Structural and Optical Properties of CdS Quantum Dots with Narrow Size Distribution

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Abstract: In the present work we report the synthesis of CdS nanocrystals. The structural investigations were carried out by XRD and TEM analyses. Its optical properties were studied by UV-VIS measurement and PL analysis.. XRD shows that the as-prepared CdS are polycrystalline having the mixture of two phases namely cubic and hexagonal which is consistent with other workers. TEM image exhibit the formation of CdS QDs with narrow size distribution. PL measurement shows prominent emission peaks at 330 nm along with 430 nm corresponding to the surface defects

Index Terms **- CdS, Quantum dots (QDs), SAED, TEM.**

I. INTRODUCTION

Nanoscale semiconductor materials or QDs have drawn much interest due to their unique mechanical, optical and electronic properties [1-3]. In recent years, controlling the morphology, shape and size of the nanomaterials has become very vital issue in nanoscience research because of their fundamental shape and size dependent properties and significant applications [2-3]. It is well known that the quantum confinement effect modifies the electronic structure of nanocrystals when diameter is comparable to Bohr excitation radius[4]. Due to this size quantization effect arising from confinement of electron, holes and phonons, there is a drastic change in materials optical and conductive properties [5].

Among metal chalcogenide, CdS is of particular interest because of its direct band gap (2.5ev) which has shown great potential applications in bioimaging[1, 5], solar energy conversion and photcatalysis[2]. The CdS nanoparticles as isolated quantum dots are subject of considerable interest due to its size dependent electronic band gap energies. It is reported that the band gap energy of the QD will be blue shifted due to the size quantization effect [6].

In recent year there has been a rapid development of growth techniques for quantum dots with high crystalinity and narrow size distribution [7]. Various methods such as PVD(Physical Vapour Deposition), sol-gel method, Chemical Bath Deposition Methods (CBD) have been reported and extensively studied[5,7]. Despite of several available synthesis methods, the reproducible preparation of CdS QDs with enhanced mechanical and optical properties still remains a fascinating area of research [5]. One particular useful low cost technique to synthesis the CdS nanoparticles is the chemical co-precipitation method or chemical bath deposition method [8]. In the present works almost uniform size of CdS QD in the range of 6-9 nm have successfully synthesized using PVA(Poly-Vinyl Alcohol) as capping agent [8-10].

II. EXPERIMENTAL:

The synthesis of CdS nanoparticles was carried out by a chemical method at room temperature [8]. The principle is the precipitation reaction of metal ions and sulfer ions in solution. First, cadmium sulphate was dissolved in deionised water separately. The Poly-Vinyl Alcohol (PVA) was also added to the reaction medium as capping agent [8, 10]. Then equimolar and equivolume of the thiourea solution was slowly dropped into the above mixed solution, along with the continuous stirring in the ambient atmosphere [3]. The light yellow colloidal nanoparticles were precipitated in the solution.

This colloidal nanoparticles solution were filtered and the nanoparticles were repeatedly washed with deionised water and methanol and then dried in hot oven at temperature 60^0 -70^0 C till it became dry [8, 10].The dry powder were finely grinded using n mortar and pressure. These fine nanoparticles were used for XRD, TEM and other characterizations.

X-ray diffraction(XRD) patterns were recorded to characterize the phase and structure of the nanoparticles using X-ray powder difractometer (Model:Seifert XRD 3003T/T) with CuK_α radiation (λ=0.15406nm) scanning in the range 20^0-80^0 .The morphology and electronic diffraction (ED) patterns of the nanoparticles were characterized by transmission electron Microscope{JEOL 200K) operated at 200KV.The UV-visible absorption of the CdS QDs dispersed in deionised water were recorded using an automated spectrometer [Model: HITACI 113210]. The room temperature PL spectra of the as-prepared sample were recorded using spectrophotometer between 330nm and 750nm with excitation wavelength 300nm [8].

III. RESULTS AND DISCUSSION:

Structural Studies

The Figure 1 represents the X-ray diffraction pattern of the prepared sample. The formation of nanocrystallinity is confirmed by broadening of diffraction peak [11]. The XRD pattern shows the formation of mixed phases, i.e. cubic phase(Zinc blende) and hexagonal phase(wurtize-type).The peak at points 30.25^0, 43.7^0, 49.95^0 corresponds to the planes(200), (220) and (311) respectively[JCPDS card 10-454] establish the formation of cubic Zinc blende structure[12]. The peaks at 36.3^0, 52.15^0 and 58.12^0 corresponds to the plane (101) , (103) and (202) respectively in the XRD pattern shows the presence of hexagonal phases in the as-prepared nanoparticles [13]. The crystal size was determined from the XRD spectrum using Debye Scherrer formula

$$D=0.9\lambda/\beta\cos\theta \quad (1)$$

Where D is the crystal size, λ is the wave length of X-ray, β is the full width at half maximum (FWHM) and θ is Bragg's angle [13]. The average grain size of the prepared sample as calculated from the above formula is found to be nearly equal to 9.7nm

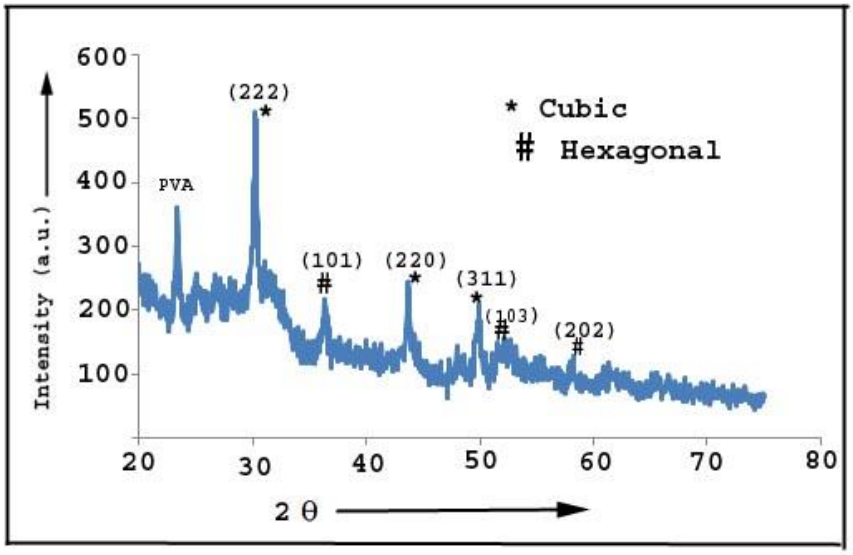

FIG.1 XRD PAETERN OF CdS QDs

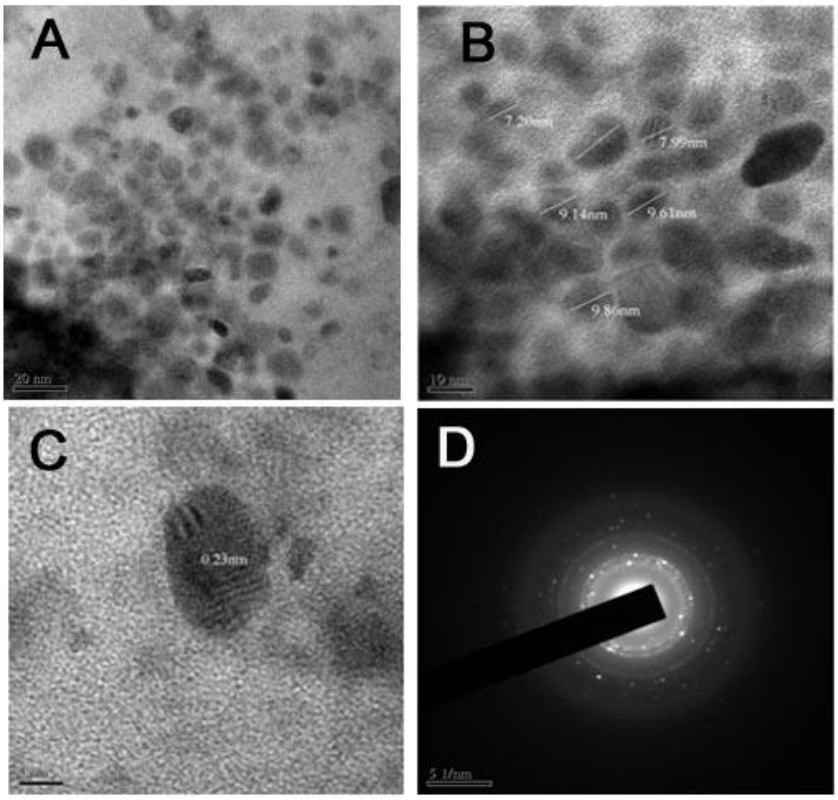

FIG. 2 (A) &(B) TEM IMAGE OF CdS , FIG. 2(C) HRTEM & 2 (D) SAED PATTERN OF CdS QDs

The Fig. 2(A) shows the low magnification TEM with the measurement of the size of the particles. It is observed that the particle size were not uniform but within the range of 5-10nm . Thus the size of the particles are in the quantum dot which exhibit particular characteristic of quantum confinement effect [6]. The low magnification TEM image Fig.1 (a) of CdS QD shows the formation of nanoparticles in spherical forms with slightly elongation along the c-axis of the hexagonal structure. It is in agreement with the XRD analyses showing the CdS QDs as the mixture of cubic Zn-blende and hexagonal structure consistent with the XRD measurement [1]. Fig 2(C) shows the HRTEM image with clear crystal lattice fringes attributing that the as-prepared specimen is well crystallized [1]. Fig. 2(D) represents SAED pattern of CdS QDs. In the figure, instead of spots diffuse rings with some degree of disorder are observed thereby attributing the specimen in the form of polycrystalline [6].

Optical Studies

The Figure 3 shows UV-visible spectra of the CdS nanoparticles .The absorption peak at 315nm in the curve of the spectra is attributed to the absorption peak of CdS nanoparticles [10]. The spectra show absorption edge of the nanoparticle at 315nm indicating these nanoparticles being blue shifted as compared to bulk CdS for which the peak is at 515nm[1-3]. This large blue shift in the absorption edge is attributed due to the quantum confinement of excitons present in the specimen resulting in a more discrete energy spectrum of the individual nanoparticles [9].

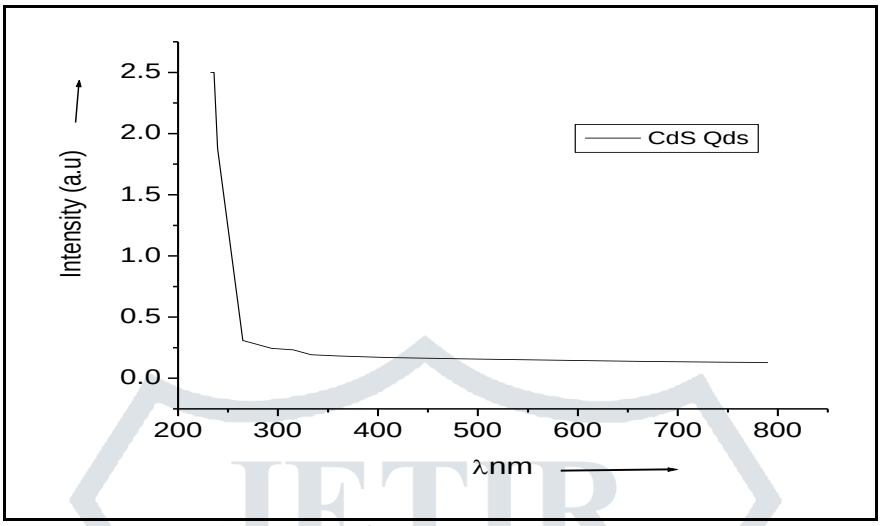

FIG.3 UV-VIS SPECTRA OF CdS QDs

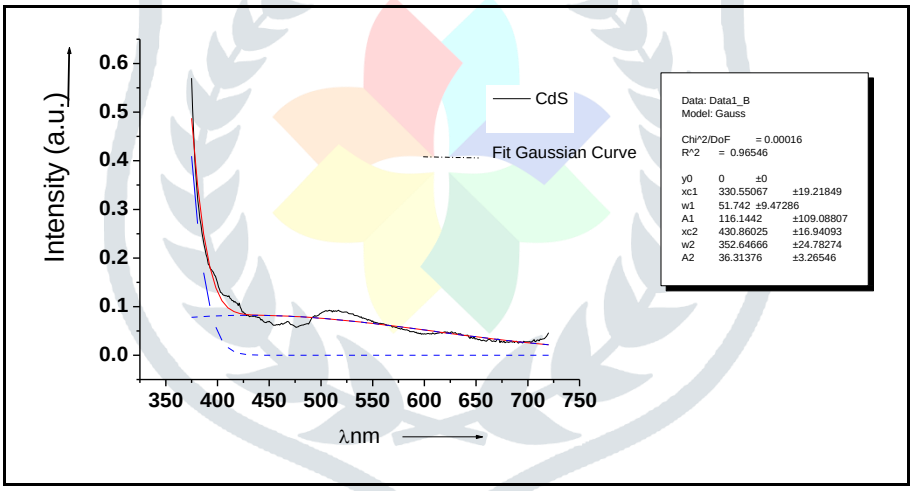

FIG.4.PL SPECTRA OF CdS QDs

From the absorption peak.the band gap energy is calculated by usng the formula

$$E_{gn}=h\,\nu_{gn}=hc/\lambda_{gn} \qquad (2)$$

Where h is Planck's constant and c is the velocity of light[8]. The estimated band gap energy of the as prepared CdS nanoparticle is found to be 3.94eV which is much more than that of the bulk CdS for which band gap is nearly equal to 2.5eV. Due to confinement of both electron and holes the lowest energy optical transition from the valence to conduction band will be increased effectively increasing in band gap[14]

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

$$Egn = \pi^2\, h^2 /2R^2/ (\,1/m_e +1/m_h) -1.8e^2/\varepsilon R \qquad (3)$$

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[12]. The size of the particle (D) is given by D=2R and the estimated sizes of CdS nanoparticle is 9.7 nm which is almost agreement with TEM measurement as shown in figure 1(A) and 1 (B)

Figure-4 represents the photoluminescence (PL) spectra of CdS nanoparticles measured at an excitation wavelength of 300nm at room temperature. The observed spectra are broad and asymmetric. So it should consist of more than one component.

The PL spectra of the specimen were subjected to the Gaussian fit which shows two peaks at 330 nm and 430nm. The difference between the PL peak and the UV-VIS absorption edge can be explained by shallow traps formed due to sulfer vacancy [10]. Further the additional peak of the PL spectra at 430nm may be attributed due to surface defects [15].

IV. Conclusion

CdS nanoparticles have been successfully synthesized by a simple aqueous chemical method using aqueous route resulting in average particle size about 5nm to 10nm.The particle sizes estimated from the Debye-Scherrer formula, TEM measurement and Effective Mass Approximation(EMA) are in quite agreement with each other. The observed PL spectra are broad and asymmetric showing two peaks at 330nm corresponding to band to band emission and at 430nm due to surface defect or interstitial sulfer vacancy. The UV_Vissible spectra showed that the absorption peak is blue shifted from the corresponding bulk counterpart. This large blue shift observed in CdS QDs could be exploited for the potential applications as smart materials in photonic nanodevice fabrications and various other applications can be explored.

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