Structural and Optical Properties of ZnS Quantum Dots synthesized by CBD method

Bhaskarjyoti Bodo[*], Ranjit Singha[**]

[*] Department of Physics, Diphu Govt College, Diphu-782462, India
[**] Department of Physics, Assam University, Duphu Campus, Diphu India

Abstract- ZnS quantum dots have been synthesized via chemical bath deposition (CBD) method. From the x-ray diffraction pattern we can observe the structure of ZnS QDs as the zinc-blende structure. TEM image shows the formation of spherical ZnS QDs. According to UV_visible spectra analyses, a large blue shift is observed which can be attributed to quantum confinement effect of the ZnS QDs. In its PL spectra measurement, the dominant emission band at peaks 438 and 521 nm are identified with optical transitions arising from vacancy and interstitial sites for both Zn and S atoms.

Index Terms- *Quantum Dots(QDs), SAED, HRTEM etc*

I. INTRODUCTION

Semiconductor QDs are very important nanomaterials with unique physical and chemical properties owing to the quantum confinement effect [1]. A variety of low dimensional nanostructures such as zero dimensional (0D) nanoparticles, one dimensional(1D) nanowire, nanotube and nanorods and two dimensional(2D) nanobelt and nanosheet are investigated extensively due to their novel and fascinating properties compared to their bulk counterparts[2-3].

Among the II-IV compound semiconductors ZnS is an important semiconductor material with direct band gap for the bulk cubic and hexagonal phase as 3.66eV and 3.8eV respectively [4]. One of the striking properties of the QDs is that tuanable optical properties can be achieved by modulating their size, their chemical composition and defects concentration etc [5]. It has been reported that quantum dots (QDs) contain only a few hundred atoms and emit only one wavelength of light when they are excited [1-6]. The color emitted is determined by the size of the quantum dots [6]. Therefore modeling of suitable material tailoring and synthesis technique is a significant part of research in this area.

The various methods of synthesis of ZnS QDs are reported [7]. Recently hydrothermal methods have been reported for the synthesis of QDs with small crystal size, narrow distribution, good crystallinity and high photoluminescence intensity [8]. More recently spherical ZnS based nanoparticles with diameter of 40nm have synthesized by using a thioglycolic and assisted hydrothermal method

In this work we report a simple CBD (Chemical Bath Deposition) method to synthesize the ZnS ODs. The morphology, structure and photoluminescence (PL) properties of the as-prepared samples are studied.

II. MATERIALS AND METHOD:

A. Synthesis

A simple chemical method was employed for the synthesis of ZnS QDs. The colloidal ZnS QDs nanoparticles were prepared by mixing equivolme and equimolar (0.5M) solution of zinc sulphate dehydrate and thiourea in the presence of ammonia at room temperature and 3% solution of poly-Vinyl Alcohol (PVA) was added to it as capping agent. The p^H vale of the reactant solution was kept at 9-11[9]. The prepared samples were kept overnight for stabilization and are then caste over glass substrate for characterization.

B. Characterization

The structural investigation of ZnS QDs was carried out using X-ray powder diffractometer (Model:Seiferi XRD 300 T/T) with CuK_α radiation (λ= 0.15406nm)scanning 2 θ in the range 20^0 -80^0 . The morphology of the nanoparticles were characterized by transmission electron microscope (TEM) [model: JEOL, jem 100CX-III] operated with an acceleration potential of 100kV. The UV-visible absorption of the samples were recorded using an automated spectrometer [Model: HITACI 113210] in the wavelength range 200nm-800nm). The room temperature PL spectra of the prepared sample were recorded by F-4500 FL spectrophotometer at excitation wavelengths of 325 nm [6].

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Structural studies

The XRD pattern of ZnS QDs is shown in the figure1. It can be identified as the cubic zinc blende structure with a comparison to the standard JCPDS file [11]. The three main peaks can be indexed with (200) (220) and (222) planes. The boarden peaks indicate

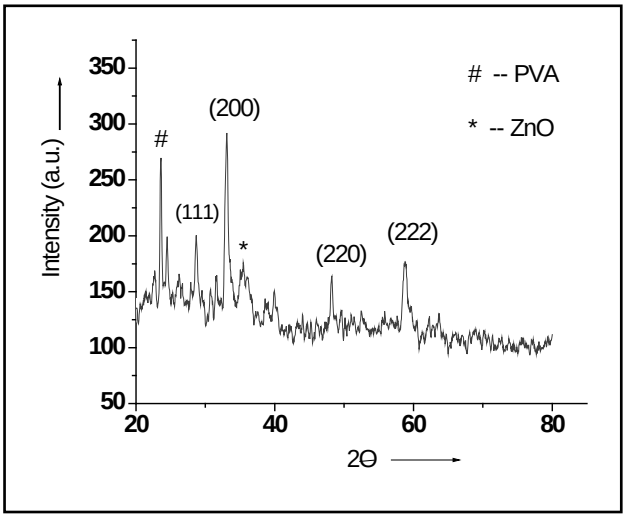


Figure 1(a) XRD Pattern of ZnS Qds

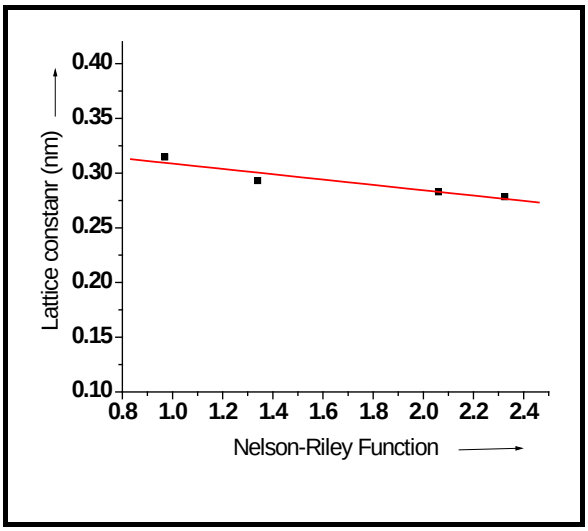


Figure 1 (b) Determination of the lattice constant by reduction Against the Nelson-Riley function

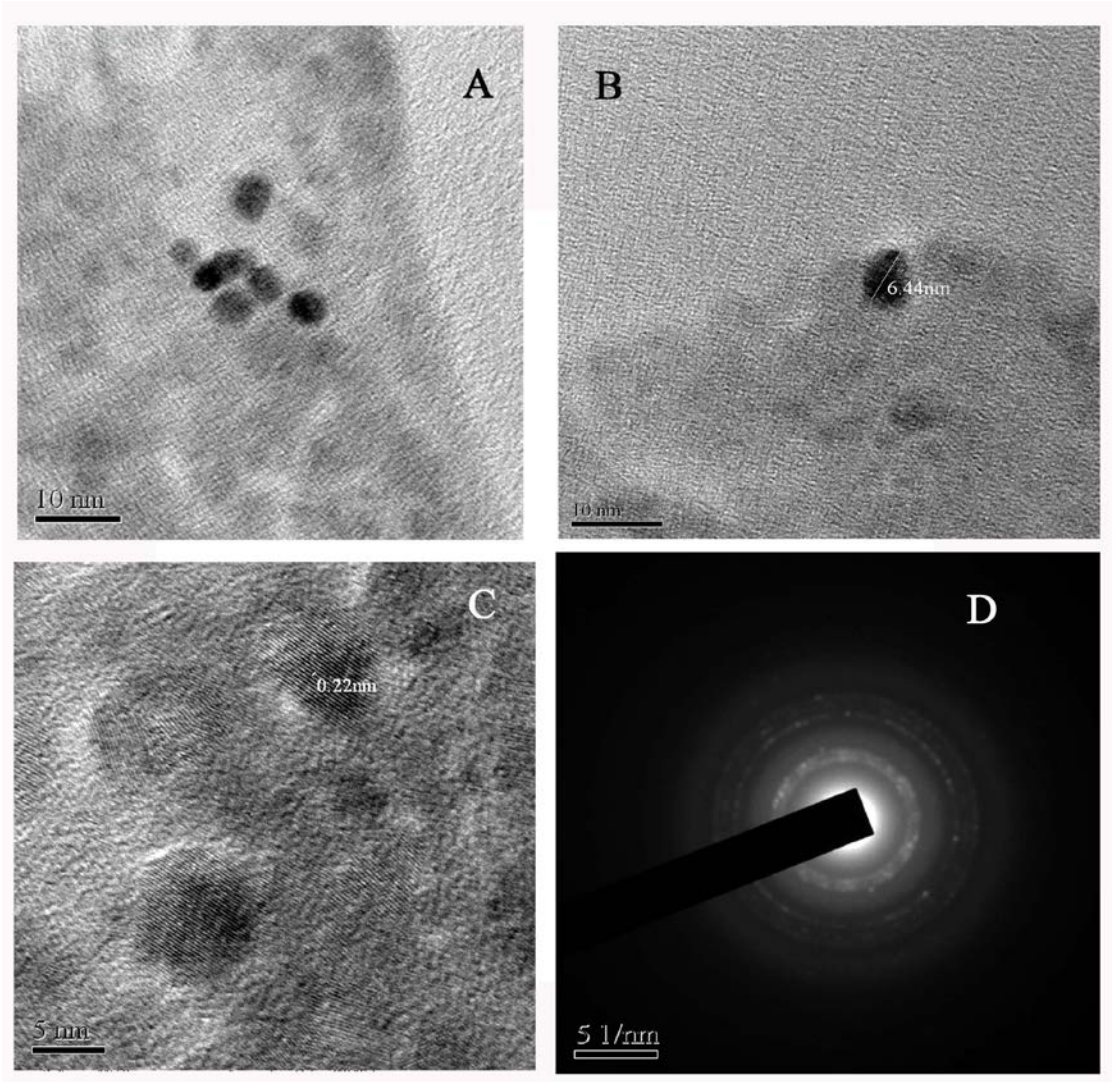


Figure 2 TEM image (A) and (B), HRTEM(C) and SEAD (D) of ZnS QDS(A),

the small particle size of the sample. The average crystalline size of the nanoparticles calculated by Debye scherrer's formula is found to be 8nm [10]. The indexed peaks were used to determine a trial lattice parameter for each peak. In through examination of error, Nelson and Riley determined that the relation

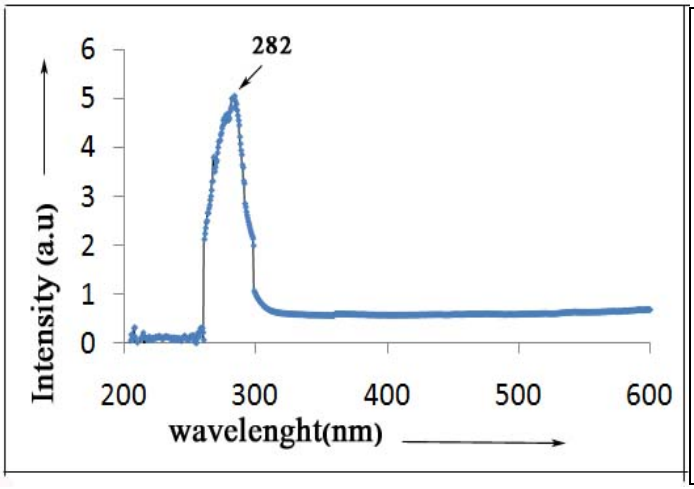
$$\Delta a/a = K(\cos^2\theta/\sin\theta + \cos^2\theta/\theta) \quad (1)$$

Accurately predicts the accuracy of a given measurement. The lattice constant is determined by plotting the calculated a values vs the Nelson-Riley function, constructing a linear regression and determining the y-intercept [11].Thus lattice constant is estimated from the intercept of the Nelson-Riley plot is 33.nm. The measured value from N-R plot is more or less free from systematic error.

The morphology and dimension of the as-prepared samples were investigated by TEM and HRTEM. Fig. 2(A) represents the TEM image of the samples and it shows the formation of cluster of ZnS nanoparticles of almost uniform size[3]. The spherical shape of nanoparticles is observed in the higher resolution of TEM in the fig. 2(b). The HR-TEM images of as prepared exhibit a fine structure with lattice spacing 0.22 nm [Fig.1(C)]. The Figure.2(d) shows SAED patterns of the ZnS nanoparticles clearly corresponding to a polycrystalline with some degree of disorder as evident by diffuse rings instead of spots[12]

B. Optical Properties:

The optical properties of ZnS QD were determined from absorption measurement in the range 200-800nm. The figure-3 represents the UV-Visible spectra of ZnS QDs. The absorption edge λ_0 of the ZnS QDs is observed at 305nm which is very much shorter than 345 nm of the bulk ZnS[13] indicating a clear blue shift . This blue shift of the absorption edge can be attributed to the quantum confinement effect of the ZnS QDs. The band gap energy of the ZnS Qds can be estimated by using Tauc equation



. Figure 3(a) UV-Visible spectra of ZnS QDs

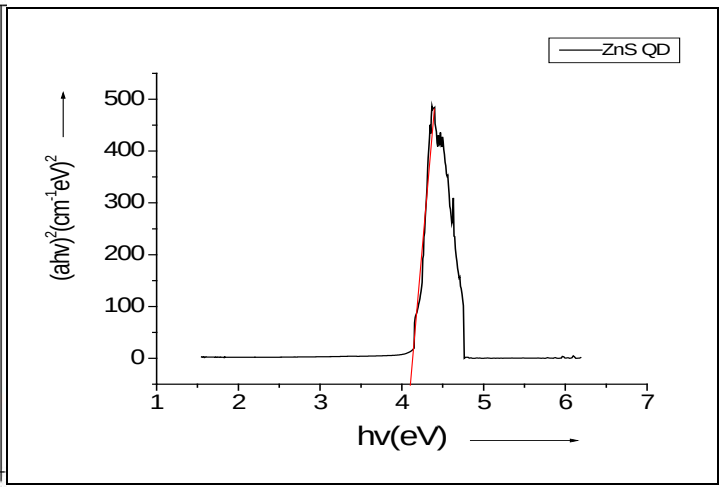


Figure 3(b) Tauc plot of as-prepared ZnS QDs

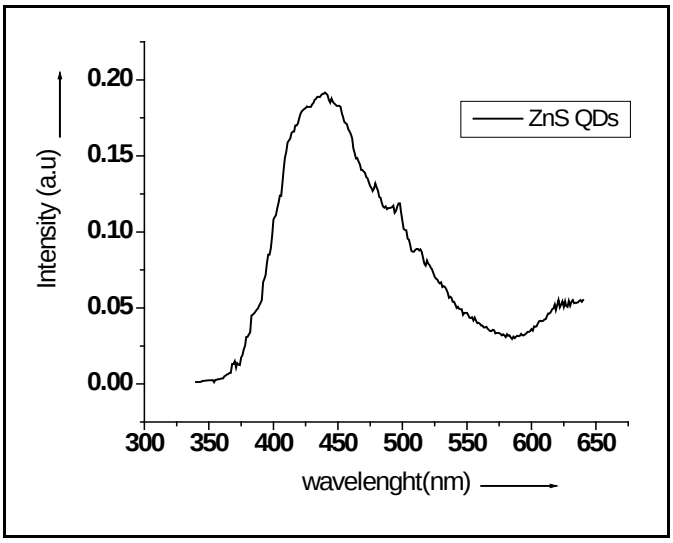


Figure 4(a) PL Spectra of ZnS Qds

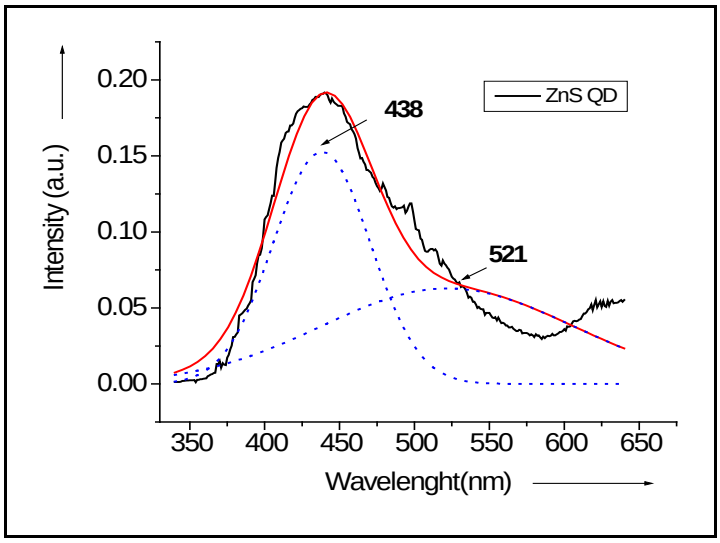


Figure 4(b) Deconvulated spectra of ZnS QDs

given in equation 2. Fig.4 (b) represents Tauc plots for estimation of band gap. Tauc formulated the following equation to determine band gap energy;

$$(\alpha h\nu)^n = B(h\nu - E_g) \quad (2)$$

Where, α is the absorption co-efficient, hν is the incident photon energy, B is a constant and E_g is the band gap energy of the material. The exponent depends on the type of the transition. Here, n=2 is taken because the transition is direct[14].

The band gap energy is calculated by extraploting the linear portions of $(\alpha h\nu)^2$ vs hν graph on the hν axis to α = 0 [15]. The estimated band gap energy is found to be 4.1 eV. From the band gap value of nanoparticle and bulk, the large blue shift of the as-prepared sample is calculated. Further from these calculated blue shift values theoretical size of the nanoparticles can be estimated by using Effective Mass Approximation (EMA) method [16]. The formula in EMA calculation as derived by I E Brus is given as

$$\Delta E_{gn} = \pi^2 h^2 / 2R^2 / (1/m_e + 1/m_h) - 1.8e^2/\varepsilon R \quad (3)$$

Where m_e = effective mass of the electron of the specimen, m_h = effective mass of hole of the specimen, h =6.58 x 10^{-16} eV and R = radius of the nanoparticle. The size of the particle (D) is given by D = 2R and the estimated sizes of ZnS nanoparticle is 12 nm which is almost agreement with TEM measurement.

Figure-4(a) shows the photoluminescence spectra of ZnS QDs in the region 350-650nm measured at room temperature.Figure-4(b) represents the deconvulated plot of ZnS QDs spectra and it shows that there are two distinct peaks situated in the blue region about 438 nm and the green region about 521 nm respectively. The 438nm blue emission is due to recombination between the conduction band and zinc vacancy related acceptor while the 521nm green peak is attributed to the recombination between the sulfer vacancy an cu related acceptor centre[17]. Since the sulfur ions are larger than the zinc ions, interstitial sulfur induces more strain to the lattice. Electron levels originating from this site will have smaller binding energies due to such strain [18] Therefore, interstitial sulfur states should be located closer to the valence band edge.

IV. CONCLUSION

We have successfully synthesized ZnS QDs using simple CVD method. This method for preparation of light emitting structure is very cheap and simple and can employed for a large scale. From the x-ray diffraction pattern we can observe the structure of ZnS QDs as the zinc-blende structure. The diameter of the QDS as measured by TEM analyses is 6.5nm. According to the UV-visible spectra; we also observed the blue shift in ZnS QDs attributing to the quantum confinement effect of the ZnS QDs. In the room temperature measurement of PL spectra , the dominant emission band at peaks 438 and 521 nm due to sulfur vacancy are observed.

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AUTHORS

First Author – Bhaskarjyoti Bodo. jyotibodo@yahoo.co.in, jyotibodo@gmail.com
Second Author –Ranjit Singha . ranjit_thingom@yahoo.com
Correspondence Author – Bhaskarjyoti Bodo, jyotibodo@yahoo.co.in, jyotibodo@gmail.com, +918471802482.