Chalcogenide Letters Vol. 9, No. 6, June 2012, p. 243 - 248

CATIONIC MICELLES CAPPED NANOSIZED CdS SYNTHESIS AND CHARACTERIZATION

K. DHANABALAN*, S.MUTHUKKUMARASAMY AND K.GURUNATHAN
Department of Nanoscience and Technology, Alagappa University, Karaikudi-630003, Tamil Nadu, INDIA-630003

The present study describes about synthesis and characterization of Cadmium Sulphide nanoparticles. CdS nanostructured materials were synthesised by aqueous method and physically characterized by spectroscopic and microscopic studies. The results reveal that absorption band edge at 475 nm is due to position dependent quantum confinement and it was observed that both cubic and hexagonal crystallographic studies were found to be present at ambient temperature. The optical properties and effect of cationic micelles in this synthesis is described in this article.

(Received April 18, 2012; Accepted June 5, 2012)

Keywords: Nanostructure, Quantum confinement, Cationic Micelle, Nano-sized CdS

1. Introduction

Semiconductor nanoparticles have attracted much interest during the past decade due to their unique size dependent chemical and physical properties [1-5]. Size, morphology and dimensionality could strongly affect the properties of nano-structured materials [4]. Recently, nanostructures of metallic and semiconducting materials with various structures and morphologies have received much attention for its novel applications due to the quantum size effects. Cadmium sulphide is an important semiconductor with a direct band gap of 2.4 eV at room temperature and has attracted considerable interest in photocatalysis [6], light emitting diode [7] and solar cells [8] due to their nonlinear properties. Unfortunately, organic phase synthetic routes are not eco-friendly. Alternatively, nanoparticles can be synthesised in aqueous phases because they are very simple, reproducible, economic and eco-friendly. CdS nanostructures such as nanoparticles, nanowires, nanorods and nano hollow sphere [9] has been intensively studied by using a wide range of synthetic methods using surfactant and variation of concentration of surfactant also affects the results. CdS nanostructures have been prepared in the aqueous phase by a number of researchers[10]. The fundamental behaviour of nanoparticles in water-surfactant system have been performed in the recent years. The interesting aspect which should be studied is micellar medium controls particle size by adsorption of surfactant onto the particle surface. The self aggregation of nanoparticles is prevented by the surfactant coating on the nanoparticle surface due to changed inter-particle potential [11]. In literature, a quite number of methods have been studied in CdS nanoparticles synthesis in the aqueous phase in the presence of surfactant (cationic and anionic). When surfactant are dissolved in water, at concentration lower than critical micelles concentration (cmc), the surfactant behaves as a strong electrolyte, whereas above the cmc the monomer forms the aggregates called micelles and the process is affected by temperature, solvent and other entities. It has been further reported that the surfactants (cationic as well as anionic) adsorbed on the surface of particles as micelle-like aggregates, and these aggregates can form even at the concentration lower than cmc due to the interaction between the polar group and nanoparticles [12]. The nature of the interaction depends specifically on the polar head-group [13]. It is virtually unknown to observe behaviour of nanoparticle–surfactant at mild temperature**.** In this paper, we

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*Corresponding author: dhanabalan_nano@yahoo.co.in present effect of the cationic micelles viz., cetyltrimethyl ammonium bromide (CTAB) mediated synthesis and optical properties of CdS nanoparticles.

2. Experimental

2.1 Materials

All chemicals (research grade) were purchased from Merck, India and used as-received without further purifications.

2.2 Methods

In this typical synthesis, 1% of 1 ml of CTAB dissolved in 100 ml of doubled distilled water and the solution was divided into two parts (A and B). 0.1 M of cadmium acetate used as a cadmium precursors and dissolved in Part A. In other hand, 0.1 M of thiourea used as sulphur precursors which was dissolved in part B solution. The Part B was added drop by drop into part A under vigorous stirring at room temperature. Finally, 25% of ammonia solution was added drop-wise into the mixture of solution till pH reaches 9.5. The solution was slowly turned to greenish yellow colour. After the completion of reaction, the solution was centrifuged using water and finally with ethanol and the sample was dried at 70°C for 2 hrs in air-oven.

2.3. Characterization

The nano CdS sample was characterized by UV-Visible-absorption spectroscopy using Lambda 35. X-ray diffraction (XRD) measurements were made with a computer controlled unit Model X'Pert, PRO, PW3050/60 using CuKα radiation (λ=1.5406 Å). FTIR measurement were made by Thermo Nicolet 380 by making pellet of sample with KBr. In order to examine the surface morphology of Nano CdS powder, scanning electron micrograph (SEM) JEOL JSM 6390 LV was employed and for the particle size determination was done by Transmission electron microscopy (TEM), Model Philips CM12.

3. Results and discussion

During the course of reaction, the color variation at the different time interval has primarily been identified by visual inspection. Quantum confinement can be possible near tip edge of the nanostructures which are smaller than or comparable to Bohr's radius of CdS (2.4 nm) because the optical properties depends lowest possible dimensions of nanocrystals [14]. As prepared nanoparticles having quantum confinement, it can be separated by band gap energy will be increased from inner wider portion to outer sharp edge of nanocrystals due to position dependent quantum size effect [15]. The absorption of CdS nanoparticles observed in the presence of CTAB at room temperature in the range of 475 nm due to excitonic transition (figure1). It is evident by the relative blue shift from the bulk that position dependent quantum size effect has actually found in our synthesised CdS nanocrystals. The band gap of nanoparticle was calculated using the Tauc relation [16]. Where ε , h, ν, P and E_g are molar extinction co-efficient, Planck constant, frequency of light, constant and band gap value of the bulk materials respectively.

$$(\varepsilon h\nu)^2 = P\,(E_g - h\nu) \quad (1)$$

By using this above formula band gap value calculated as 2.62 eV through plotting $(\varepsilon h\nu)^2$ Vs $h\nu$.

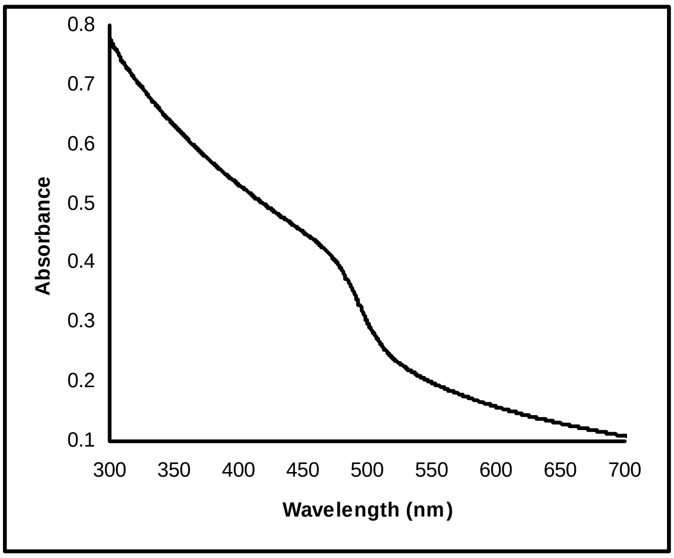

Fig.1. Optical spectrum of the CdS nanoparticles.

Cd (II) ions react with S^{2-}, forming CdS molecules which are associated with nucleation and growth of CdS nanoparticles. While this stage reached, the surfactant molecules are adsorbed on the surface of nanoparticles. Now, this can be explained by Fourier transform infrared (FTIR) spectroscopy in figure (2), the peak range of 3383 cm^{-1} shows that some adsorbed moisture in the sample. The peak at 1484 cm^{-1} and 1462 cm^{-1} are corresponding to asymmetric and symmetric C-H scissoring vibrations of the –N-CH_3 moiety of free CTAB have been shifted at 1411 cm^{-1}, 1558 cm^{-1} and 1652 cm^{-1} and suppressed in the presence of CdS nanoparticles indicating the interaction of surfactant through the head group [17]. From FTIR results, it is clear that peaks due to surfactant head group regions are shifted significantly without any significant shift in hydrocarbon tail region. The adsorption of surfactant via ion pairing passivates the surface of nanoparticles once formed, since the pH of resulting solution is 9.5, it is expected that the synthesized nanoparticles are negatively charged due to an excess of S^{2-} ions on the particle surface and therefore draw the cationic surfactant (CTAB) by long-range electrostatic attraction, inducing the CTAB adsorption through the headgroup.

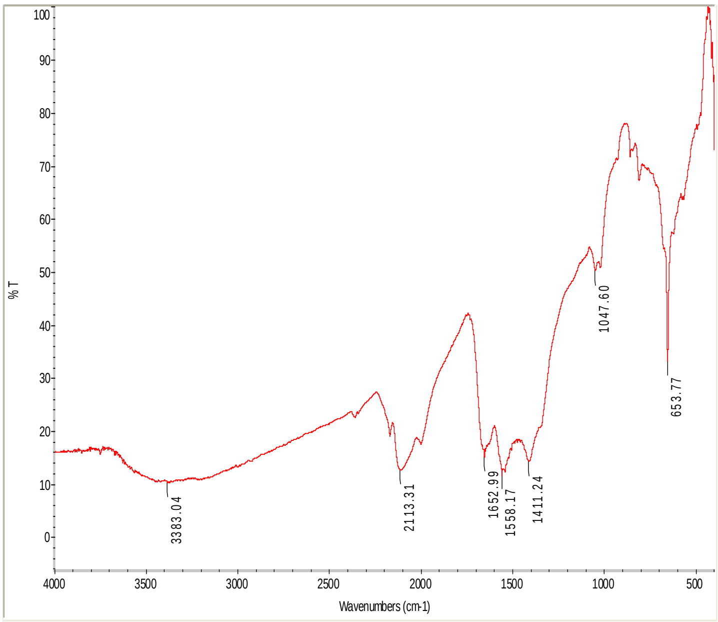

Fig.2. FTIR studies of CdS nanoparticles.

Fig. 3 shows that X-ray diffraction (XRD) of CdS. The broadness of XRD lines indicated reduced particle size as well as some inhomogeneous particle distribution. The obtained diffraction patterns show predominant peak $2\theta = 26.82°$ which can be assigned to the (111) plane of CdS. we observed three diffraction peaks at 26.82°, 44.31°, 52.50° and are assigned to be the(111), (220), (331) reflections planes respectively in the CdS cubic structure. A comparison of Inter-planar spacing (d_{hkl}) calculated from X ray diffraction patterns with the standard JCPDS card No 10-0454 and 41-1049 shows close agreement with the reported result in the literature [18]. From the XRD pattern, the average grain size is estimated by using the Scherer formula is around 10 nm. All diffraction peaks from sample can be readily indexed to wurtzite structure of nano CdS. Anisotropic nature of CdS nanoparticle causes a sharp peak (002) with high intensity then all other peaks in the peaks with strong preferential orientation along (001) direction The XRD pattern of the sample reveals the presence of the zinc blende crystal structure as well as the wurtzite crystal structure. This can be inferred from the intensity of the peaks corresponding to the (220) and (331) planes of the zinc blende structure, which also correspond to the (110) and (112) planes of the wurtzite structure. These are much more prominent than the wurtzite (103) peak that occurs between them[19&20]. The thermodynamic growth regime is driven by high energy (temperature), yielding isotropic nanocrystals, whereas in the kinetic condition, low temperature and high monomer concentration are the governing factors yielding anisotropic structures such as cubic phase (zinc blende) or hexagonal (wurtzite).

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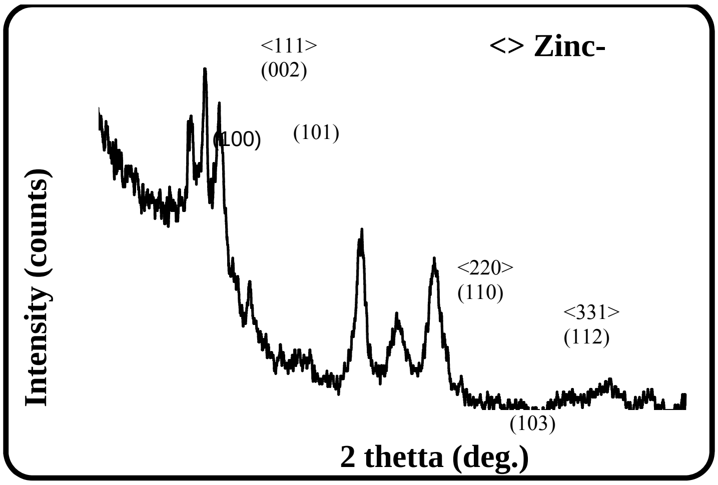

Fig.3 XRD pattern of CdS nanoparticles.

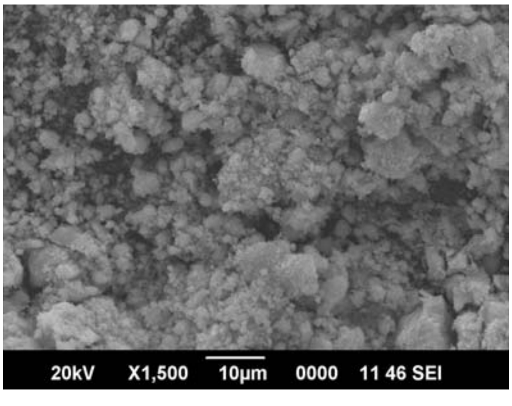

Fig.4 SEM image of CdS nanoparticles

In order to examine the microstructures and nanoparticles distribution within the nanoparticles SEM and TEM analysis were conducted. Figure 4 SEM micrographs of the CdS nanoparticles presented a homogenous microstructure, however it should be noted that some irregularities in size and shape because the growth of particles had some difference. The particle size and distribution from TEM image, most of the CdS nanoparticles were aggregated to a larger structure of average diameter 150 nm (Figure 5a). The TEM image (Figure 5 b) confirms the average particle diameter of the CdS to be 5 nm.

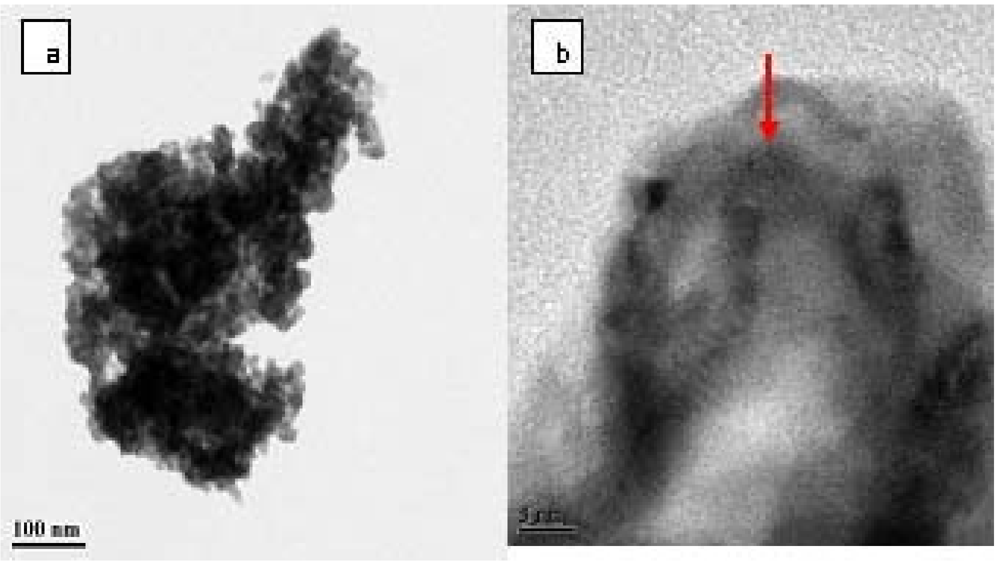

Fig 5 TEM (a and b) images of CdS nanoparticles.

4. Conclusion

In summary, this paper enumerated the cationic micelle, CTAB capped synthesis of CdS nanoparticles, the CTAB played significant role in capping CdS nanoparticle for its ensuring its stability and it exerted good blue shift value. XRD Result proved that as-prepared CdS nanoparticles were having both cubic and hexagonal structures at ambient temperature.

Acknowledgement

Authors thankfully acknowledge UGC, New Delhi Govt of India for financial support and department Physics Alagappa University, Karaikudi, India for XRD characterization

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