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Structural and optical characterization of CdS nanoparticles synthesized using a simple chemical reaction route

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Cadmium sulphide (CdS) nanoparticles have been successfully synthesized by a simple chemical reaction route using ammonium hydroxide as a complexing agent. X-ray powder diffraction, Scanning electron microscopy, Energy dispersive analysis using x-rays and UV–Visible spectroscopy. X-ray diffraction analysis confirms the formation of hexagonal wurtzite structure of CdS with average grain size of 10 nm. SEM images depict the presence of spherical nanoparticles and pores in the sample. From the optical absorption measurement, it is supposed that the blue shift in the absorption peak of 480 nm from that of bulk is at 512 nm may be due to the quantum confinement effect.

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1. Introduction

In the recent years, II-VI nanocrystalline semiconductor materials have been under intense research due to their exciting unique properties, which are absent in bulk materials since nanoparticles have a wide number of surface atoms than that of bulk [1-4]. In such nano-regime, nanoclusters with imperfect surfaces have interesting effects is a major challenge among the researchers. It is feasible to design materials of required optical, chemical and magnetic properties by controlling the surface and size effect, such as enhancement of photo catalytic properties and quantum size effects of the nanoparticles with decreasing crystallite size [5]. A semiconductor crystallite with exciton Bohr diameter exhibits a blue shift in the exciton energy, which is the so-called quantum size effect [6]. It is explained that the continuous energy band of the bulk crystal transforms into a series of discrete energy states resulting in the broadening of the band gap due to the finite size of the nanocrystals. Among II-VI compounds, CdS with a direct band gap, Eg=2.40 eV, is an important semiconductor with non-linear optical properties have been extensively studied and has potential applications such as solar battery, photoelectrocatalysis, Biological sensors and photodiodes [7-11]. Cadmium chalcogenides have been under intense investigation for their size dependent optical absorption properties and core/shell nanoparticles of CdS showed excellent emisssion properties makes them as an outstanding material for their practical applications in optoelectronics and photonics [12-14]. Many synthetic methods have been employed to prepare CdS nanoparticles including solid-state reaction, sol-gel process and microwave heating [15-17]. Moreover, preparation of CdS nanoparticles using solution growth techniques at low temperature possessing hexagonal wurtzite structure is still a great challenge among the researchers.

In this investigation, we have synthesized CdS nanoparticles using a simple chemical reaction method using Cadmium acetate dihydrate ($C_4H_6O_4Cd{\cdot}2H_2O$), Thiourea [$(NH_2)_2CS$] and ammonium hydroxide (complexing agent). CdS nanoparticles were analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM), Energy dispersive analysis using X-rays (EDAX) and UV–VIS absorption spectroscopy in order to study the structural and optical properties of the CdS nanopowders.

2. Experimental

In the present work, cadmium sulfide nanoparticles synthesized using a simple chemical reaction method involves a reaction between metastable precursors. All the chemicals used were of analytical grade. The precursor solution was prepared by dissolving 0.025M cadmium acetate ($Cd(CH_3COOH)_2$) and 0.05 M of thiourea ($(NH_2)_2$ CS) into 25 ml of sodium hydroxide. Thiourea acts as source of S and cadmium acetate acts as source of Cadmium Sodium hydroxide (NaOH) acts as the alkaline medium in order to yield cadmium and suphur ions in the solution. Mixed solution was then kept under constant magnetic stirring and 0.1M ammonium hydroxide was added to the stirring solution. Since the solubility product of CdS is low, ammonium hydroxide is used as a complexing agent in the reaction [18] which acts as a buffer, keeping the pH value of the solution at a desired level. In the beginning a white solution was obtained, which gradually become transparent and the colour changed from white to orange yellow. The precipitate was then filtered and washed with ethanol. The obtained

precipitate was dried at 80°C for 30 minutes in air. Free standing powder obtained as final product was used for further characterizations.

The crystallinity and the phase purity of the CdS nanoparticles were examined by X-Ray powder diffraction analysis (XRD) with (PAnalytical Model: X'Pert PRO). Scanning electron Microscope (SEM) (HITACHI Model: S-3400N) was used to observe the microstructure of the CdS nanoparticles. The purity and the composition of the sample was analysed using Energy Dispersive analysis using X-rays (EDAX). The optical property of the sample was studied using UV-Visible absorption spectroscopy.

3. Results and discussion

Structural analysis of synthesized CdS nanoparticles was studied using X-ray diffractometer. XRD pattern of the CdS nanoparticles illustrated in Fig. 1. can be indexed as hexagonal wurtzite structure of CdS (JCPDS – file No. 10-0454) with prominent peaks corresponding to the reflections at (100), (002), (101), (220) (103) and (112) planes. The broadened peaks are indicating that the sizes of the particles are in nanorange. The average paticle size of the CdS nanoparticles calculated using Scherer formula is 10nm.

$$t=0.9\lambda / B\cos\theta \qquad (1)$$

Here, t is the average particle size, λ is the wavelength of X-ray radiation, *B* is the full-width at half-maximum (FMWH) of the peak, and θ is the angle of diffraction. The lattice constant of prepared CdS nanoparticles are found to be equal to a=4.0726 A° and c=6.6895A° which is close to that of reported values of hexagonal CdS [19].

The morphology of the CdS nanoparticles has been investigated using Scanning Electron Miocroscopy (SEM) with different magnification as shown in Fig.2. It can be seen from SEM micrograph in Fig.2.(a) spherical CdS nanoparticles in the form of nanoclusters. In Fig.2.b the presence of pores in the form of black holes may be developed due to release of gases during the preparation process.

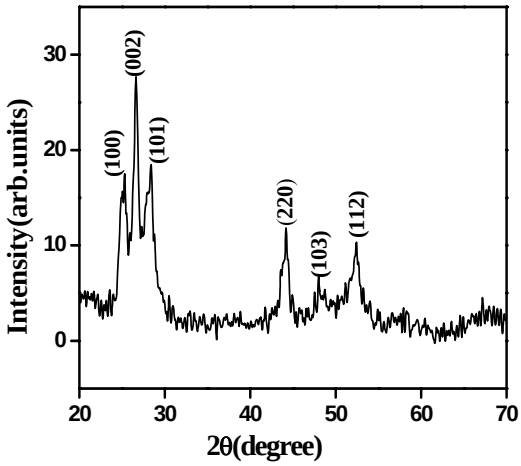

Fig.1. X-ray diffraction pattern of CdS nanoparticles.

Elemental composition of the sample and its purity has been verified using EDAX shown in Fig.3. The formation of atoms of Cd and S are 46.06 and 53.94 respectively. From the EDAX analysis of CdS nanoparticles prepared using the present technique are free from impurities is well understood.

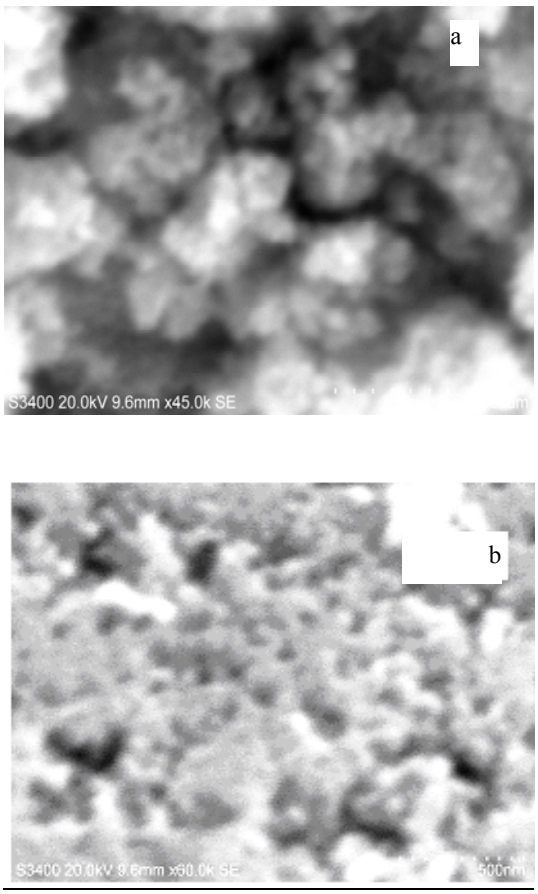

Fig.2. SEM micrographs of nanoparticles of CdS

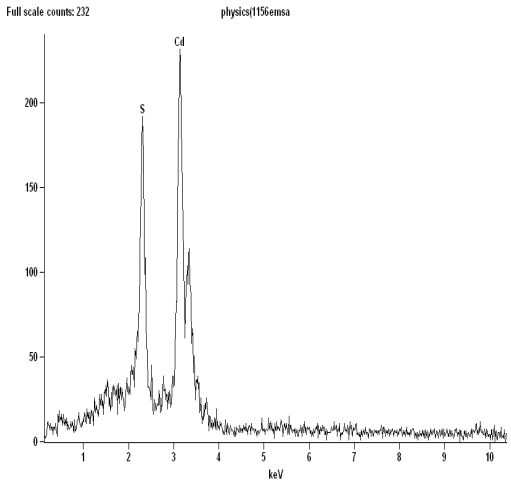

Fig.3. Elemental analysis of CdS nanoparticles using EDAX

The most remarkable property of the optical absorption spectrum is its sensitivity to the size of the nano regime. Many researchers have reported that there is an appreciable shift of band head with the size of the particles when the particle size changes from bulk to nano size. The optical absorption property of the CdS nanoparticles studied using UV-Vis-NIR spectrophotometer in the range 200-800nm is shown in Fig. 4.

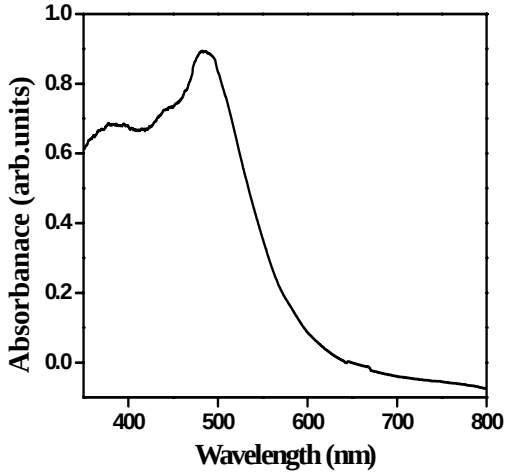

Fig.4. Optical absorption spectrum of CdS nanoparticles

CdS is a direct band gap material, with absorption edge for the bulk hexagonal CdS is at 512 nm which has the band gap energy ~ 2.4 eV [20]. From the absorption spectrum of CdS nanoparticles of our present study, a well-defined absorption peak at 480 nm is observed. The exciton absorption observed at about 480 nm, which is blue shifted compared with the characteristic absorption of bulk CdS may be due to quantum confinement effects.

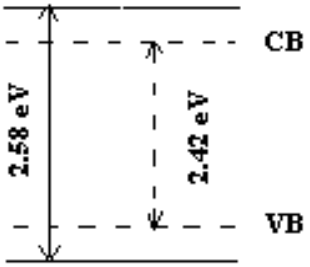

Fig. 5. Energy Band diagram for CdS. Dotted lines are for bulk CdS and straight lines are for the prepared CdS nanoparticles.

The band diagram shown in Fig. 5 explains the energy difference for the bulk and the nanoparticles of CdS. The absorption peak at 480 nm corresponds to the optical transition of the first excitonic mode with energy band gap of 2.58 eV, shows a difference of 0.16eV energy greater than that of bulk, indicating quantum size effect [21-22]. Normally it is stated that the broadening of the band gap of semiconductor nanoparticles are explained to be due to discrete energy level distribution. It is the famous quantum size effect of nanoparticles [23]. V.P. Singh *et.al* [24] reported that no absorption peak was observed for CdS material prepared using solution growth method because of their larger crystallite size. In our present study, optical investigation of CdS nanoparticles prepared using solution growth method showed a blue shift in optical absorption spectra as a result of quantum confinement effects.

4. Conclusions

CdS nanoparticles have been successfully prepared using a simple chemical solution method. CdS prepared using this method exhibits nano size regime with a predominantly hexagonal phase.with broadened diffraction peaks. SEM analysis showed the presence of nanoclusters and pores in the sample. EDAX analysis confirmed the purity of the sample. Optical absorption property of CdS nanoparticles showed a blue shift in their absorption band edge and it is explained due to the quantum size effect of the CdS nanoclusters. Thus, the present method is a simple and efficient for the preparation of nano-crystalline CdS nanoparticles at low temperature with excellent structural and optical properties which could find their applications in optoelectronic devices.

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