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Effect of the organic solvent on the formation and stabilization of CdS and PbS nanoclusters

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Abstract

Nanoclusters of CdS and PbS were prepared using two different organic solvents as stabilizers in order to understand the factors affecting their formation and stabilization. Growth of the nanoclusters was monitored by optical absorption spectroscopy at regular intervals of time. Mean cluster size was characterized by X-ray diffraction (XRD). The surface structure of nanoclusters was analyzed using infrared (IR) spectroscopy. Spectroscopic studies under identical experimental conditions reveal interesting correlations between the stability of the nanoclusters formed, the nature of the solvent and the size of metal ion involved, leading to a better understanding of nanocluster formation.

Keywords: CdS nanocluster; Optical properties; Exciton Bohr radius

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1. Introduction

Semiconductor nanoclusters are known to show properties which are much different from those of the corresponding bulk materials [1]. Significant deviations from optical and electronic properties are observed when the dimension of the confined particle approaches the excitonic Bohr radius (r_B). Such nanoclusters are also called quantum dots due to their extremely small size as well as the strong quantum confinement effects observed. In view of their potential in opto-electronic device applications based on their enhanced nonlinear optical response [2], there is considerable interest in understanding the fundamental physics and chemistry of quantum dots of II–VI and IV–VI semiconductors [3,4].

Cadmium sulphide (CdS) is a wide gap semiconductor with bulk bandgap energy of 2.41 eV, corresponding to an optical cut-off of 515 nm, with exciton Bohr radius (r_B) of 3 nm. CdS has been used in photodetectors and for solar cell applications [5]. By tuning the size of CdS nanoclusters, it is possible to engineer the bandgap from the visible region to the UV region of the spectrum. Lead sulphide (PbS) is another interesting material with an exciton Bohr radius of 9 nm and a bulk bandgap of 0.41 eV, corresponding to an optical cut-off of 3020 nm [6]. PbS has been used in IR detectors. Strong quantum confinement effect in PbS nanoclusters permits the tuning of the optical absorption edge from IR region to the UV–vis region leading to remarkable changes in its optical properties across the spectrum.

Nanoclusters can be prepared using stabilizers such as thiols, phosphates and phosphine oxides or by restricting the reaction space by using matrices such as zeolites, glasses, polymers, reverse micelles, vesicles, LB films. Irradiation with sonochemical, microwave, ultraviolet or γ-irradiation has been attempted in order to increase the rate of nucleation in solution phase synthesis [7–13].

The present work focuses on the synthesis of CdS and PbS nanoclusters using dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) as solvents as well as stabilizers. An understanding of the stabilizing mechanism involved in the formation of CdS and PbS prepared under identical conditions and its correlation with the physical properties of the

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solvent would help in making the proper choice of the solvent for nanocluster stabilization. With this in view, such a correlation study was undertaken systematically.

2. Experimental method

Lead acetate trihydrate (LAT) and cadmium acetate dihydrate (CAD) were used as the source for lead and cadmium, respectively, and thioacetamide was used as the source for sulphur. LAT and CAD were purchased from Merck (99.9%, AR grade), thioacetamide from CDH chemicals. DMF and DMSO received from CDH chemicals were of HPLC grade and used without further purification.

In all the experiments, equal volume of 10 mM of the CAD (or LAT) in organic solvent was added to 10 mM TA with constant stirring. Immediately after the addition, the solution was poured into 1 cm quartz cuvette for optical absorption using Cary 5E UV-VIS-NIR Spectrophotometer. Optical absorption spectra were carried at regular intervals of time in order to monitor the size growth of nanoclusters.

XRD analysis was done using XD-D1 Shimadzu Horizontal Diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å). The samples used were in the form of flocculated powders (using acetone) in the case of CdS and precipitated powder in the case of PbS. IR spectrum was taken using Perkin Elmer Spectrum One FT-IR spectrometer on the pellets made by mixing the sample with KBr (weight ratio 1 mg:100 mg).

3. Results and discussion

3.1. Formation and stabilization of CdS nanoclusters

Fig. 1 shows XRD pattern of CdS nanoclusters prepared from DMF (a) and DMSO (b). Broad peaks observed in both the cases indicate the formation of CdS nanoclusters. Three major peaks were observed at 26.7°, 44° and 52.5° corresponding to the cubic phase of β-CdS (JCPDS No. 10-454). Although the appearance of symmetric peak around 26.7° suggests the formation of cubic β-CdS, the presence of small amount of hexagonal phase cannot be ruled out as the free energy difference between cubic and hexagonal phases is very small [14]. Mean cluster size was calculated by Scherrer's formula:

$$D = 0.9\lambda/\beta \cos\theta$$

where D is the diameter of the nanocluster, λ the wavelength of the incident X-rays, β the full-width at the half-maximum and θ the diffraction angle. The mean cluster size was found to be 5 nm for the samples prepared using either DMF or DMSO.

Optical absorption spectra for DMF- and DMSO-stabilized CdS nanoclusters with time are shown in Fig. 2a and b. Spectra were taken at various time intervals after mixing the reactants. The curve marked '0' corresponds to a freshly prepared solution of 0.01 M CAD in the corresponding solvent for comparison. The rest of the curves were recorded after different durations of reaction times from 1 to 60 min. The absorption onset for the samples got blue-shifted from the bulk value of 515 nm suggesting the formation of stabilized nanoclusters. Since either the pure solvent or metal ion dissolved in that solvent does not show any significant absorbance in the wavelength range shown, the spectra correspond to the formation of CdS nanoclusters and their growth. Absorbance value for nanoclusters in DMSO seems to be slightly more than in DMF prepared under identical condition. This can be attributed to the formation of the slightly larger number of nanocluster in DMSO than in DMF. Absorbance of the nanoclusters showed little change after 1 h. The size of the nanocluster formed was calculated by Brus formula [5,13]:

$$E = E_g + [\hbar^2\pi^2/2R^2]\,[1/m_e^* + 1/m_h^*] - 1.786e^2/\varepsilon R$$

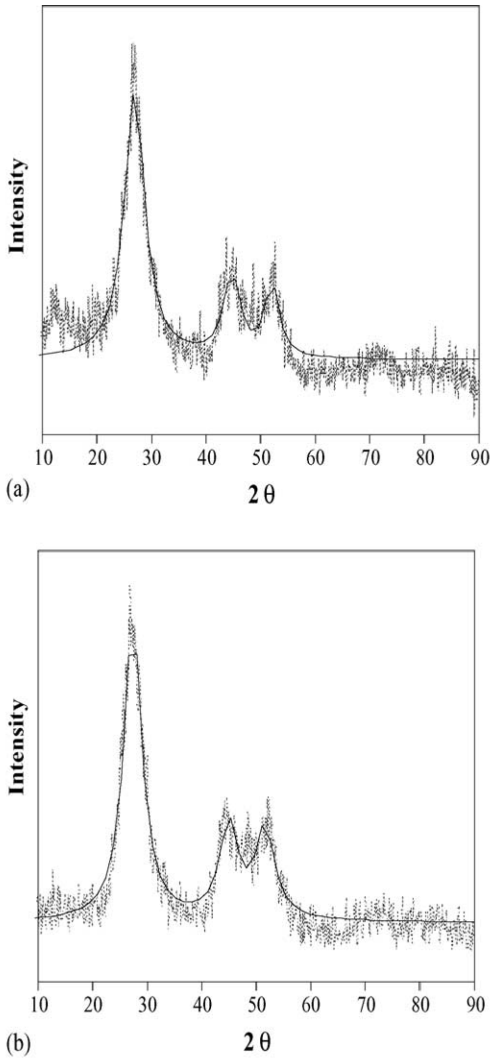

Fig. 1. XRD pattern of flocculated powder after 1 h for (a) DMF-stabilized and (b) DMSO-stabilized CdS nanoclusters (dotted lines indicate the pattern and solid indicates the Lorentzian fit).

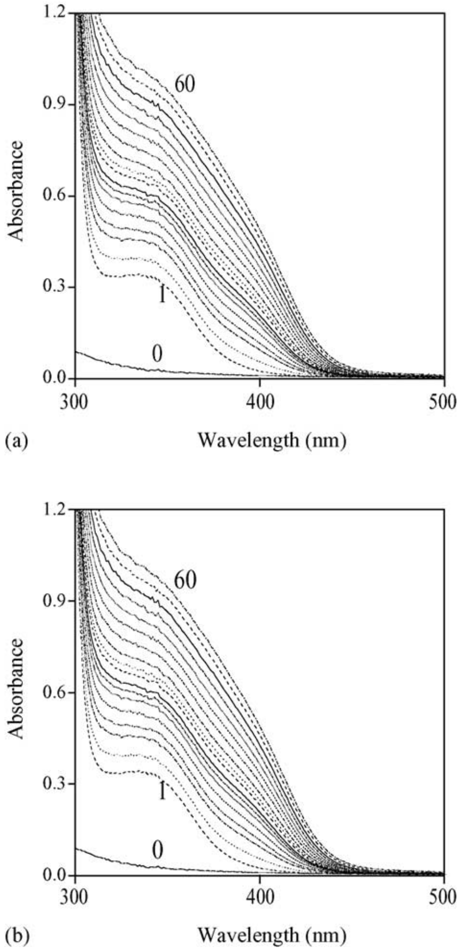

Fig. 2. Optical absorption spectra of CdS nanoclusters prepared in (a) DMF and (b) DMSO. The curves were recorded after different reaction time and are marked 0 to 60 accordingly.

where E_g is the bandgap of bulk CdS, m_e^* and m_h^* are the effective masses of the electron and hole, respectively, R and ε are the radius and dielectric constant of CdS, respectively. E_g is estimated from the absorption onset obtained by extrapolating the linear region of the optical absorption spectrum to intercept the wavelength axis. The mean cluster size estimated using the above formula was found to be 4.6 nm for the sample after reacting for 1 h, in good agreement with XRD results.

In order to find out the role of solvent on the nanocluster formation, IR study was carried out on the extracted powders. In Fig. 3a, 1651 cm^{-1} corresponds to C–O stretching frequency of CdS-DMF. Although pure DMF showed C–O stretching at 1674 cm^{-1}, this decrease in stretching frequency can be attributed to the coordination of O (from C–O in DMF) to the cadmium ion as shown below:

$$\mathrm{C=O} \longrightarrow -\mathrm{Cd}^{2+}\cdots\cdots\mathrm{O} \doteq \mathrm{C}$$

Coordination through O, leads to weakening of C–O bond and hence the observed reduction in stretching frequency which was in good agreement with earlier studies [15].

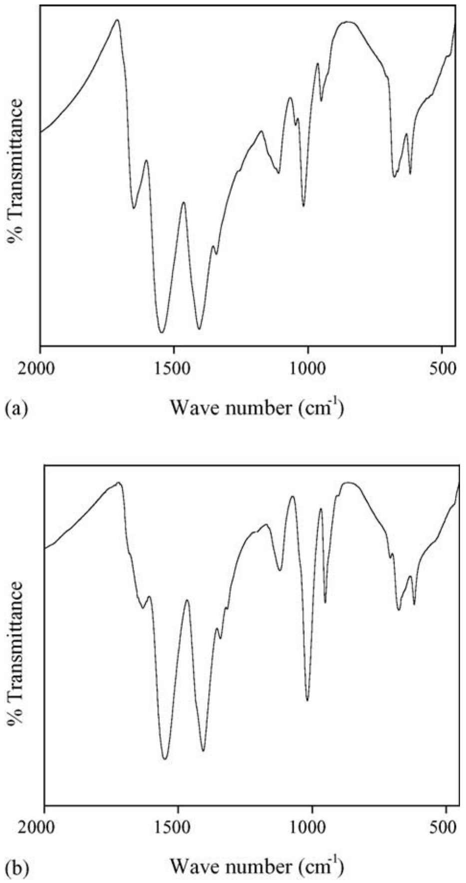

Fig. 3. IR spectra for CdS nanocluster stabilized in (a) DMF and (b) DMSO.

Fig. 3b shows IR spectra for CdS nanocluster prepared in DMSO. On comparing with pure DMSO it was found that S–O stretching frequency at 1050 cm^{-1} shifted to 1018 cm^{-1}. This is possible only if there is coordination of solvent to Cd^{2+}. Coordination to oxygen leads to weakening of S–O and corresponding decrease in stretching frequency. On the other hand, S coordination leads to strengthening of S–O and hence increasing stretching frequency. Since there is a decrease in frequency, O coordinates to the cadmium ion as shown:

$$\mathrm{S=O} \longrightarrow -\mathrm{Cd}^{2+}\cdots\cdots\mathrm{O} \doteq \mathrm{S}$$

Peaks were observed around 1550 and 1410 cm^{-1} in IR spectra of the nanoclusters where there is no peak for either of the pure solvent. These were attributed to acetate C=O asymmetric and symmetric stretching, respectively [15,16].

In case of pure CAD, peaks appeared at 1558 and 1419 cm^{-1}; the small reduction in stretching can be attributed to acetates weakly adsorbed onto the CdS nanocluster surface, thereby weakening the stretching frequency. Further, when IR was performed with samples washed thoroughly with methanol these peaks disappeared suggesting that nanocluster surface was capped with O atom of the organic solvent and small amount of adsorbed acetate was present in the as-prepared condition.

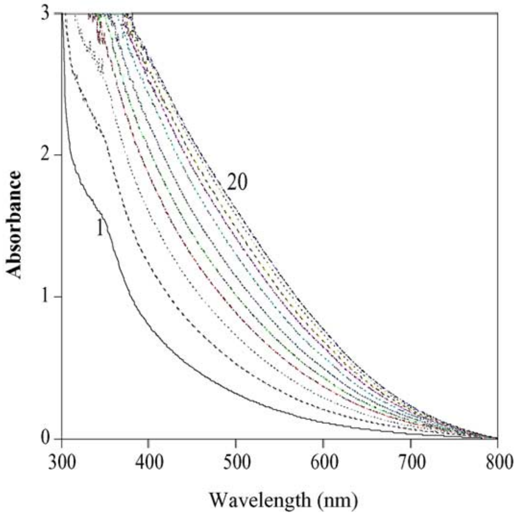

Fig. 4. Optical absorption spectra for PbS nanoclusters prepared in DMF (numbers indicate time in minute).

3.2. Formation and stabilization of PbS nanoclusters

Optical absorption spectra of PbS nanoclusters prepared in the presence of DMF are given in Fig. 4. The curves from left to right are in the order of increasing reaction time during which the spectra were recorded. The left most curve is after 1 min and the right most one is 20 min after mixing the reactants. Initially the sample was light reddish-brown in colour which quickly changed to deep brown and then black. Accordingly, the cut-off wavelength in the optical absorption spectra was found to shift to a larger value indicating the cluster growth. Although there is a large shift in bandgap compared to the bulk cut-off value (3020 nm), a large amount of scattering was observed in the sample after 20 indicating the formation of larger clusters. The material got precipitated completely within 30 min.

XRD pattern of PbS nanoclusters prepared with DMF as the solvent is shown in Fig. 5. All the peaks matched with those of cubic rock salt PbS (JCPDS No. 5-0592) and the appearance was similar to that of bulk PbS material. This could be due to quick precipitation into bulk form by the time XRD was recorded. Similar results were obtained also for PbS nanoclusters prepared with DMSO.

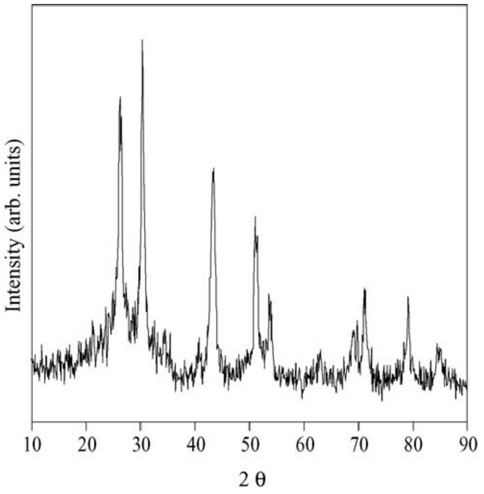

Fig. 5. XRD pattern of PbS prepared in DMF as the solvent.

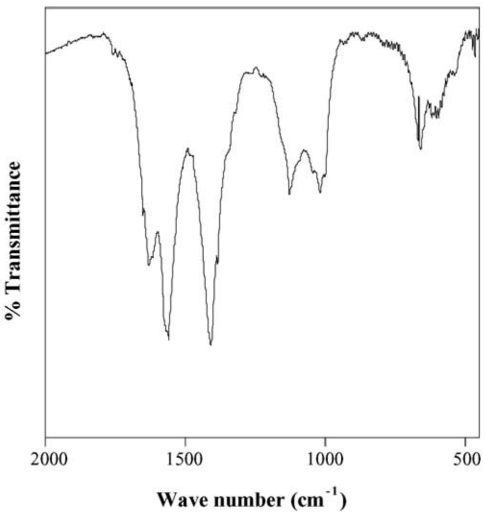

Fig. 6. IR spectra of PbS prepared in DMF.

IR spectra of PbS prepared in DMF (Fig. 6) showed no shift in peak position unlike CdS nanoclusters prepared in DMF. It is likely that there was no stabilization of Pb^{2+} ions by DMF (a similar trend was observed in DMSO).

Optical absorption spectra of PbS nanoclusters prepared with DMSO as solvent are shown in Fig. 7. Since neither of the pure solvent nor LAT dissolved in DMSO show any significant features, this can be attributed to the formation of PbS nanoclusters which grow in size with time. Features in optical absorption spectra are similar to those of PbS nanoclusters stabilized with polyvinyl alcohol having size in the range of 3.5–4 nm [17], indicating the formation of PbS nanoclusters

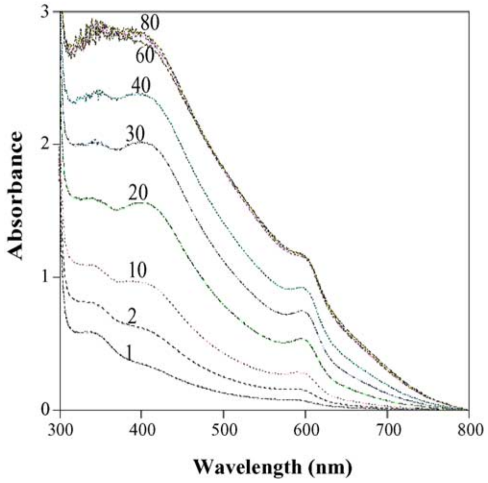

Fig. 7. Optical absorption spectra of PbS clusters prepared in DMSO (numbers indicate time in minute).

with DMSO as solvent. Three peaks were observed around 600, 400 and 300 nm which were significantly enhanced after 10 min. Absorbance values at these three different wavelengths are shown in Fig. 8. All the cases show an increase in absorbance with time up to 60 min and saturation thereafter. Observation beyond this period was difficult, as there was large scattering. Although there seems to be formation of PbS nanoclusters, it was difficult to stabilize these beyond a period of an hour, as they got precipitated as bulk PbS. However, stabilization appears to be slightly better with DMSO when compared to DMF.

3.3. Effect of solvent on the stabilization of cation

Cadmium and lead salts form corresponding solvated ions on dissolution in DMF and DMSO. Since solvent can easily polarize the cadmium ions, it coordinates well to the solvent molecules compared to lead ion due to latter's larger size [18]. Since Pb^{2+} ions were not stabilized strongly by the solvent coordination, it resulted in the formation of bulk PbS compared to cadmium ions which form stabilized CdS nanoclusters. In order to compare the effect of solvent properties such as dielectric constant and the donor and acceptor numbers, water was used instead of organic solvent under the same experimental conditions. Precipitation was found to be immediate and XRD results clearly indicated the formation of bulk CdS and PbS.

Water having higher dielectric constant, lower DN, higher AN (Table 1) and strong hydrogen bonding ability seems to have poor coordinating ability resulted in the formation of bulk form of both CdS and PbS material rather than stabilized nanoclusters. On the other hand, since organic solvent coordinates to the metal ion they can stabilize the nanocluster easily.

In spite of having the same anion (S^{2-}) and similar charge on the cation, there seems to be a large difference as far as the stabilization of CdS and PbS nanoclusters is concerned. This is probably due to the larger size of the Pb^{2+} ion, where the charge is spread over a large volume, making it more difficult to get polarized easily. Although optical absorption spectra show the formation PbS nanoclusters in the presence of organic solvents, the product was found to be unstable due to weak solvent coordination resulting in the formation of bulk PbS. Solvents having high donor number (and hence increased polarizability) could be a better choice for the stabilization of PbS nanoclusters.

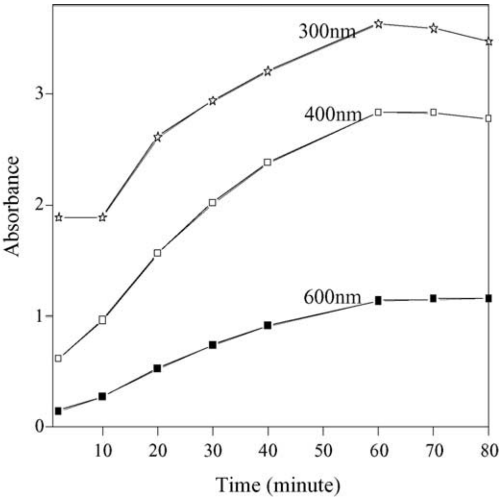

Fig. 8. Absorbance change plotted as a function of time.

Table 1
Physical properties of solvents [19,20]

Solvent property	Water	DMF	DMSO
Nature of solvent	Protophilic H– bond donor	Aprotic protophilic	Aprotic protophilic
Dielectric constant (ε)	78.5	36.71	46.45
Dipole moment (Debye)	1.84	3.86	3.96
Donor number (DN)	16.4	26.6	29.8
Acceptor number (AN)	54.8	16.0	19.3

The optical absorption spectra of PbS nanoclusters in DMF did not show any specific peak (Fig. 4) whereas the spectra of PbS in DMSO showed clear absorption peaks (Fig. 7), similar to those reported in PVA [17]. These peaks correspond to exciton transitions and clearly formed peaks are indicative of a narrower size distribution. Variation in the size of nanoclusters leads to a distribution in the exciton peak positions, smearing the peaks and rendering the spectrum featureless. Thus DMSO appears to help in the formation of PbS nanoclusters of a narrower size distribution compared than that obtained with DMF as solvent. This is attributed to the larger donor number (Table 1) and the resulting improved stabilization in the case of DMSO as compared to DMF. In the case of PVA, the PbS nanoclusters are likely to be wrapped around by PVA which prevents them from further aggregation.

4. Conclusions

A systematic approach is employed to prepare CdS and PbS nanoclusters under identical conditions using two different organic solvents and to compare the effect of solvent properties on the stabilization of nanoclusters. Spectroscopic studies help to delineate the stabilizing mechanism of both the solvents in the formation and stabilization of CdS nanoclusters. However, no effective stabilization was possible in the case of PbS nanoclusters with either of these solvents. It appears that while moving from a smaller to a larger cation, a stronger stabilizing solvent environment is required. Donor number is one of the parameters that can be used as a guideline for selecting the proper solvent for stabilization of nanocluster. Understanding the correlations between the mechanism of nanocluster stabilization and the physical properties of the solvents appears to be of crucial significance in nanocluster synthesis and further experiments in this direction are in progress.

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