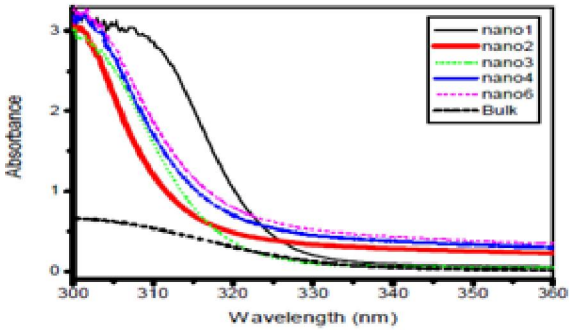

Fig 4: UV-Visible absorption spectrum of ZnS quantum dots

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. In the spectrum of ZnS quantum dots 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. The XRD patterns of prepared samples were taken by Seifert XRD (3003TT) operating at 40KV-30mA. Fig 5. shows the XRD patterns of ZnS thin films of various concentrations (1M, 0.75M). The three broad peaks observed in the diffractogram at around 28.58°, 48.29° and 56.17° for 1M and 28.61°, 47.96° and 56.31° for 0.75M reveals a cubic lattice structure of ZnS (Zincblende). These peaks could be easily assigned to the planes (111), (220) and (311) respectively of the cubic phase. The peak broadening in the XRD patterns clearly indicates the formation of ZnS nanocrystal of small size. The increase in diffraction angle is clearly a result of lattice contraction expected to occur because of higher surface to volume ratio. From X-ray diffraction study, average particle size has been calculated by using Debye Scherrer formula and the calculated size is found to be 4.05 nm for 0.75M and 3.80 nm for1M.

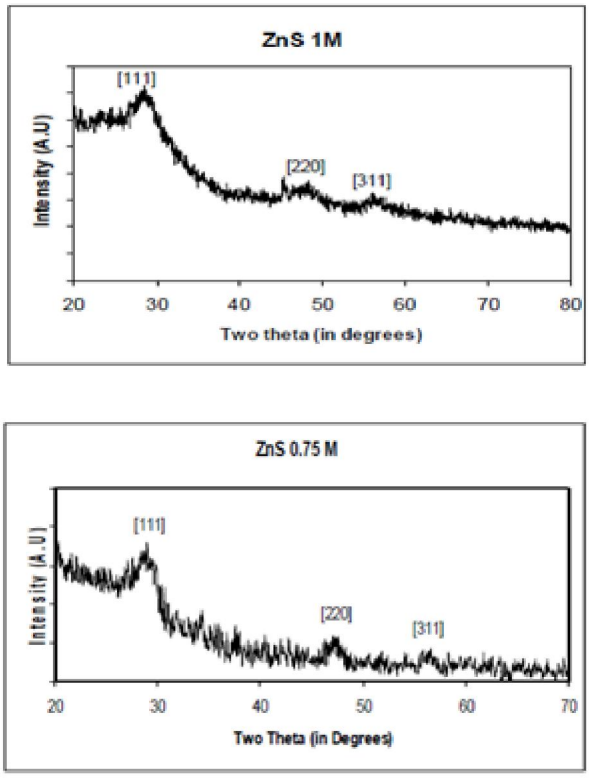

Fig 5. XRD patterns of ZnS Thin films

4. Conclusion

Thus we conclude that the absorption spectrum of Synthesized ZnS quantum dots shows a blue shift with decrease of quantum dot size. The peak broadening in the XRD patterns clearly indicates the formation of ZnS nanocrystal of small size. The increase in diffraction angle is clearly a result of lattice contraction expected to occur because of higher surface to volume ratio From X-ray diffraction study, average particle size has been calculated by using Debye Scherrer formula and the calculated size is found to be 4.05 nm for 0.75M and 3.80 nm for 1M.

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