

Synthesis and Characterization of PVA Capped CdS Nanoparticles

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Abstract-I In the present work CdS nanoparticles were prepared by chemical co-precipitation method at room temperature. The structural properties of CdS nanoparticles were determined by XRD, TEM and its optical properties by UV-Visible and PL spectra measurement. XRD analysis showed that the prepared samples were the mixture of both the cubic and hexagonal structure with particles' size in the ranges 30nm -50nm. The TEM analysis revealed the formation of CdS nanoparticles with almost uniform shape and size. UV-visible spectra revealed a blue-shift with green emission indicating the quantum confinement of the particles. In PL analysis, an enhanced PL emission was observed.

Keywords- CdS, TEM, SAED, PVA

I. INTRODUCTION

Size controlled synthesis of semiconductor nanoparticles has attracted significant interest in research because of their excellent luminescent properties, quantum size effects and other unique physical and chemical properties. [1] A major feature of semiconductor nanoparticle is the quantum confinement effect [2,3] Controlling the size, shape, composition and various parameters affecting the shape and size of the materials, the physical and chemical properties of the nanomaterials can be controlled. [4]

The synthesis of binary metal chalcogenides of group II-VI semiconductor in a nanostructure form has been a rapidly growing area of research due to their important non-linear optical properties, luminescent properties and quantum size effect [5]. CdS is one of the most important II-VI semiconductor compound having their unique photochemical and photophysical properties[6]. It is a direct band gap semiconductor of energy band gap of 2.42 eV at 300 K.[7-8]. In recent years significant research efforts have been devoted to the synthesis and investigation of size dependent optical properties of CdS semiconductor nonmaterial [5,9] Attempts were also made in the successful construction of some devices based on these materials [10-11]. In the present work an effort has been made to study the structural and optical properties of CdS nanoparticles prepared through a chemical co-precipitation method. This chemical method is a simple and

inexpensive technique to obtain homogeneous and stoichiometric CdS nanocrystals.

II. SYNTHESIS AND CHARACTERIZATION

A. Synthesis

An aqueous solution of 0.1 M of CdCl₂ has been prepared by dissolving 0.80528 gm of CdCl₂ in 40ml of distilled water aided by magnetic stirrer. Aqueous solution of 0.1 M of NaOH is obtained by dissolving 0.8 gm of NaOH on 200 ml distilled water. NaOH solution was slowly added to methanol and H₂S gas was liberated in the solution. The resultant solution was stirred for more than one hour before adding CdCl₂ solution in it. After three hours of constant stirring of these solution of NaOH and CdCl₂ along with PVA (Poly-Vinyl Alcohol) using as capping agent, a yellow solution was obtained. The precipitate was separated from the solution by filtration, washed several times with distilled water and dried at room temperature for several days to obtain yellow CdS nanoparticles [5].

B. Characterization

The structural investigation of as prepared CdS nanoparticles were carried out using X-ray powder diffractometer (Model: Bruker D8 Advance powder diffractometer) with CuK_α radiation ($\lambda=0.15406$ nm). The morphology of the particles were investigated by transmission electron microscope (TEM) [Model: JEOL JEM 100 CX-II] operated at accelerating potential 100 kV. The UV-Visible absorption spectrum of the sample was recorded using an automated spectrometer (Model: HITACHI 1113210). The room temperature PL spectra of the prepared sample were recorded by F-4500 FL spectrophotometer at excitation wavelengths of 325 nm .

III. RESULTS AND DISCUSSION

A. Structural Studies

The Figure1 depicts the X-ray diffraction pattern of the as-prepared CdS nanoparticles. The XRD patterns show a mixture

of cubic phase (zinc blende) and hexagonal phase (wurtzite-type) [3]. It has been reported that chemically synthesized CdS nanoparticles exhibit either hexagonal or cubic phase [3, 12]. The peaks at points 26.74, 30.23, 43.57 and 51.7 corresponding to the planes (111), (200), (220) and (311) respectively [JCPDS card 10-454] established the formation of Cubic zinc blende structure.[13]. Further, the peaks at points 28.30, 53.62 and 58.46 corresponding to plane (101), (103) and (202) respectively in the XRD patterns show the presence of hexagonal wurtzite phase in the prepared samples. [12-14]. The size of CdS nanoparticles can be estimated by using Debye-Scherrer formula: [12-13]

$$D = 0.93\lambda / \beta \cos\theta \quad (1)$$

Where D is the diameter of the particles, $\lambda = 1.518\text{\AA}$ (CuK α radiation wavelength), β = full width at half maxima, θ is the Bragg's angle. By substituting these values, the size of the nanoparticles were estimated to be about 45nm which is in very close agreement with HR TEM measurement.

The morphology and dimension of the as-prepared samples were investigated by TEM and HRTEM. Figure 2(A) represents the TEM image of the samples and it shows the formation of cluster of CdS nanoparticles of almost uniform size [3]. The spherical shape of nanoparticles capped with PVA is observed in the higher resolution of TEM in the figure 2(b). The HR-TEM images of as prepared exhibit a fine structure with lattice spacing 0.24-30nm [Figure 1(C)]. The Figure 2(d) shows SAED patterns of the CdS nanoparticles clearly corresponding to a polycrystalline with some degree of disorder as evident by diffuse rings instead of spots [15].

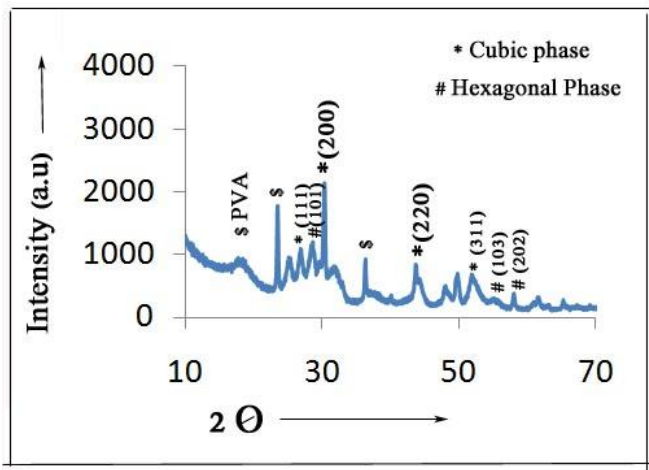
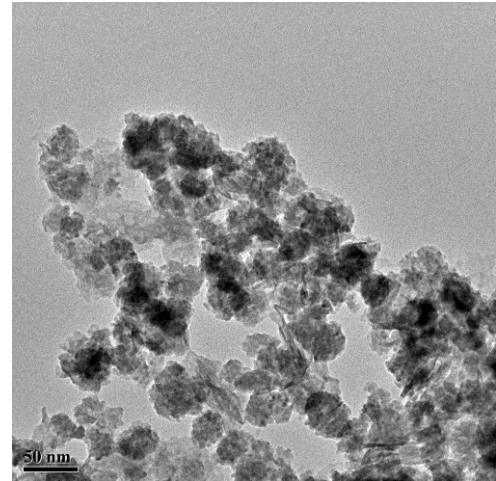
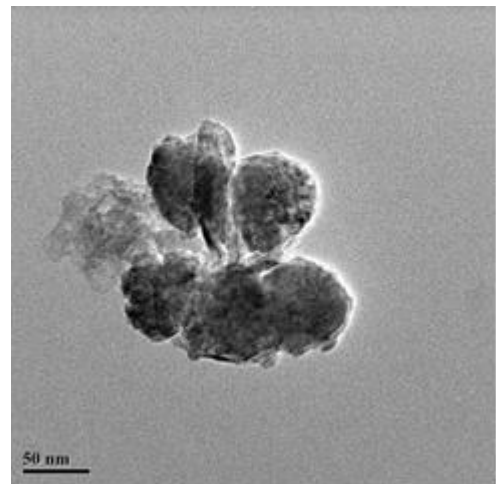


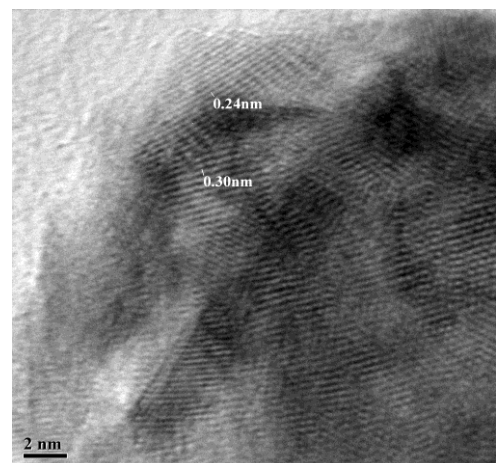
Figure 1. XRD pattern of CdS nanoparticles (in PVA matrix)



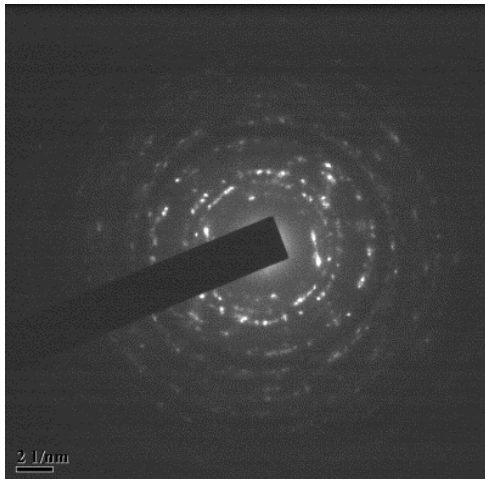
(a)



(b)



(c)



(d)

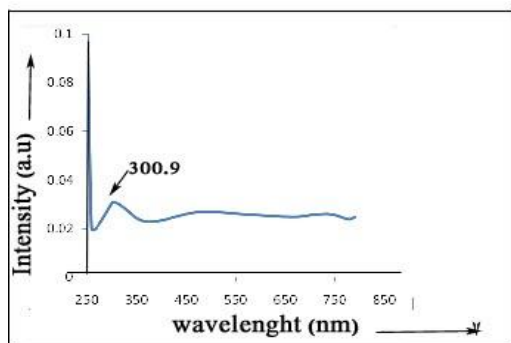
Figure 2. (a) TEM image of CdS Nanorod structure. (b) TEM image (higher resolution) of CdS Nanoparticles. (c) HRTEM image of CdS Nanoparticles. (d) SAED patterns of CdS nanoparticles

B. Optical Studies

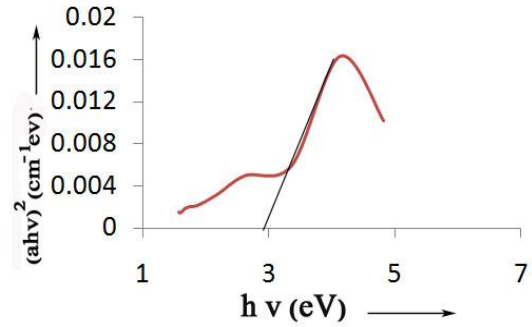
It has been reported that optical properties of semiconductor are structure sensitive and dependent on the nature and amount of impurities present in the structure [16]. The UV-visible spectra of the CdS nanoparticles are shown in the Figure 3(a). In the figure 3(a), CdS nanoparticles display the absorption edge in the range of 300.9 nm which is at shorter wavelength of band gap energy 2.42eV for bulk CdS [17]. The blue shifted absorption edge is due to the quantum confinement of the exciton present in the sample, resulting in more discrete spectrum of the individual nanoparticles [19]. 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, $h\nu$ 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.



(a)



(b)

Figure 3. (a) UV-Visible Spectra of CdS nanoparticles. (b) Tauc plot of as-prepared CdS nanoparticles

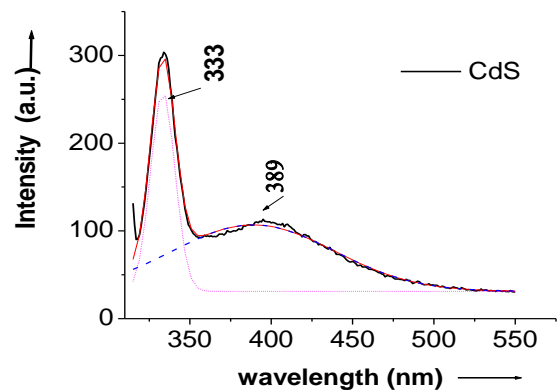


Figure 4. PL Spectra of CdS and deconvoluted spectra of CdS, red line shows the fitted curve.

The band gap energy is calculated by extrapolating the linear portions of $(\alpha h\nu)^2$ vs $h\nu$ graph on the $h\nu$ axis to $\alpha = 0$ [18]. The estimated band gap energy is found to be 2.92 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 [19]. The formula in EMA calculation as derived by I E Brus is given as

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

Where m_e = effective mass of the electron of the specimen, m_h = effective mass of hole of the specimen, $\hbar = 6.58 \times 10^{-16}$ 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 42 nm which is almost agreement with TEM measurement.

The room temperature PL spectra were measured with 325 excitation wavelength. Figure 4 shows the PL spectra of the CdS nanoparticles. The deconvoluted spectra of CdS show two peaks at 333nm and 389nm. It is well known that the luminescent peak centered at 333nm could be assigned to the UV-excitonic emission and other peaks attributing to the sulfur vacancy. 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 [15]. Therefore, interstitial sulfur states should be located closer to the valence band edge. Consequently the peak 389nm may be attributed to the interstitial sulfur.

IV. CONCLUSION

In summary nanoparticles of CdS are successfully synthesized through a chemical precipitation technique using PVA as capping agent. This technique is very simple and also can be adopted for a large scale preparation. The crystal structure and grain size of the particles were estimated by XRD and TEM measurement. UV-visible spectra revealed a blue-shift thereby indicating the quantum confinement of the particles. The PL spectra recorded at excitation wavelength of 325nm show a fine structure on the higher energy side of the spectrum which has been attributed as due to selectively excited photoluminescence. Thus the analyses of structural and optical properties of the sample reveal its immense potential applications in various opto-electronic and photo-luminescence nanodevices.

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