Preparation, structural and linear optical properties of Zn doped CdS nanopowders

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Abstract. A series of Zn doped cadmium sulfide (CdS:Zn) nanopowders were prepared by a simple co-precipitation method at room temperature by mixing the stoichiometric amount of reactants in a Milli Q water solvent. The composition of nanopowders was accurately adjusted by controlling the molar ratio of Cd, Zn acetate in the mixed reactants. Spectroscopic studies on as prepared nanopowders were investigated by using XRD, Raman, UV-Vis absorption, FE-SEM-EDAX and photoluminescence. Extremely broad reflections of XRD peaks of as prepared powders establish the nanometer scale dimensions and cubic structure. Doping with Zn in CdS does not lead to any structural phase transformation but introduces a decrease in the lattice constants. Two characteristics of LO phonon peaks were observed in pure and Zn doped CdS samples. Raman peaks of Zn doped CdS nanopowders shifts slightly towards higher energy side compared to the pure CdS nanopowders. Exciton-phonon confinement factor (S) varies in between 0.3-0.4. At lower wavelength excitation we observed a broad emission peak maximum centered at 404 nm is attributed to localized band edge emission.

1. Introduction
Colloidal semiconductor nanoparticles or quantum dots (QDs) have generated enormous attention in the past decade because their optical and electronic properties, which are dramatically different from those of the corresponding, bulk crystals, as well as their wide applications in the fields of optoelectronic and biological technology. Chalcogenide semiconductors such as cadmium sulfide is a II-VI compound semiconductor with a wide direct band gap of 2.42 eV (bulk CdS) and a small exciton Bohr radius of 2.5 nm. When the nanoparticle radius is comparable to the Bohr exciton radius in the corresponding bulk material, it leads to splitting of continuum of electronic energy levels into discrete states with the effective band gap energy blue shifted from that of the bulk. II-VI semiconductor nanostructures have been investigated widely and demonstrated for potential applications in solar cells, light emitting diodes, IR photodetectors, electrically driven lasers, optical limiters, biological fluorescent labels and upconversion luminescent materials.

Most of the efforts are focused on equal valence charge doping. Recently, transition metal ions doped II-VI nanoparticles have attracted keen interest because transition metal ions incorporated into II-VI nanoparticles can improve significantly the optical properties of nanoparticles. The optical properties of doped nanomaterials differ from the corresponding host nanomaterials [1]. Thrust of recent research has been the synthesis of quantum-dot sized doped CdS nanoparticle powders. Recently, attempts were made on the use ofCd_{1-x}Zn_xS nanoparticles for production of hydrogen from water under visible light irradiation with greater efficiency than using pure ZnS and CdS nanoparticles [2-4]. Cd_{1-x}Zn_xS film was shown to have good photovoltaic efficiency [5].
The present work is focused on the cost-effective synthesis and its physical properties of the cubic structure Zn-doped CdS nanoparticles at room temperature. The synthesis method presented is an easy, inexpensive, and single-step method.

2. Experimental section
2.1 Preparation technique
Pure and doped CdS nanoparticles were prepared by the colloidal chemical precipitation method at room temperature [1]. Three different molar ratios of cadmium acetate to zinc acetate, 10:0, 9:1, and 8:2 were prepared. About 15 ml of polyvinyl pyrrolidone (PVP MW-55,000) solution in methanol (0.5M) was added to 30 ml of the aqueous solution of Cd - Zn mixture solution with vigorous stirring. At room temperature 0.1 M Na$_2$S aqueous solution was added slowly drop wise to the Cd - Zn mixed solution under vigorous stirring. After 1 hour and 30 minutes stirring precipitate particles were isolated from the solution by centrifugation at 6000 rpm for 15 min. The product was washed by milli Q water and absolute ethanol through multiple cycles of centrifugation and redispersion. The yellow precipitate obtained was air dried.

2.2 Characterization
Crystal structure of the powder sample was determined using powder X-ray diffractometer (Inel C120) which is equipped with a curved position sensitive detector and data was collected using Co-K$_\alpha$ radiation of wavelength 0.17889 nm. Raman spectra, was obtained using Horiba Jobin Yvon LabRam HR high resolution micro-Raman spectrophotograph with 514 nm of Argon ion laser as the excitation source. FE-SEM-EDAX analysis was carried out using Carl Zeiss Ultra 55 model. UV-Visible spectral analysis was carried out on a JASCO UV-Visible absorption spectrophotometer with a resolution of 1 nm in the range of 200 to 1200 nm with a scanning speed of 200 nm/min. Steady-state photoluminescence (PL) characteristics of as prepared powders dispersed in chloroform placed in a 1 cm path non-fluorescent quartz cuvette, were measured by Jobin Yvon Inc., Fluorolog 3 spectrofluorometer with a spectral resolution of 1 nm.

3. Results and Discussions
3.1 XRD
X-ray diffraction (XRD) peaks of pure and doped CdS powders reflection were broadened and as shown in Fig. 1 and its lattice parameters were calculated. The broadening can be attributed to a very small grain size of the particles. The reflection peaks of as synthesized powders can be indexed to be cubic phase, with JCPDS data card no 800019 at Co-K$_\alpha$ radiation of wavelength 0.17889 nm. Since we did not observe any characteristic peaks of the impurity phases in the XRD spectrum, we have concluded that the dopant is distributed homogenously without clustering or segregation with increase
of the doping percentage, the XRD peak position shifts slightly towards higher angle relative to that of the pure CdS powders. Similar patterns were observed in Mn, Zn co-doped CdS nanowires [6]. Lattice parameters of pure and doped (Zn 10%, 20%) CdS were 5.7941, 5.7836 and 5.7001 Å. The ionic radius of Zn$^2+$ (0.74 Å) ion are smaller than Cd$^2+$ (0.97 Å) ion. So doping with Zn in CdS does not lead to any structural phase transformation but introduces a decrease in the lattice constants.

3.2 Raman Studies
A Raman spectrum of as synthesized powders is shown in Fig. 2. Bulk CdS has two characteristic LO phonon peaks, 1-LO (300 cm$^{-1}$) and 2-LO (600 cm$^{-1}$) vibrations [7]. These two characteristic LO phonon peaks were observed in pure as well as in Zn doped CdS samples, however at lower energies (pure CdS 293, 593 cm$^{-1}$) compare to their bulk CdS, which could be due to quantum confinement. With increase of Zn content, 1-LO and 2-LO modes shift towards higher energy side compared to their pure CdS nanopowders which is consistent with the Cd$\rightarrow$Zn substitution in the nanopowders. The intensity ratio of the 2-LO to 1-LO modes ($I_2^{LO}/I_1^{LO}$) is the parameter used to specify exciton-phonon coupling strength ($S$) in semiconductors. Calculated exciton-phonon coupling strength ($S$) for pure and doped (Zn 10%, 20%) CdS powders were 0.3914, 0.3414 and 0.3005. Our observations are in agreement with an earlier reported decrease in ratio from 0.88 to 0.42 from bulk to nanospheres at 514 nm excitation [7]. The phenomenon was attributed to lowering of the exciton-phonon coupling due to quantum confinement.

3.3 FE-SEM-EDAX Studies
Field Emission Scanning Electron Microscope (FE-SEM) images and Energy-Dispersive X-ray Analysis (EDAX) were obtained from as synthesized powders mounted on double sided carbon tape. Fig. 3 shows a FE-SEM image of as synthesized pure CdS powders. The grains are found to have aggregated to form clusters. Fig. 4 shows EDAX analysis of as synthesized powders. From the clear peaks of Cadmium (Cd), Zinc (Zn) and Sulphur (S), it can be noted that our sample did not show any trace elements other than cadmium, zinc and sulphur. The compositional ratio of Cd:Zn in the nanocrystals is approximately equal to that reactant mixture over a large composition range.

3.4 UV-Vis absorption spectroscopy
UV-Vis Absorption spectrum of pure and doped CdS powders dispersed in chloroform at same concentration is as shown in Fig. 5. The band gaps for pure and Zn doped CdS powders are blue-shifted relative to bulk CdS, which has a band gap at ~ 2.42 eV (512 nm), suggesting the formation of
nanometer-sized CdS particles. The broad absorption peak around 462 nm is attributed as due to the surface states of the aggregated particles [7] and the narrow peak around 280 nm is attributed as due to the exciton peak of CdS. Absorption peak at 280 nm shows broadening in the case of Zn doped CdS compared to their pure CdS, which could mean that the exciton peaks energies in the doped system are distributed over wide energies.

3.5 PL studies
Emission spectra were recorded by exciting as prepared solid nanopowder dispersed in chloroform (4×10^{-4}M) through 15 minute ultrasonication and as shown in Fig. 6. At lower wavelength excitation we observed a broad emission centered at 404 nm from all samples. It was reported that this kind of band-edge luminescence is caused by the recombination of shallow region trapped electron-hole pairs and/or excitons [7]. The absence of emission from trap (defect) states, which normally appears around 635 to 675 nm range, suggests the stoichiometric nature of CdS, without a surface excess of Cd^{2+} or S^{2-} vacancies. Another interesting feature is that at low doping concentrations of ~ 10 % of Zn, the emission intensity increases but at higher dopings of 20%, the emission intensity slightly decreases as shown Fig. 6. The increase in the emission intensity is attributed as due to ZnS. The attenuation of the fluorescence is attributed to possible self quenching.

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