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Characterization of CdS,CdXZn1-XS and ZnS Nanocrystallites Grown by Chemical Route

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Abstract

A simple chemical reduction route at room temperature is adopted for the synthesis of CdS, CdXZn1-XS and ZnS nanocrystallites. Anhydrous $CdCl_2$ or $ZnCl_2$, S and $NaBH_4$ react in organic solvent THF. The nanoparticles are characterized by X-ray diffraction, UV-Vis absorption, Photoluminescence and TCSPC study. The particle size ranges from 5 to 10 nm. There is a change of phase from CdS to CdXZn1-XS and finally to ZnS. The lattice changes from hexagonal phase to cubic phase with an increasing percentage of Zn in the ternary compound. The nanoparticles exhibit an absorption peak that shifts towards the lower wavelength side with an increasing percentage of Zn in CdXZn1-XS. The band gap increases as the phase changes from CdS to CdXZn1-XS. Also, the band gap is found to be greater than the bulk value due to the formation of nanoparticles. Photoluminescence and Fluorescence Lifetimes are determined through PL and TCSPC measurements for each composition. The composition-controlled growth of CdXZn1-XSnanostructures is essential for utilizing them in the fabrication of laser diodes.

Keywords: Nanoparticles; Optical; Absorption; Particle Size ; Photoluminescence

Public Interest Statement

While many of the advances in materials science have been driven by breakthroughs in material design and fabrication, understanding the changes that occur in a material during its utilization or operation in devices is of immense importance for its successful integration. Considering these aspects and the continued growth in materials research, there is a clear need for new topical journals which can serve researchers to understand the phase transitions and exploit the phenomena to current, state-of-the-art research in the field of materials science, moreover with full accessibility.

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Introduction

The synthesis and characterization of semiconducting nanoparticles are important because of their novel properties and three-dimensional confinements [1-5]. Nanofilms of CdS and ZnS are attractive materials in optoelectronic devices such as Solar Cells and Photodetectors. Also, CdXZn1-XS is an important material for blue and ultraviolet laser diodes [6-8] and is based on quantum well structures. Thus CdXZn1-XS can be the ideal material for laser diode applications in the lower wavelength region. Group II-VI semiconductors form defects at high temperatures. Therefore, low-temperature growth of II-VI semiconductors is preferred. Most of the methods utilized for growing nanocrystalline CdS and ZnS have some limitations. Either high temperature is required, or they employ toxic precursors [9-10]. We prefer a simple chemical route to grow nanocrystalline CdS, CdXZn1-XS and ZnS at room temperature. CdCl2, ZnCl2, Sulphur, NaBH4 powders act as reactants. The reaction is carried out in solvent THF (Tetrahydrofuran). THF acts as capping agent (11). Optical absorption spectra of CdS nanoparticles show the quantum size effects while Photoluminescence spectra of nanoparticles give the information of the surface (12).

For any applications based on the optical properties of nanocrystals, it is essential to use high-quality nanocrystals. In principle, high-quality nanocrystals should possess at least two characteristics, high emission color purity and high photoluminescence quantum yield (PL QY)[13-14]. The color purity of the emission is strongly dependent on the size distribution of the nanocrystals. The narrower the size distribution, the purer the color of the emission light, which can be reflected by the narrow PL emission bandwidth and/or the narrow UV/Vis band-edge absorption bandwidth. Very recently, Pan et al. developed a two-phase approach to successfully synthesize highly luminescent and nearly monodisperse CdS nanocrystals. Based on the work by Pan et al., we developed a new two-phase approach to synthesize high-quality CdS nanocrysals in an autoclave. Compared with the earlier results, the CdS nanocrystals obtained by the new approach exhibit a narrower size distribution and a higher PL QY[15-17].

Experimental Details

A stoichiometric amount of $CdCl_2$ is added to a beaker containing THF and a white suspension is formed due to stirring. After 5 minutes of stirring,an appropriate amount of sulfur powder is added to the beaker. After that, $NaBH_4$ is added. The suspension turned light yellow. The mixture was stirred for three and half hours. A yellow precipitate wasformed, which was filtered and washed with ethanol. After that, it was washed with distilled water several times to remove impurities. Then the sample was dried at room temperature for 12h and kept for further characterization. $ZnCl_2$ was used instead of $CdCl_2$ for synthesizing ZnS nanoparticles. For the preparationof $Cd_XZn_{1-X}S$, stoichiometric amounts of $CdCl_2$ and $ZnCl_2$ powders were used according to the molar ratios of the target compound like $Cd_{0.7}Zn_{0.3}S$, $Cd_{0.5}Zn_{0.5}S$, $Cd_{0.3}Zn_{0.7}S$. X-ray diffraction patterns were obtained by using a Rigaku X-ray diffractometer with CuK_L radiation in the range of 20 to 70^0. Absorption spectra were recorded using a Shimadzu UV-Vis spectrophotometer with a 1 cm quartz cell. PL spectra of CdS and $Cd_XZn_{1-X}S$ were measured using pulsed laser excitation. Fluorescence lifetime was measured for each sample using TCSPC.

Results and Discussion:

Figure 1 below displays the XRD patterns obtained from CdS nanoparticles as well as for all compositions like $Cd_{0.7}Zn_{0.3}S$, $Cd_{0.5}Zn_{0.5}S$, $Cd_{0.3}Zn_{0.7}S$ and finally ZnS. The pattern well matches with the diffraction profile of standard CdS and ZnS. XRD pattern of CdS nanoparticles show

peaks around scattering angles (2θ) at 25 and the planes from which scattering takes place are (100), (002), and (101). The multiple peaks of CdS transform into single peak as we move towards ZnS with gradual increase of Zn content[18]. The XRD pattern of the as prepared ZnS nanocrystals matches well with the bulk ZnS. CdS nanoparticles have hexagonal phase. It goes to cubic phase for ZnS. Average particle size is estimated using Scherrer equation:

$$P=k\lambda/B_{1/2}Cos\theta.....(1)$$

Where λ is the wavelength of X-ray, $B_{1/2}$ is the width at half of maximum intensity, θ is the Bragg angle. The particle size calculated from the peak at 2θ around 25 for each sample shows that it varies from 5 to 10 nm.

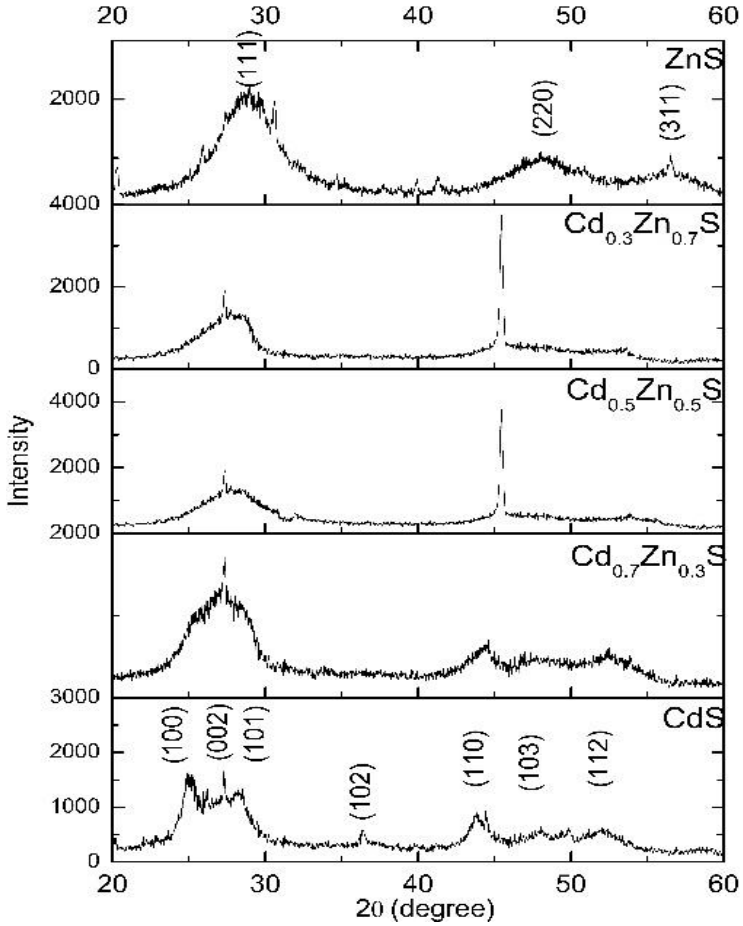


Fig.1: XRD patterns of CdS, $Cd_{0.7}Zn_{0.3}S$, $Cd_{0.5}Zn_{0.5}S$, $Cd_{0.3}Zn_{0.7}S$ and ZnS nanocrystallites.

In **Figure 2**, optical absorption data shows absorption peak gradually shifts towards lower wavelength as we shift from CdS to ZnS through $Cd_{0.7}Zn_{0.3}S$, $Cd_{0.5}Zn_{0.5}S$, and $Cd_{0.3}Zn_{0.7}S$. The shift of the absorption peak indicates that there is increase of band gap as we move from CdS to ZnS through different compositions.

The direct band gap relation involving band gap and frequency of incident wave shows that

$$(\alpha h\nu)^2=Const(h\nu-E_g).....(2)$$

Where α is the optical absorption coefficient and E_g is the direct band gap.

The band gap was determined from $(\alpha h\nu)^2$vshv plot and is shown in **Figure 3**.The band gap increases as we go towards ZnS from CdS with the increase of Zn content. The change in band gap energy is due to compositional change. Also, there is a simultaneous increase in band gap due to the formation of nanoparticles at each composition.

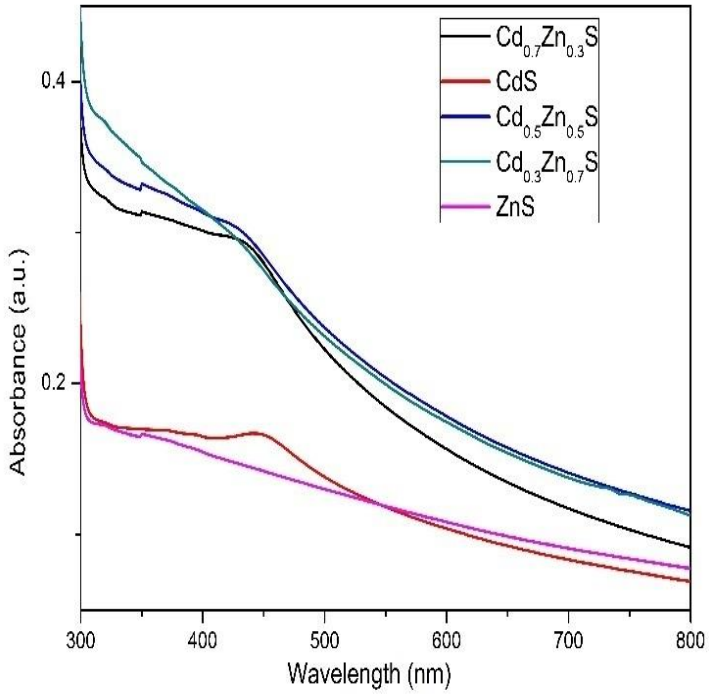


Fig 2: UV-Vis absorption spectra of the CdS,$Cd_{0.7}Zn_{0.3}S$, $Cd_{0.5}Zn_{0.5}S$, $Cd_{0.3}Zn_{0.7}S$ and ZnS nanocrystallites.

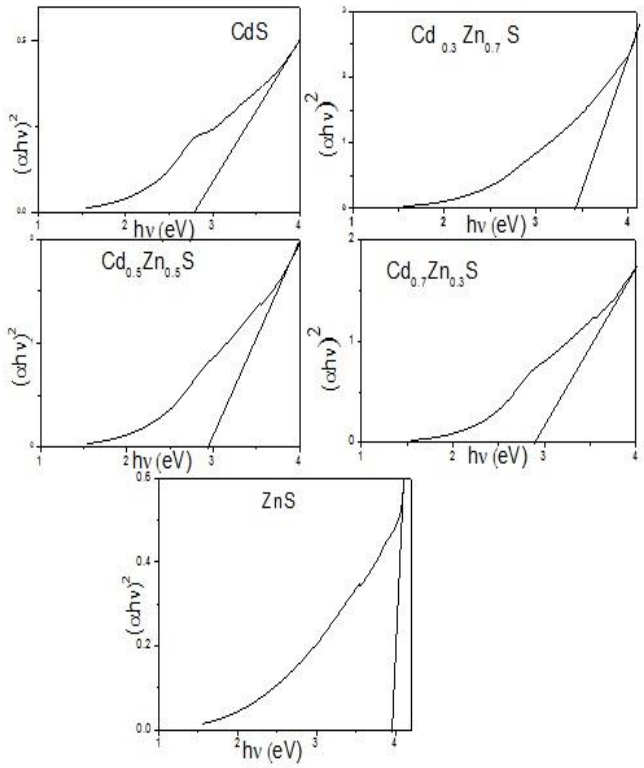


Fig 3: $(\alpha h\nu)^2$vshv plots for CdS and $Cd_xZn_{1-x}S$ nanocrystals.

Figure 4 shows the PL spectrum of CdS nanoparticles which revealed a strong emission band around 550 nm. The excitation wavelength varied between 370 and 440 nm. The PL excitation is varied for different materials since the band gap changes from 2.78 eV for CdS to 3.97 eV for ZnS. The position of the PL emission band shifts towards a lower wavelength as we move towards ZnS from CdS. Time-correlated single-photon counting (TCSPC) was used to measure the fluorescence decays in the time domain.

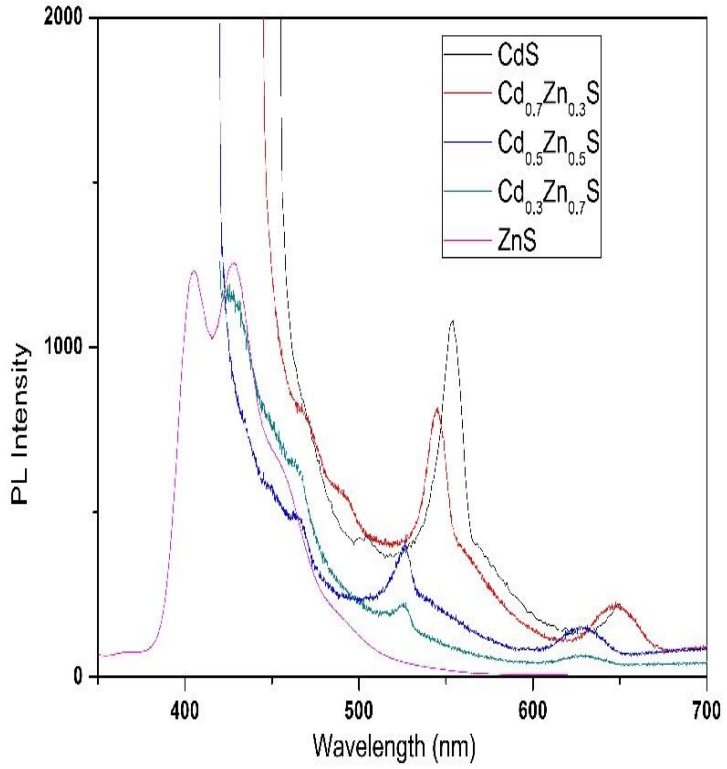
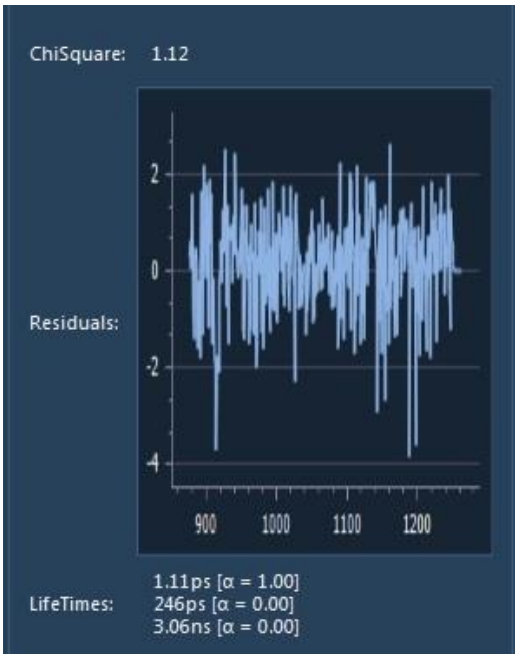


Fig 4: PL spectra of the CdS and $Cd_xZn_{1-x}S$ nanocrystals

Figure 5aand **5b** shows that fluorescence lifetime increases from 3.06 ns for CdS to 5.19ns for ZnS. We have shown the best Chi-Square fit for CdS and ZnS.The fluorescence lifetimes are found to be 3.06 ns and 5.09 nsrespectively. This indicates that with the increase of band gap energy, the fluorescence lifetime increases to a small extent.

Thus, we have successfully grown CdS, ZnS nanostructures as well as different phases i.e., $Cd_{0.7}Zn_{0.3}S$, $Cd_{0.5}Zn_{0.5}S$, $Cd_{0.3}Zn_{0.7}S$ in a simple cost-effective way at room temperature. The different phases could be achieved by gradual substitution of Cd atoms by Zn atoms in the CdS lattice. The control of the composition of $Cd_XZn_{1-X}S$ may lead to the application of these nanostructures in different optoelectronic devices.

The results below (Table 1) are typical characteristics of CdS or ZnS nanocrystallites obtained from the thermal decomposition. Some of the results using other single-molecule precursors and other synthetic conditions their band gap as well as PL peak position are summarized in Table 1. The absorption edge of CdS obtained did show a slight red-shift as compared to CdS samples obtained from the other precursors.



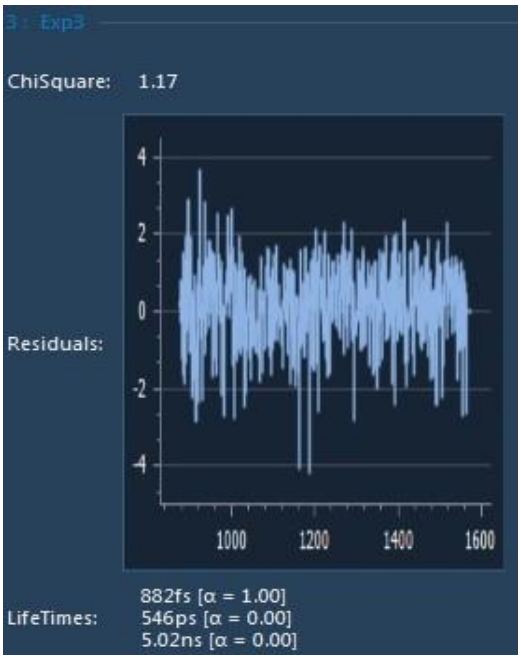


Fig.5a Fig.5b

Fig. 5: a) Chi square 1.12 fit for CdS; b): Chi square 1.17 fit for ZnS.

Table-1 Characteristics of grown samples

Sample	Band gap (eV)	PL peak position (nm)	Fluorescence lifetime (ns)
CdS	2.78	554	3.06
$Cd_{0.7}Zn_{0.3}S$	2.88	545	4.29
$Cd_{0.5}Zn_{0.5}S$	2.93	526	4.4
$Cd_{0.3}Zn_{0.7}S$	3.42	525	4.64
ZnS	3.97	427	5.09

Conclusion

In conclusion, a new two-phase approach has been developed for synthesizing high-quality CdS nanocrystals with a relatively narrow size distribution and a high PL. By using a seeding-growth technique, a relatively wide controllable size range of nanocrystals can be achieved and a focusing of the size distribution can be maintained throughout the whole size range. Compared with the traditional route, the approach can be performed at relatively low temperature without the need for stirring and hot injection. In addition, the approach may be applied to the synthesis of other semiconductor nanocrystals; in particular, the seeding-growth technique also provides a novel and feasible approach for the synthesis of high-quality nanocrystals with core/shell structure, work on which is currently underway.

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