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Two Step Hydrothermal Synthesis of Nanocrystalline CdS

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Abstract: *Cadmium sulphide nanocrystals of predominantly hexagonal shape have been synthesized using a two-step hydrothermal method. In this method, a wet chemical process and a hydrothermal process were grouped together. In the first step, the precursor solutions along with hydrazine hydrate were thoroughly mixed together and preheated at 50 °C for 30 minutes. The resulting sol was then transferred to a metal bomb which was maintained at 150°C for six hours to produce nanocrystalline CdS. X-ray diffraction (XRD) studies confirm that synthesized nanocrystals are highly crystalline CdS having the wurtzite structure. Transmission electron microscopy (TEM) show fine polygon shaped crystallites of size around 30-50 nm. Raman results confirm the characteristic phonon vibrational modes of CdS. Room temperature Photoluminescence spectra indicate that the optical band gap of the synthesized particles is around 2.53 eV.*

Key words: *Nanoparticles, two step solvothermal method, band gap, TEM, photoluminescence.*

1. INTRODUCTION

The small size and high surface to volume ratio of nanocrystals of inorganic compound semiconductors exhibit interesting physical, chemical and optical properties [1].CdS have two different crystal structures cubic zinc blende and hexagonal wurtzite. Cadmium sulphide is extensively used in various applications such as in non-linear devices, solar cells, display devices, x-ray detectors, in the pigments and plastic industry, and as photo-catalysts [1-10].It is well known that the properties of nanocrystals of cadmium sulphide are controlled by the growth process and different growth conditions [4]. It is necessary to develop various approaches to prepare high quality nanoparticles CdS nanocrystals. CdS nanoparticles are synthesized by various approaches, like chemical precipitation method with or without template agent [3, 4], electrochemical method [5], mechanical alloying [6], wet chemical method [7-8], solvothermal method [9-10] and other chemical methods [13-17]. Among all these methods, the new solvothermal method is more suitable and has many advantages as it is a simple and cheap method and the growth can be controlled by controlling the growth temperature.
In this work we report on a new simple and environmental friendly two step hydrothermal technique for synthesis of CdS nanocrystals. The first step involves a wet chemical process for uniform mixing of constituent solutions and template agents and the second step is a solvothermal process or high pressure synthesis at constant temperature heating, using a metal bomb. A uniformly mixed solution of cadmium acetate, thiourea and hydrazine hydrate was used as precursor solution for hydrothermal synthesis. The two step solvothermal method is a suitable technique for the synthesis of polygon shaped CdS nanocrystals.

II. EXPERIMENTAL PROCESS

Cadmium acetate dehydrate [$(CH_3COO)_2Cd.\ 2H_2O$], thiourea (NH_2CSNH_2) and hydrazine hydrate (N_2H_4) were used as starting materials. At room temperature, cadmium acetate and thiourea were dissolved in distilled water separately. Both the solutions of cadmium acetate and thiourea were mixed together in such a way as to maintain the atomic ratios of cadmium and sulpher at 1:1 with stirring and heating. The hydrazine hydrate was added to this solution drop wise, stirred well and heated at 50 °C for 30 minutes. Then the reaction bath was poured in to the metal bomb which was packed airtight and put into an oven for high pressure hydrothermal synthesis. The reaction temperature was maintained at 150 °C for six hours. The sample was then cooled down naturally to room temperature. The yellowish precipitate was separated out from the liquid phase and washed with ethanol and distilled water by centrifugation at 5000 rpm. The precipitate was vaporized and dried at 100°Cin hot air oven and stored for further analysis. The dried samples are called as synthesized.

The XRD pattern of the as-synthesized freshly dried CdS powder was recorded by a Rikagu Miniflex 600 X-ray diffractometer in the 2θ range 5° to 70° using copper Kα radiation (1.5406Å). An STR 500 micro Raman spectrometer was used for recording the phonon spectra of CdS nanoparticles using a diode laser. A Simadzu RF 6000 spectroflurometer was used to record the photoluminescence spectra of the as-synthesized CdS powders. The SEM images were obtained on a NOVA NANO FESEM 450. The TEM and HRTEM images and SAED patterns were obtained on a FEI Tecnai transmission electron microscope G2 S-Twin 300 kV instrument.

III. RESULTS AND DISCUSSION

3.1 XRD results

The diffraction pattern of cadmium sulphide nanocrystals is shown in Figure 1. The pattern shows the characteristic features corresponding to (100), (002), (101), (102), (110), (103), (112 and (203) planes of hexagonal wurtzite structure of CdS (JCPDS no.41-1049, a= 4.140Å and c=6.719 Å).The values of crystallites size and lattice parameters are calculated using the value of full width at half maximum (FWHM) of the (002) plane. The average crystallite size is around 34.8 nm calculated from the Scherer formula. The calculated values of lattice parameters are a = 4.135Å, c = 6.721 Å and the volume of unit cell is 35.027 $Å^3$.

3.2 Raman results

The Raman spectrum of the CdS nanoparticles is shown in Figure 2.The characteristic peaks of 1LO and 2LO of phonon vibrations are observed at 300 $cm^{-1}$and 597cm^{-1}. The 1LO peak (at 300 cm^{-1}) represents the prominent signature of CdS, but the 2LO peak of phonon vibrations is obtained at 597 cm^{-1}, a slightly higher frequency than the reported value (600 cm^{-1}) [13-15].it is may be due to the interactions between particles may give rise an apparent broadening and shift of various surface phonon modes [15].

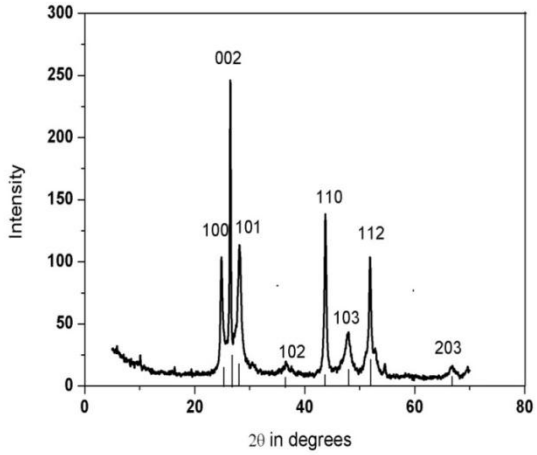


Figure 1 XRD pattern for CdS nanocrystals

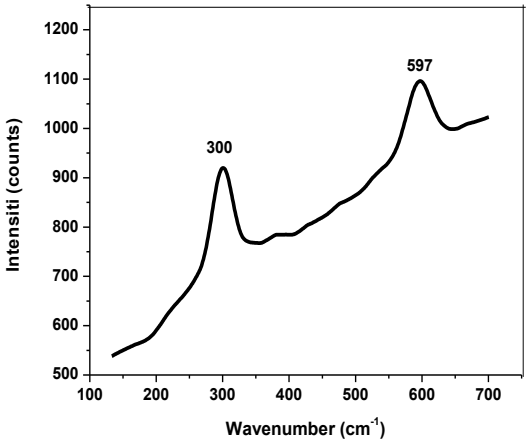


Figure 2 Raman spectrum of CdS nanocrystals

3.3 PL Results

Photoluminescence emission is the resultant of the recombination of electrons and holes and thus, in general, PL spectra give information regarding the excitonic levels in a semiconductor. Figure 3 shows the room temperature PL spectra of the CdS nanocrystals excited at 300 nm. The figure shows a sharp emission peak centered at 490.5 nm, which may represent the recombination of free excitons [1, 18]. This puts the band gap value at slightly higher than 2.5 eV.

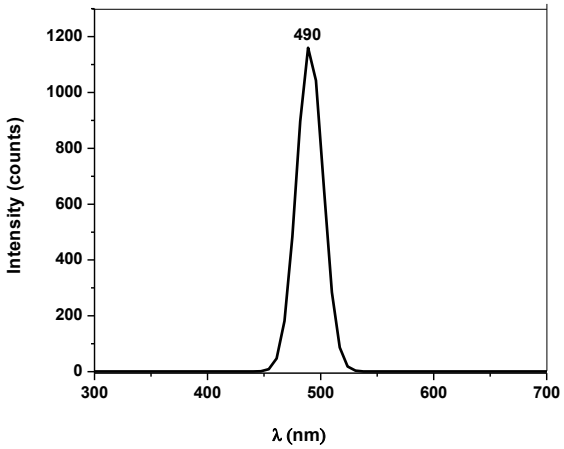


Figure 3 PL spectrum of CdS nanocrystals

3.4 SEM Images

Figure 4(a) and (b) shows the SEM micrographs of the CdS nanoparticles with different magnifications. The images show that the synthesized particles are in the size range 50-300 nm size. Considering that the calculated crystallite size is around 30 nm, each particle must be made up of a few to several crystallites.

3.5 TEM images

TEM is a suitable technique for the analysis of size and shape of nanocrystals. Figure 5 (a) and (b) shows the TEM image of CdS nanoparticles. The grains of the CdS nanocrystals appear polygon shaped and their size ranges from30-50 nm which is in agreement to the crystallite size obtained from XRD. Figure 7(b) shows the HRTEM image in which the lattice planes are clearly evident. The magnified view of the part of the image clearly show the interlayer distance of 0.357 nm (inset of figure 7(b)) which is close to the d-value in XRD of the CdS hexagonal lattice corresponding to the separation of the(100) planes.

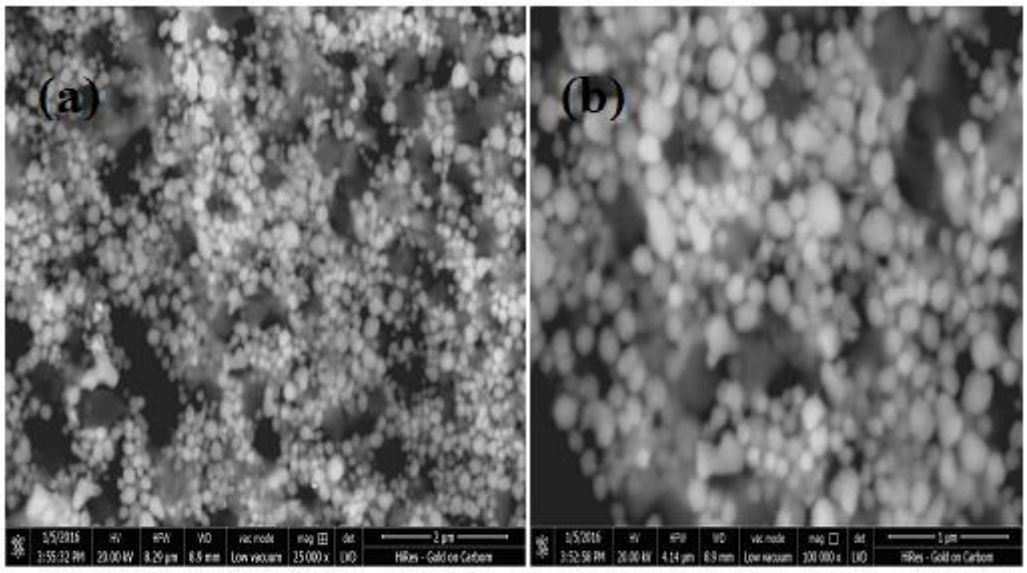


Figure 4 (a)& (b) SEM images of CdS nanocrystals

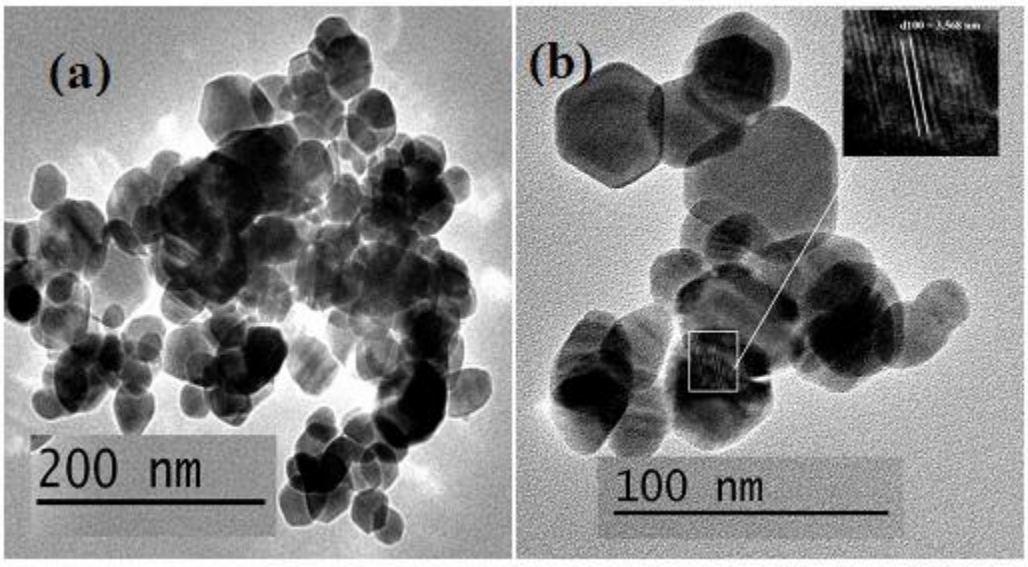
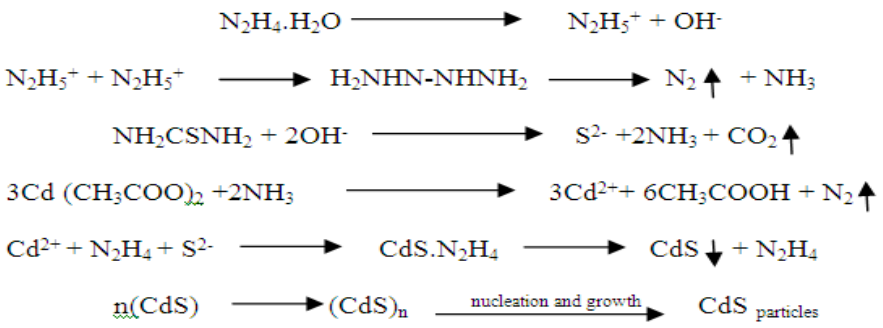


Figure 5 (a) & (b) TEM images of CdS nanoparticles

IV. GROWTH MECHANISM

The exact mechanism for the formation of CdS nanocrystals is still unclear, but on the basis of observation during synthesis the reaction mechanism of nanocrystalline CdSe is proposed. The solution bath was containing cadmium precursor solution, sulpher precursor solution and hydrazines hydrate. During the wet chemical process the constituent solutions were mixed well with stirring and heating at 50 °C for 30 minutes. The solution is then poured into the metal bomb for high pressure hydrothermal synthesis, in which the reaction temperature is maintained at 150°C for a few (six) hours to produce nanocrystalline CdS. Initially hydrazine hydrate in aqueous solution form hydrazil ions. The hydrazil ions undergoes dimerization and form an intermediate species that generates ammonia [12, 19] which acts as a reducing agent and reduce the cadmium acetate and thiourea in Cd^{2+} ions and S^{2-} ions. As the nucleation starts at high pressure the hydrazine hydrate also act as a coordination agent and form a CdS co-ordination compound which gives CdS

nanoparticles. The reaction continues till the completion of the formation of CdS nanocrystals. The possible reaction steps during the solvothermal synthesis are proposed as follows:



V.CONCLUSIONS

In summary, we report on a new two-step hydrothermal method for the synthesis of luminescent cadmium sulphide nanocrystals in an aqueous medium. In comparison to several other growth techniques, the method presented here is a simple and straightforward method. The analysis reveals that the synthesized CdS nanocrystals have the hexagonal wurtzite phase with crystallite size around 35 nm, which is in agreement with the particle size observed from TEM micrographs. The Raman spectrum confirms the characteristic phonon vibrational modes of CdS. The room temperature PL spectra show the optical band gap is around 2.53 eV, which is close to the reported values for CdS. Hence we can say that this new hydrothermal method is suitable for the synthesis of polygonal shaped CdS nanoparticles.

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