RESEARCH ARTICLE   OPEN ACCESS

Tuneable Optical Properties of CdS Nanopaticles through Different Mole Ratio by Simple Chemical Method

N. Om Muruga [1], A. Balamurugan [2]

1(Research & Development Centre, Department of Electronics, Bharathiar University, Coimbatore – 641 046, Tamilnadu, India.)

1(Department of Electronics, Government Arts College, Udhagamandalam – 643 002, Tamilnadu, India.)

2 (Department of Physics, Government Arts College, Udhagamandalam – 643 002, Tamilnadu, India.)

Abstract:

The cadmium sulphide (CdS) nanoparticles were prepared using simple chemical method under room temperature by changing the different mole ratio. The synthesised NPs structural, morphological, optical properties were characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet visible spectroscopy (UV) and photoluminescence spectroscopy (PL) techniques. A cubic crystal structure was observed from the XRD analysis and their calculated crystallite sizes were approximately ±15 nm. A blue-shifted optical absorption nature was observed from UV spectrum and their calculated bandgap energy value was approximately 3.8 eV.

Key Words: CdS Nanoparticles, Simple Chemical Method, Mole ratio change and Optical properties.

I.   INTRODUCTION

The semiconductor nanocrystals also known as quantum dots (QDs) has drawn enormous research attention in the past decade because of their great potential in electronics, photonics, opto-electronics and bio-applications [1-4]. The optical properties of QDs are strongly depending upon the quantum size effects [5]. Moreover, the size, shape and surface morphology plays pivotal roles in controlling the physical, chemical, optical, and electronic properties of these nanoscopic materials. The CdS is one of the well known wide band gap and light sensitive semiconducting material. The bandgap energy increases when the materials absorption takes a blue-shift and it is one of the interesting optical behaviours, occurred due to the quantum confinement effect [5-7]. Generally, the well known narrow bandgap semiconducting CdS nanoparticles has an excellent luminescence property. There are several reports on the preparation, characterization and application of CdS nanoparticles. Actually, CdS nanoparticles was showed photoluminescence from red to blue region which was due to deep level sulphur vacancy states resulted from the deviation in the stoichiometry [8-13]. In the present work, the CdS nanoparticles were prepared by changing the different mole ratio of 0.5 M, 1 M and 1.5 M.

Further their deviated emission behaviours were investigated.

II.   EXPERIMENTAL TECHNIQUES

A. Chemicals:

All chemicals used were standard analytical grade (AR) and not further treated. Cadmium acetate ($Cd(CH_3COO)_2$) and sodium sulphide (Na_2S) are the precursors with the solvent of double distilled water (DDW). The detailed samples preparation is described as follows.

B. Synthesis of Nanoparticles:

The freshly prepared 0.5 mole of $Cd(CH_3COO)_2$ solution was taken and stirred well using magnetic stirrer under room temperature. Then the freshly prepared 0.5 mole of Na_2S solution was slowly added dropwise into the $Cd(CH_3COO)_2$ solution. After the addition of Na_2S, the clear solution turns into white colour which indicates the formation of CdS. The mixture was stirred vigorously and further, the solution was stored without any disturbance until the particles sedimentation was obtained. The sedimentation was washed several times to remove unreacted compounds. After centrifuge, the particles are separated from the solution and then dried. Finally, a yellow color CdS powder was obtained. Hence, different mole ratio of CdS nanoparticles was
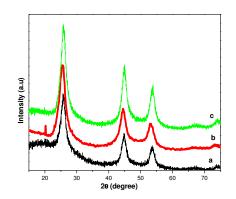
prepared using 1 and 1.5 mole. The obtained nanoparticles were characterised to know their structural, morphological and optical properties.

C. CHARACTERIZATION TECHNIQUES:

The crystalline nature of the synthesized nanoparticles was analysed by using X-ray diffractometer (XRD, Shimadzu-6000). The formation of nanoparticles size and surface morphology of the nanoparticles were studied by scanning electron microscope (SEM, JOEL JSM-6390). The functional group present in the CdS nanoparticles were recorded using FTIR spectrophotometer (FTIR, Brucker-Tensor 27). The absorption of the nanoparticles was measured using spectrophotometer (UV-VIS, Jasco V530). The emission spectra of the nanoparticles were measured using spectrofluorometer (Horiba Jobin, Flouromax-4).

IV. RESULTS AND DISCUSSION:
A. XRD-Structural analysis:

Figure 1 shows the XRD patterns of (a) 0.5 M, (b) 1 M and (c) 1.5 M of CdS nanoparticles. The obtained diffraction peaks are matched with the standard CdS cubic crystal structure (JCPDS card no.: 10-0454 and 41-1049, which was similar to the previous report [14]. The obtained (111) peak broadening indicates, the formation of particles are in nanometer scale range. The crystalline size or average particle sizes (D) were calculated using Debye-Scherer's formula [15] and their calculated sizes were approximately 14-16 nm. The lattice parameter values were calculated using Bragg's relation and their calculated sizes were approximately 0.33 nm.

Figure 1. XRD patterns of (a) 0.5 M, (b) 1 M and (c) 1.5 M of CdS nanoparticles.

Debye-Scherer's formula was used to calculate the crystalline size (D),

$$D = \frac{K\lambda}{\beta\cos\theta}$$

Bragg's relation was used to calculate the inter planar spacing (d),

$$d_{hkl} = \frac{n\lambda}{2\sin\theta}$$

The calculated crystalline sizes and their corresponding d-spacing values are given in **Table 1.**

Table 1. XRD parameters calculated at (1 1 1) plane of CdS nanoparticles

Mole ratios	2θ (degree)	Crystalline sizes (nm)	d spacing (Å)
0.5 M	26.44	14.86	3.380
1 M	26.34	15.23	3.368
1.5 M	26.63	16.14	3.344

B. SEM-Surface Morphology analysis:

Figure 2 shows the SEM images of (a) 0.5 M, (b) 1 M and (c) 1.5 M of CdS nanoparticles. A clear surface morphology was not observed, due to the formation of very small sized particles. However, the appearances looks like the growing stage of spherical structure. Therefore, to know the clear observation of surface morphology TEM measurement is required.
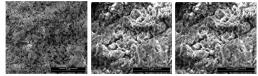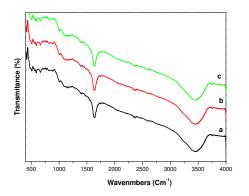
Figure 2. SEM images of (a) 0.5 M, (b) 1 M and (c) 1.5 M of CdS nanoparticles.

C. FTIR-Chemical bonding analysis:

Figure 3 shows the FTIR spectrum of (a) 0.5 M, (b) 1 M and (c) 1.5 M of CdS nanoparticles. The as prepared CdS nanoparticle FT-IR spectrum shows the Cd-S vibration of bands around 620 Cm^{-1} and 1120 Cm^{-1}. Therefore, the vibration of bands confirmed from the Cd-S stretching and they are well matched with previous report [16].
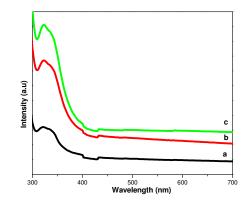

Figure 3. FTIR spectrum of (a) 0.5 M, (b) 1 M and (c) 1.5 M of CdS nanoparticles.

D. UV-Optical analysis:

Figure 4 shows the UV absorption spectrum of (a) 0.5 M, (b) 1 M and (c) 1.5 M of CdS nanoparticles. The absorption band was obtained at approximately 323 nm which was blue-shifted absorption behaviours when compared with the bulk CdS spectrum, because of quantum confinement effect were occurred. Moreover when increasing the mole ratio from 0.5 M to 1 M and 1.5 M, an absorption quenching effect were observed and it may be to the transition nature occurs between valence band and conduction band.

Figure 4. UV absorption spectrum of (a) 0.5 M, (b) 1 M and (c) 1.5 M of CdS nanoparticles.

The bandgap energy value was calculated using the relation of
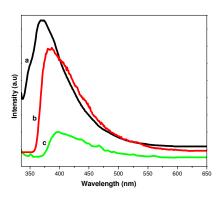
$$E_{bg} = hc/\lambda$$

The calculated bandgap energy values were increases because of decreased particle size when compared with bulk CdS (E_g=2.42 eV). The calculated bnadgap energy values and their corresponding absorption values are given in **Table 2.**

Table 2. UV bandgap energy values of CdS nanoparticles

Mole ratios	Absorption wavelength (nm)	Bandgap energy (eV)
0.5 M	319	3.88
1 M	321	3.86
1.5 M	322	3.85

E. PL-Emission analysis:

Figure 5 shows the PL emission spectrum of (a) 0.5 M, (b) 1 M and (c) 1.5 M of CdS nanoparticles. From the emission spectrum, a strong violet emission bands were observed which is due to the absence of sulphur vacancy states [17]. These emission behaviours indicate defect reduced levels obtained in the prepared CdS nanoparticle samples. It may be the chance of stoichiometric nature of CdS through Cd and S chemical composition and therefore the excitonic transition or band to band transition were possible due to the formation of nano-sized particles [18].

Figure 5. PL emission spectrum of (a) 0.5 M, (b) 1 M and (c) 1.5 M of CdS nanoparticles.

Moreover when increasing the mole ratio from 0.5 M to 1 M, the emission band takes quenching effect and slightly moves towards violet to blue region (that is, red-shift). When increasing the mole ratio from 1 M to 1.5 M, the violet emission band getting more suppressed and enhancing the blue emission which may be the slight formation of sulphur vacancy states **[19]**.

V. CONCLUSION:

The cadmium sulphide (CdS) nanoparticles were successfully prepared using simple chemical method by changing different mole ratio of 0.5 M, 1 M and 1.5 M. Then their structural, morphological, optical properties were investigated. From the XRD analysis, a cubic crystal structure was observed and their calculated crystallite sizes were approximately ±15 nm. From the SEM analysis, a spherical shaped surface morphology nature was observed. From UV spectrum analysis, a blue-shifted optical absorption nature was observed and the bandgap energy value was approximately 3.8 eV. From the PL emission spectrum, an enhanced emission nature was observed.

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