Synthesis of CdS nanoparticles through colloidal rout

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Colloidal nanoparticles of CdS were prepared by mixing 1.86×10^{-3} M $Cd(NO_3)_2$ and 2.5×10^{-3} M $(NH_4)_2S$ solutions of different proportions in acetonitrile solvent. UV-VIS optical absorption spectra revealed the size-dependent shift of excitonic transition in the nanoparticles. Variation of excitonic transition shift with the growth of nanoparticles in the mixture with time and with the variation of cation (Cd^{++}) or anion (S^-) contents in the solution have been studied. In general, the size of the nanoparticles is smaller for the solutions containing excess cations. However, the growth of particles in the solution terminate rapidly when either of the ions were in large excess, due to the formation of double dielectric layer around the initially grown particles. Evolution of particle size with time and with the variation of cation/anion ratio has been studied. The structure, crystallinity and size distribution of the nanoparticles are presented.

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1. Introduction

The study of nanometer size crystallites provides an opportunity to observe the evolution of material properties with size. The study of intermediate size regime gives the information about the collective behaviour of bulk materials which emerges from the discrete nature of molecular properties.

Semiconductor microcrystallites are among the promising materials for future applications in nonlinear optical devices, because they poses a large third-order optical nonlinear susceptibility $\chi^{(3)}$ as a result of quantum confinement effect in the microcrystallites. Quantum confinement, the widening of the HOMO LUMO gap with decreasing crystallite size, and its applications for the electronic structure and photophysics of the crystallites have generated considerable interest in recent years [1-5]. Several methods have been adopted to grow nanometric semiconductor particles. For example, CdS, CdSe, CdTe, CdS_xSe_{1-x} nanoparticles have been grown by chemical techniques [6,8]; Au, GaAs, Si nanoparticles embedded in SiO_2 or ZnO matrix have been grown by ion-implantation and r.f. co-sputtering techniques [9-13]. Both the linear and non-linear optical properties of those nanoparticles are being studied extensively at present in view of finding their applications in optoelectronics.

In this work, we present the preparation of CdS nanoparticles of different size through a colloidal rout. The size of the particles could be controlled either by terminating the chemical reaction at different time interval or by varying the cation/anion ratio in the reaction mixture. The structural and optical properties of the nanoparticles have been studied.

2. Experimental

One of the methods of preparing semiconductor nanoparticles is the chemical reaction of corresponding cationic and anionic solutions to prepare colloidal particles. The method is simple and relatively cheap. The colloidal rout permits to obtain relatively pure nanoparticles, and as the matrix is liquid, the separation of particles is not difficult. The dynamics of the formation of nanoparticles in colloidal form based on the dissociation of the species present in the mixture solution and the parameters like dielectric constant of the solvent, temperature, and the concentration of the solutions play important roles.

In a colloidal system, consist of two ionic solutions, the stability of the colloidal particles is influenced by chemical equilibrium. In case of CdS, the chemical equilibrium is defined by the reaction:

$$(CdS)_{crystal} \leftrightarrow (Cd^{++})_{solv.} + (S^{--})_{solv.} \quad (1)$$
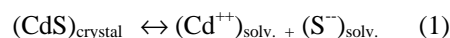
This equilibrium (eq. 1) is a function of size of the crystallites and the dielectric constant of the solvent. The reaction is favored to the right hand side due to the low energy of bonding in the small crystals and the dissolved ions can recrystallize to bigger particles. So, the thermodynamic stability is more in bigger crystals. This mechanism of transferring mass from smaller crystals to bigger crystal is known as "Ostwald" ripening [14], where the higher surface energy of small crystallites makes them less stable with respect to dissolution in the solvent than larger crystallites. The net result of this

Table I. Volumetric ratio of the solutions mixed to prepare the final colloidal mixtures and the % of ions in them.

$Cd(NO_3)_2 : (NH_4)_2S$	% of Cd^{++} : % of S^{--}
10 : 1	88.15 : 11.85
4 : 1	74.85 : 25.15
2 : 1	59.80 : 40.20
1 : 1	42.66 : 57.34
1 : 2	27 .12 : 72.88
1 : 3	19.87 : 80.13
1 : 4	15.70 : 84.30
1 : 6	11.03 : 88.97
1 : 10	6.93 : 93.07

stability gradient within a dispersion is a slow diffusion of material from small particles to the surface of larger particles [14]. The "Ostwald" ripening process decreases with time and permits a longer lifetime for the bigger crystals. The process of forming bigger crystals from the smaller crystals depends strongly on the dielectric constant of the solvent. Generally, a lower dielectric constant solvent is preferred, as the dissolved ions in it are less stable. The magnitude of the electrostatic force between the ions of charge Q_1 and Q_2 separated by a distance r in a medium of dielectric constant ε is given by:

$$F= Q_1Q_2/4\pi\varepsilon_0\varepsilon r^2 \qquad (2)$$

Where ε_0 (8.854 x 10^{-12} C^2/Jm) is the dielectric permeability of vacuum and ε is the dielectric constant of the medium. So, when the ε is low, the electrostatic force between the ions is high and the ions unite strongly [15].

The size of the colloidal particles can also be controlled by regulating the volume fraction of one of the components in the solution. Generally a very low concentration of the solution is recommended to minimize the collision between the particles and to avoid their agglomeration and sedimentation .

In this work we used acetonitrile as the solvent which has a lower dielectric constant (ε = 36) in comparison to water (ε = 84) [16]. By changing the content of either of the ions in the solution we studied the evolution of CdS particles in it.

Using acetonitrile as the solvent, we prepared 1.86×10^{-3} M $Cd(NO_3)_2$ and 2.5×10^{-3} M $(NH_4)_2S$ solutions of 20 ml each. The solutions were mixed in different volumetric proportions and agitated vigorously. In Table I the volumetric ratio of $Cd(NO_3)_2$ and $(NH_4)_2S$ solutions used to prepare the mixture solutions and the percentage of Cd and S ions in them are given. The freshly prepared colloidal mixtures were used for optical absorption measurement. A Shimadzu UV-3101PC double beam spectrophotometer was used for this purpose. The absorption spectra were recorded at different interval of time to monitor the change in the size of the CdS particles in the mixture. The measurements were carried out for several days or until there was any significant change in the absorption spectra. For XRD measurement, the aged
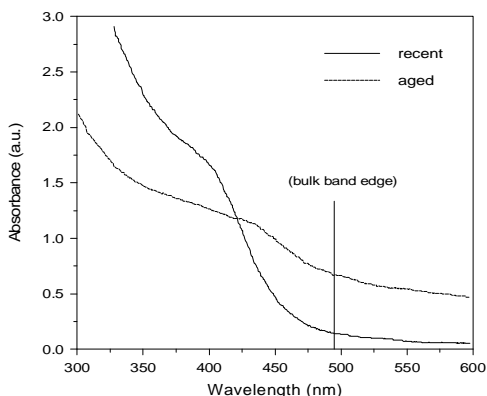
colloidal solutions were dropped on a quartz substrate and evaporated subsequently in a vacuum chamber backed by a mechanical pump. The process was repeated several times to prepare a thick film of CdS on the substrate. A Rigaku, RAD-C x-ray diffractometer with CuK_α radiation was used to record the diffraction pattern of the samples. For transmission electron microscopy (TEM) and transmission electron diffraction (TED) measurements, the colloidal solutions were spread on the carbon coated Cu grids and dried in a vacuum chamber. A JEOL JEM2000-FXII electron microscope was used for TEM and TED observations on the samples.

3. Results and discussion

In figure 1, the absorption spectra of a sample prepared with a 2:1 volume ratio of $Cd(NO_3)_2$ to $(NH_4)_2S$ are presented for fresh and aged solutions. We can see a clear shift of band edge in the colloidal particles from the bulk CdS band edge (490 nm) due to quantum confinement effect in them. With time, the growth of particles continues and the band edge shifted towards lower energy. Other workers [17] have observed a similar shift of band edge with the increase of CdS crystallite size. There appeared a hump or peak correspond to the "exciton" transition in all the optical absorption spectra. The excitonic peak position shifted with the increase of particle size, i.e. with time after the preparation of a fresh colloidal mixture. Depending on the concentration of the ions in the mixture the growth process continue for a finite time. In figure 2 the time evolutions of the exciton peak position for the colloidal particles prepared with three different proportions of
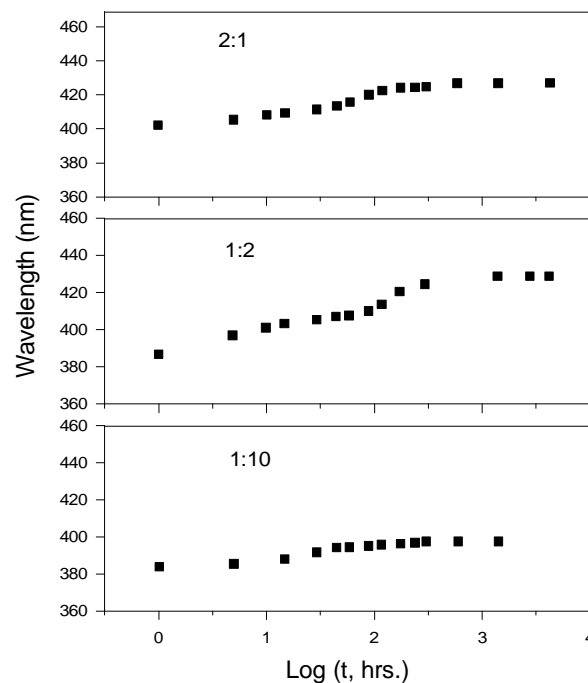

Figure 1. Absorption spectra of recent and aged colloidal CdS particles prepared with 2:1 :: $Cd(NO_3)_2$: $(NH_4)_2S$.

Figure 2. Time evolution of exciton peak position for the colloidal CdS particles prepared with different ratio of $Cd(NO_3)_2$ to $(NH_4)_2S$.

anions and cations are presented. We can clearly see that the growth process strongly depends on the relative concentration of cations and anions. The final size of the particles also depends on the initial concentration of two ions. In figure 3, the TEM micrographs of the colloidal CdS particles extracted form the aged solutions prepared by mixing 2:1 proportion of $Cd(NO_3)_2$ and $(NH_4)_2S$ and its TED pattern are presented. In figure 4, the size distribution of the particles obtained by mixing different proportions of $Cd(NO_3)_2$ and $(NH_4)_2S$, obtained from TEM micrographs are presented. A clear hexagonal symmetry for the particles is revealed. As all those TEM samples were prepared from the aged solutions, we can observe the effect of cation/anion ratio on controlling the final size of the nanoparticles. In figure 5, a typical XRD pattern of the nanocrystalline CdS particles is presented. Though CdS crystallize in both cubic and hexagonal phases, the hexagonal phase is the preferable one. The XRD spectrum revealed only a week (002) peak correspond to its hexagonal phase. The attenuation and broadening of the peak are characteristic of the finite size of the particles and stacking faults along the (002) axis [18,19].

To study the effect of cation/anion ratio on controlling the particle size, we measured the excitonic peak position in freshly prepared colloidal solutions containing different cation/anion ratio and after aging for a long time (about two months latter). The shift of excitonic peak positions were measured by:

$$\Delta\lambda = \lambda_{aged} - \lambda_{recent}$$

In figure 6, the shifts of excitonic peak positions are plotted against the percentage of anion present in the final mixture. It is revealed that the shift is small when either of
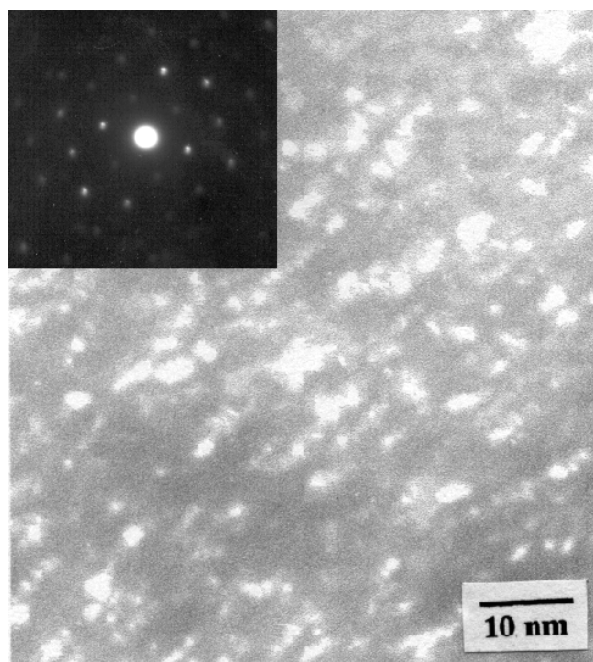
the ions was in large excess in the solution, which indicates that the presence of either ion in large excess in the solution terminates the crystallite growth process rapidly. The phenomenon can be explained by considering the formation of double electric layer at the crystallite interface. Generally when two ionic solutions are in contact, a potential difference establishes at the interface of the two mediums. There are three ways by which the double electric layer can be formed:

1) Due to the difference in the escape velocity of positive and negatively charged particles from one medium to other, i.e. from crystallite to the solution and vice versa.
2) Another possible origin of the double electric layer is the orientation of neutral molecules (electric dipole), over the crystallite surface. Though this double electric layer is not diffusive, it can induce a secondary diffused double electric layer from the attraction of mobile charge particles.
3) When one of the positive and negative ions is not in appreciable quantity in the medium and the ions of one type absorbed more than the other type at the crystallite surface.

As the $\Delta\lambda$s are very small for the mixtures containing large excess of either ions in our case, we assume that the third mechanism was responsible to form the double dielectric layers at the crystallite surfaces in our samples. The $\Delta\lambda$ is even smaller at the left extreme of the figure 7, where Cd^{++} were in large excess. As the ionic radius of Cd is lesser than that of S, the Cd^{++} ions are more mobile and weakly bound to the crystalline lattice and hence it has higher tendency of
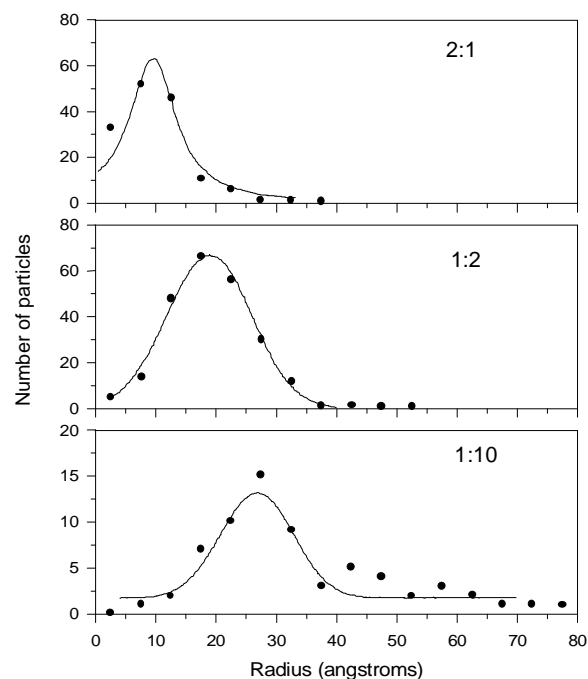

Figure 3. Typical TEM and TED micrographs of the sample prepared with 2:1:: $Cd(NO_3)_2$: $(NH_4)_2S$.

Figure 4. Size distribution of CdS particles prepared by mixing different ratios of $Cd(NO_3)_2$ and $(NH_4)_2S$ (all the samples extracted from aged mixtures).
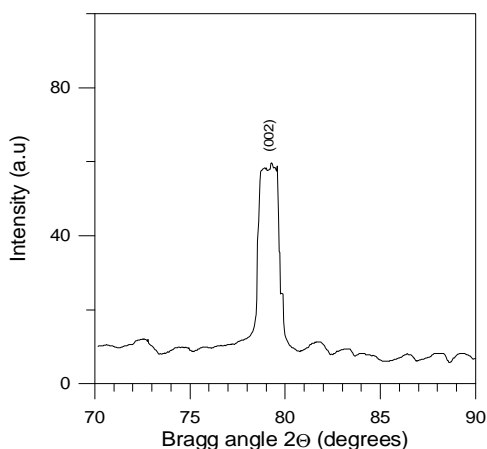
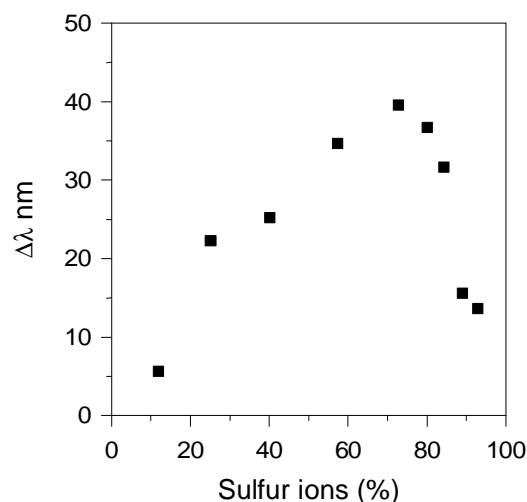Figure 5. Typical XRD pattern of the CdS nanoparticles.

Figure 6. Change in exciton peak position between the recently prepared and aged colloidal CdS particles for different percentage of anions/cations.

being absorbed at the crystallite surfaces. So, the accumulated Cd^{++} ions form the double dielectric layer with the other Cd^{++} ions at the surface preventing a further growth of the crystallites and hence the growth of the crystallites terminates rapidly.

4. Conclusions

Colloidal CdS nanoparticles were prepared using acetonitrile as the solvent. The growth kinetics of the particles has been studied. The size of the particles could be controlled either by terminating the growth process at different intervals of time or by controlling the proportions of cations and anions in the growth mixture. Being the smaller ionic radius and higher mobility of the Cd^{++} ions, its presence in large excess in the mixture solution forms the double dielectric layers over the crystallite surfaces and terminate the growth of crystallites rapidly. So, by controlling the ratio of cations and anions in the mixture solution we could control the size of the CdS particles.

Acknowledgements

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