



Influence of Ethylene Diamine Capping on the Structural and Optical Properties of Hydrothermally Synthesized Cadmium Sulphide Nanoparticles

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One dimensional nanoparticles of cadmium sulphide were prepared using ethylene diamine assisted solvothermal synthesis. X-ray diffraction result confirms that the nanorods are of hexagonal structure and the selected area electron diffraction identifies its single crystalline nature. The sample was characterized by UV-VIS absorption, photoluminescence spectrum, scanning electron microscopy, transmission electron microscopy and thermal analysis. The UV-VIS absorption spectrum indicates the narrow size distribution of the cadmium sulphide nanorods. The absorption band edge is seen shifted to 490 nm than the bulk material and the corresponding band gap is found to be 2.53 eV. The photoluminescence emission peak is detected around 503 nm. From SEM and EDAX analysis, the morphology of the aggregates and the composition of the obtained product are identified. The TEM micrographs show that the cadmium sulphide nanorods have well defined morphology and high crystalline quality with narrow size distribution of lengths and widths. The thermal behaviour of the as prepared nanopowder was studied by thermogravimetric analysis.

Key Words: Nanostructures, Cadmium compound, Semiconducting II-VI materials, Solvothermal, Capping agent.

INTRODUCTION

Semiconductor nanoparticles are of great interest both for fundamental research and technological applications as a consequence of the large ratio of surface to volume atoms and quantum confinement of the excitons^{1,2}. Recently, the synthesis of inorganic nanocrystals has attracted much interest due to their strong size dependent, special optical, electronic properties and potential applications in electronics, optics, catalysis, *etc.*^{3,4}. As a typical semiconductor material of the II-VI group, cadmium sulphide (CdS) nanocrystals have been widely investigated^{5,6}. It is a direct band gap semiconductor with its band gap of 2.4 eV for bulk hexagonal (Wurtzite) structure and 2.38 eV for bulk cubic (zinc blende) structure^{7,8}. Cadmium sulphide nanoparticles are considered to be one of the model systems for investigating the unique optical and electronic properties of quantum confined semiconductors. Cadmium sulphide shows interesting optical properties, for example, upon optical excitation, the surface defect states rapidly trap the electrons and holes and quench the radiative band gap recombination⁹. The optical properties of CdS nanoparticles are strongly dependent upon the preparation conditions. It is now widely used for photoelectric conversion in solar cells, in light emitting diodes for flat-panel display, photocatalysis, non-linear optical materials, optoelectronic and biological labelling.

Over the past few years, tremendous efforts have been made to control the size and shape of the CdS nanocrystals and a huge number of new methods have been reported, especially on one-dimensional CdS nanostructures. Modifying the surface of nanoparticles with various organic and inorganic species is projected to remove their surface defects and subsequently, influence their property. Organic capping of nanoparticles with surfactants would give rise to a barrier to aggregation and electronic passivation of the particles. Numerous colloidal chemistry (or solution chemistry) methods have been developed for the preparation of cadmium sulphide nanocrystals⁹. The solution chemistry synthesis of CdS nanocrystals utilizes the organic stabilizers to cap surface atoms of nanoparticles in order to control the growth process. The kind of stabilizers is of great importance, since, it affects the chemical as well as the physical properties of the semiconductor nanocrystals, from stability to solubility to light emission.

Phuruangrat *et al.*¹⁰ synthesized CdS nanorods and nanoparticles by solvothermal method at 200 °C for 24 h using ethylene diamine (EDA) and water as pure and mixed solvents in different ratios. The phase and its vibrational modes were clearly detected and the influence of the dielectric constants of the solvents in determining the shapes of the final product was interpreted. In pure EDA, hexagonal structure CdS

nanorods with 0.2-2.0 μm long and 30 nm diameter were obtained. Li and Zhang¹¹ reported the formation of large scale CdS nanorods with high quality employing solvothermal method at 160 °C using aqueous EDA as a solvent. EDA is proved to be the best solvent to promote the selective anisotropic growth of CdS and provide an appropriate CdS monomer concentration for the preferential growth of 1D CdS nanostructure¹². It was proved that EDA molecule played a chelating role in the formation of CdS nanorods in aqueous solution¹³. Without the addition of EDA, only CdS nanoparticles were obtained¹⁴. Yu *et al.*¹⁵ proposed that the reaction mechanism in EDA is different from that in the other solvents since the coordination ability of EDA is much stronger than those of other solvents and thiourea and the complex ion $[\text{Cd}(\text{en})_2]^{2+}$ will form in the solution instead of $[\text{Cd}(\text{TU})_2]^{2+}$. It is believed that thiourea reacts with a small amount of H_2O in the system to produce S^{2-} , which bonds with $[\text{Cd}(\text{en})_2]^{2+}$ in the solution which loses EDA molecules to form CdS.

In the present work, solvothermal synthesis of CdS nanoparticles has been carried out under mild conditions and the influence of the EDA on the crystalline quality, morphology, size and crystalline phase has been investigated. The sample was systematically characterized by powder XRD, UV-VIS absorption and photoluminescence spectroscopy, SEM and TEM and thermal analysis.

EXPERIMENTAL

Cadmium nitrate $[\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$ (Merck, 98 % purity) and thiourea (H_2NCSNH_2) (Merck, 98 % purity) are used as the starting materials with ethylene diamine as a solvent. All chemical were used as purchased and no further purification was done.

Synthesis: Ethylene diamine (EDA) was used as the capping agent as well as a solvent. A stoichiometric ratio of 1:3 for $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and H_2NCSNH_2 was maintained. The cadmium precursor solution was initially mixed with 75 mL of EDA solution and followed by the addition of thiourea-EDA solution and the pH was found to be 8. The solutions were mixed thoroughly and transferred into a 200 mL capacity autoclave. The autoclave was maintained at 180 °C for 6 h and then allowed to cool naturally to room temperature. The resulting product was collected and filtered out. It was washed in Millipore water and ethanol and then dried at 180 °C for 24 h.

Characterization: The room temperature powder XRD pattern for the as prepared sample was done using RICH SEIFER with monochromatic nickel filtered $\text{CuK}\alpha$ ($\lambda = 1.5461 \text{ \AA}$) radiation. The UV-VIS absorption spectral study was carried out using VARIAN CARY 5E UV-VIS-NIR spectrophotometer in the spectral region of 200-800 nm. The photoluminescence spectrum of the sample was recorded with a VARIAN CARY 5E UV-VIS-NIR spectrophotometer. Particles size and distribution analyses were carried out with TEM model JEOL JEM 3010 at an accelerating voltage of 200 kV. For the TEM observations, the sample was dispersed in ethanol and ultrasonicated for 0.5 h and then it was kept on a carbon coated grid. Scanning electron microscope (SEM) was employed for morphological study using JEOL JSM 6310 operated at 10 kV with Energy Dispersive X-ray analyzer (EDAX).

Thermogravimetric (TG) and differential thermal analysis (DTA) for the air dried sample was performed on a SDT Q600 with a heating rate of 20 °C min^{-1} .

RESULTS AND DISCUSSION

Powder XRD analysis: Fig. 1 shows the typical XRD pattern of the as prepared CdS nanoparticles capped with ethylene diamine (EDA). It is evident from the pattern that (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 3), (1 0 3), (2 0 0), (1 1 2), (2 0 1) and (2 0 3) peaks are corresponding to hexagonal phase of CdS. Thus the presence of the bidentate ligand (EDA) has not affected the structure of the CdS crystallites formed. It has been reported that for CdS nanoparticles synthesized at temperature below 150 °C, usually leads to mixed phases of cubic and hexagonal¹⁶ and in addition to temperature, the lower concentration of capping ligand is also expected to contribute to such mixed phases in CdS. It is believed that in the present case a relatively high reaction temperature of 180 °C with appropriate concentration of EDA resulted in fully hexagonal phased nanoparticles of CdS. The obtained data was compared with the standard data for CdS (JCPDS card No. 80-0006) and the lattice parameters are found to be; $a = b = 4.121 \text{ \AA}$ and $c = 6.682 \text{ \AA}$.

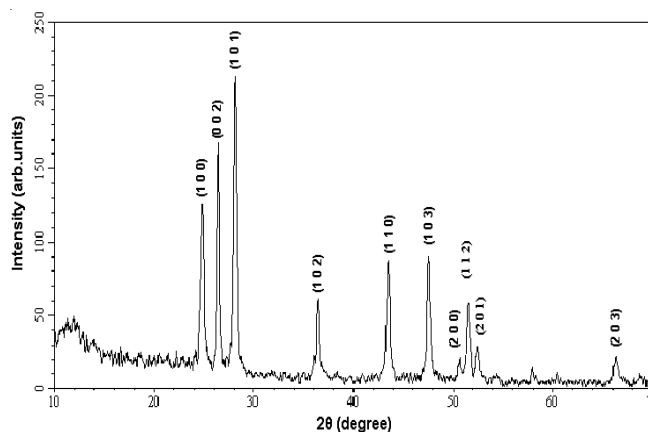


Fig. 1. Powder XRD pattern of EDA modified CdS nanoparticles

UV-VIS near infrared spectral analysis: The controlling and tuning of band edge emission and surface traps state emission of CdS nanocrystals are obviously very important to realize the tunable optical properties and laser emission. Fig. 2 shows the absorption spectrum of CdS nanoparticles prepared with EDA. The band edge absorption is seen at 490 nm. The relatively sharp absorption indicates the narrow size distribution of the nanoparticles. The shift of the absorption edge to *ca.* 22 nm (compared to bulk CdS) towards lower wavelength is due to confinement of charge carriers in CdS nanocrystallites. The corresponding optical band gap of CdS nanocrystallites is 2.53 eV.

Photoluminescence study: One of the interesting aspects of the photo-physical properties is the photoluminescence (PL) of CdS nanocrystallites. The photoluminescence studies on CdS nanocrystallites have been investigated by various research groups¹⁷. In general, the reported emission spectra consist of two broad bands in the range 400-520 nm and then at 520-800 nm.

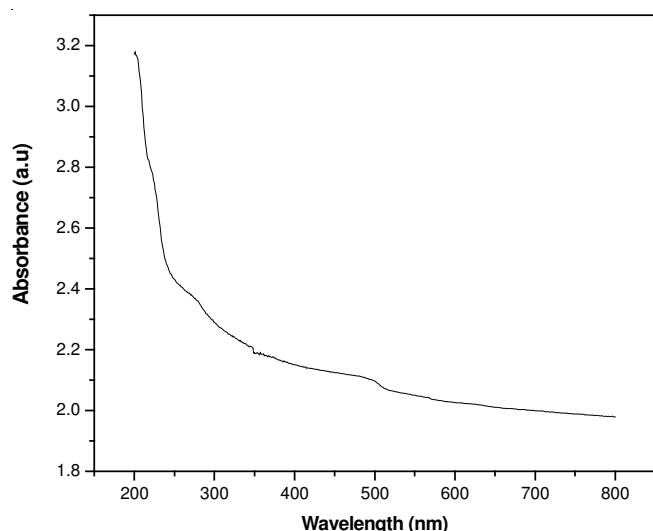


Fig. 2. UV-VIS spectrum of EDA capped CdS nanoparticles

The photoluminescence property is influenced by the structure, composition, particle size and morphology of the CdS nanoparticles. In addition, the method of preparation has marked influence. In the case of CdS nanoparticles prepared with EDA capping, Zhan *et al.*¹⁸ have observed the presence of a strong emission peak at *ca.* 503 nm, which can be ascribed to a high level transition in CdS semiconductor crystallites. This kind of band edge luminescence arises from the recombination of exciton and/or shallowly trapped electron-hole pairs. In the case of CdS nanorods with Cd²⁺ rich surface, S⁻ surface traps are not expected. Instead, surface electron traps, such as Cd⁺ or sulphur vacancies (V_s⁺) are expected to influence luminescence¹⁹. Fig. 3 shows the photoluminescence spectrum of CdS nanoparticles prepared with EDA. The emission peak observed at 503 nm can be assigned to the surface trap induced fluorescence which involved the recombination of electrons trapped inside a sulphur vacancy with the hole in the valence band of CdS nanoparticle.

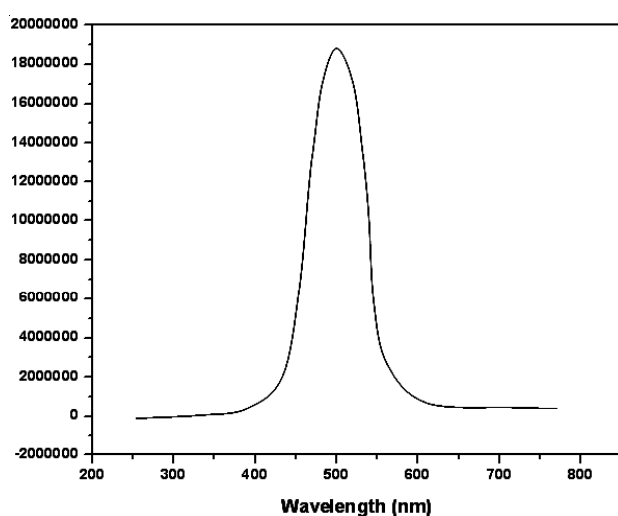


Fig. 3. Photoluminescence spectrum of EDA capped ZnS nanoparticles

Scanning electron microscope (SEM) study: Fig. 4 shows the high magnification SEM image of the CdS nanoparticles synthesized with EDA. It shows that the products

are composed of predominantly irregular shapes and a few prickly spheres, dendrites, tiny rods as well as long rods. The observed length of the long rod is about 380 μm .

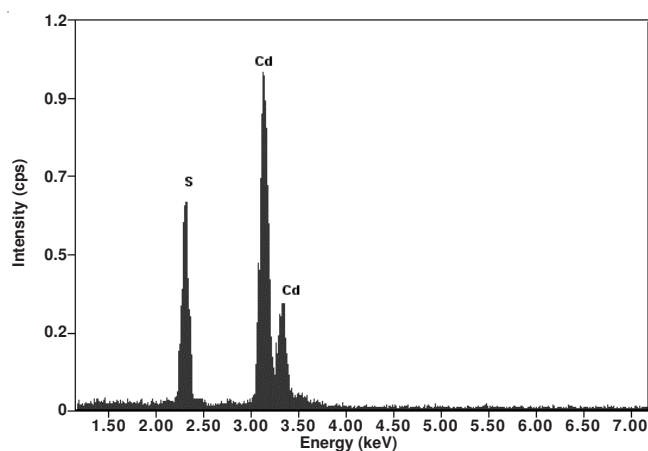
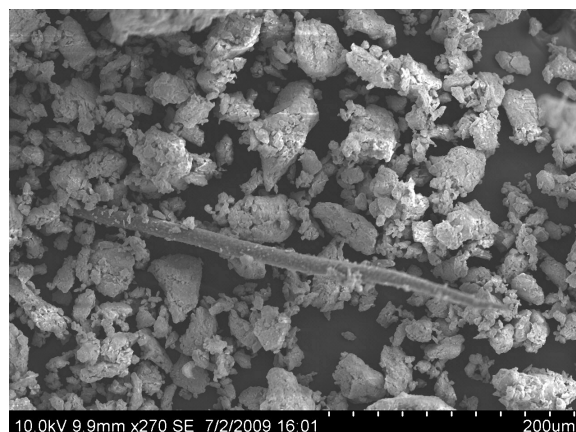


Fig. 4. SEM and EDAX spectrum of EDA capped CdS nanoparticles

Energy dispersive X-ray (EDAX) analysis: EDAX is an important technique to analyze the composition of elements quantitatively and solve the chemical identity of any nano-material. It is inferred from the result of the EDAX spectra (Fig. 4) that the sample is composed of only Cd and S and is exactly CdS nanoparticles and no trace of other elements is observed. Figure further shows that the sample is cadmium rich even though a relatively higher concentration of sulphur was used than the cadmium to synthesize CdS nanoparticles.

Transmission electron microscopy (TEM) study: The transmission electron microscopic analysis allows one to visualize particles at nanosize regime with high degree of accuracy, it offers better understanding about growth aspects and helps to analyze the actual size of the particles, shape and growth pattern.

In the presence of EDA, CdS nanoparticles show high content of agglomeration with particles of irregular size and morphologies (Fig. 5 (i)) and the individual particles are not visible. However, with higher magnification, it is evident from the TEM micrographs (Fig. 5 (ii)) that majority of the products appear as nanograins and a few short nanorods are also visible. The spherical particles have an average size of nearly 18 nm and there is also limited number of spherical particles with size around 10 nm. Li *et al.*¹⁶ suggested that a higher temperature favours the growth of nanorods and the length of the

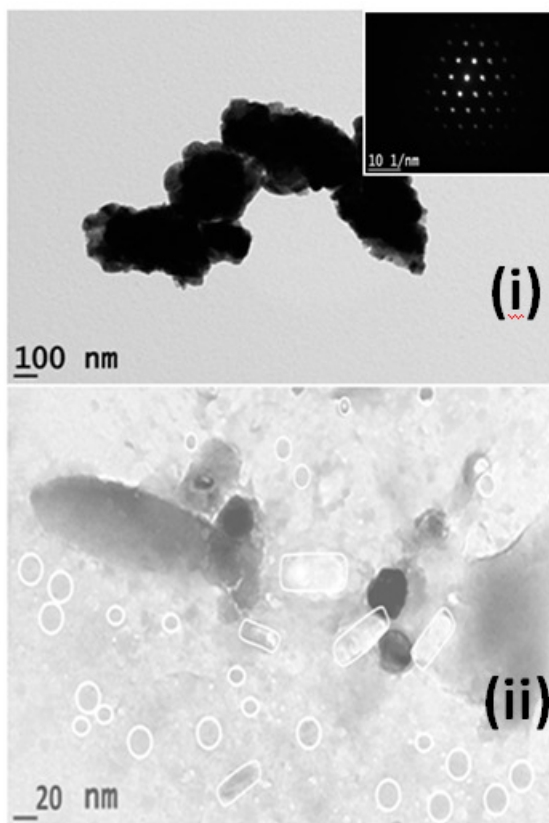


Fig. 5. TEM images of EDA capped CdS nanoparticles

nanorods increases with increase in the reaction temperature. EDA functions as a solvent and as a bidentate chelating ligand, it can play the role in improving the aspect ratio of the product. In general, a solvent with low dielectric constant promotes the growth of particles in the shape of rods¹⁰. The present study confirms the formation of CdS nanorod with the aspect ratio *ca.* 4 to 5. The SAED pattern of the sample reveals the crystallization of the particles in hexagonal structure and the diffraction spots indicate the slightly larger size of the nanopowder.

Thermal analysis: The thermal behaviour of the semiconductor nanoparticles of CdS was studied by employing TG/DTA analysis. Since the temperature plays an important role in the formation of nanostructured materials, temperature induced phase changes are important for the utility of these nanoparticles for various applications.

The TGA trace (Fig. 6) of CdS nanopowder confirms the three stages of weight loss. The first stage starts around 425 °C with 12.46 % weight loss. This is followed by the second and third stages at 625 °C and 745 °C with the weight loss of 6.975 and 9.334 %, respectively. After reaching 745 °C, no significant weight loss is observed in the sample.

Conclusion

A cost effective synthesis procedure was successfully employed to prepare CdS nanorods of good crystalline quality and moderate aspect ratio. Cadmium sulphide nanorods were obtained under solvothermal conditions at 180 °C with a short reaction time of 6 h. The optical properties of the CdS nanorods were studied using UV-VIS absorption and photoluminescence

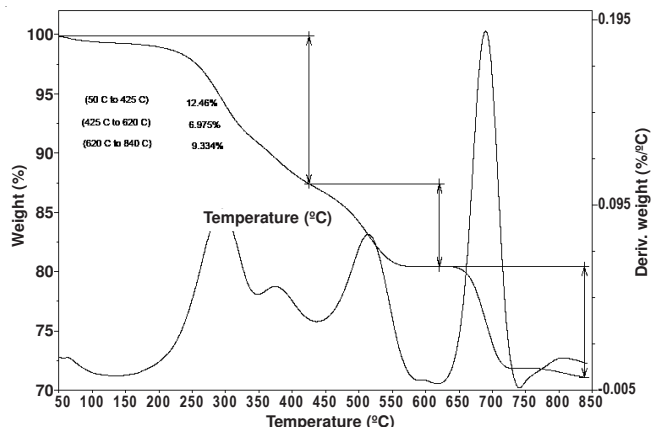


Fig. 6. TG-DTG thermogram of EDA capped CdS nanoparticles

spectroscopic techniques. The emission peak at 503 nm for the sample can be assigned to the surface trap, induced fluorescence which involved the recombination of electrons trapped inside a sulphur vacancy with the hole in the valence band of CdS nanoparticle. TEM study indicates that the CdS nanoparticles exhibit 1D nanostructure and the aspect ratio of the nanorods was 4-5. Thus, the mild condition synthesis of CdS nanorods with EDA makes the present work as a promising approach and it could be extended for large scale production of 1D CdS nanostructures.

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