

Luminescence Properties Of Semiconductor Nanocrystals Synthesized In Organic Phase

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Abstract—The present work provides a potentially efficient and a simple chemical route for the synthesis of CdS & $Cd_{(1-x)}Mn_xS$ nanocrystals in organic phase at ambient room temperature. The nanostructures of the prepared undoped CdS and Mn^{2+} doped CdS:Mn nanoparticles have been analysed using UV-vis spectrophotometer, Fourier Transform Infrared studies and fluorescence emission spectra have been studied. There is a wavelength shift in the emission of manganese doped samples. The size and shape of the synthesized nanoparticles have been studied using the Transmission Electron Microscope.

Chemical manipulation towards both size and shape tunable preparation is achieved successfully.

Keywords—Quantum confinement, absorption, emission, Doping, Capping agent, organic phase

I. INTRODUCTION

Development of synthesis protocols for nanomaterials over a range of sizes, shapes and chemical compositions is an important aspect of nanotechnology. In recent years, we have witnessed impressive advances in understanding the unusual physico-chemical and opto-electronic properties of nanomaterials, their synthesis, assembly and packaging for commercial applications [1]. One important area of nanotechnology is involved in the development of reliable processes for the synthesis of nanomaterials over a range of sizes with good monodispersity and chemical composition [2]. Due to high surface area, the nanostructured materials possess a high surface energy and therefore are thermodynamically unstable or metastable. One of challenges in fabrication and processing of nanomaterials is to overcome the surface energy and to prevent the aggregation of nanomaterials. Due to high surface energy of the nanoparticles, they are extremely reactive and most systems without protection or passivation of their surfaces undergo aggregation [3]. Organic stabilizers are usually used to prevent nanoparticles from aggregation by capping their surfaces [4].

Metal nanoparticles have attracted considerable interest in fields such as optics and catalysis, because of their size and shape dependent physico-chemical properties [5]. Among such procedures, those that require an aqueous medium are the most convenient to develop because of water's ability to solubilize a variety of ions and stabilizing molecules. On the other hand, nanoparticles prepared in organic media are interesting for

applications to catalytic processes and for surface modifications with organic functional groups to fine tune their properties [5-8]. Differently sized and shaped metal nanoparticles can be obtained in organic media either by preparing them directly in those media [9] or by transferring nanoparticles from aqueous phase to organic phases [10-13]. The first approach is very sensitive and difficult to achieve convenient size and shape controllable processes. The second approach has the advantage that there are many well developed procedures available for the preparation of well-defined metal nanoparticles in aqueous media.

Phase transfer of metal nanoparticles from aqueous phase to an organic phase can be achieved by capping the nanoparticles with thiols and amines [10], or by using phase-transfer reagents, such as surfactants to improve the solubility of nanoparticles in organic media.

CdS is a II-VI semiconductor. CdS nanoparticles exhibit size dependent properties. It has a band gap energy, E_g , of 2.42eV [14] at room temperature and pressure. Since CdS has wide band gap, it is used as window material for hetero-junction solar cells to avoid the recombination of photo-generated carriers which improves the solar cell efficiency [15]. It has applications in Light Emitting Diodes [16], Photo detectors [17] and sensors [18].

The paper highlights the method of synthesis of cadmium sulphide nanocrystals in chloroform with Octa Decane Thiol as the capping agent.

II. EXPERIMENTAL DETAILS

A. Chemicals

Cadmium Nitrate- $Cd(NO_3)_2$, Stearic Acid- $C_{18}H_{36}O_2$, Chloroform- $CHCl_3$, Octadecane Thiol - $C_{18}H_{38}S$, Manganese chloride- $MnCl_2$, Yttrium Carbonate- $Y_2(CO_3)_3$ were of analytical grade and were used as received..

B. Sample Preparation

For synthesis, 50 mL of $10^{-3}M$ aqueous $Cd(NO_3)_2$ solution whose pH was adjusted to 8.5 was mixed with 50 mL of $10^{-3}M$ stearic acid in chloroform. The mixture is stirred vigorously using a magnetic stirrer for 5 hours at room temperature.



This leads to the transfer of the cadmium ions from the aqueous phase to the organic phase. The phase transferred cadmium ions present in organic medium were separated from the stirred solution. Equal volumes of phase transferred cadmium ions and 5×10^{-3} M ODT dissolved in chloroform were added. ODT behaves as a capping agent so that the cadmium ions do not agglomerate.

The solutions were mixed well by shaking and the mixture was kept aside for 15 minutes. Then H_2S gas was bubbled through the mixture for 15 minutes. As the reaction proceeds, a yellow coloration is observed in the solution, indicating the formation of CdS particles in organic phase.

For Manganese-doping, the corresponding aqueous salts of Mn and Cd were homogeneously mixed in required weight proportions. 10^{-3} M solution of $MnCl_2$ in proportions of 2%, 4%, 6%, 8%, and 10% in weight proportions are prepared and added along with Cd $(NO_3)_2$ solutions.

III. RESULTS AND DISCUSSIONS

Figure 1(A), shows the absorption spectra of the CdS nanocrystals in chloroform (organic phase).

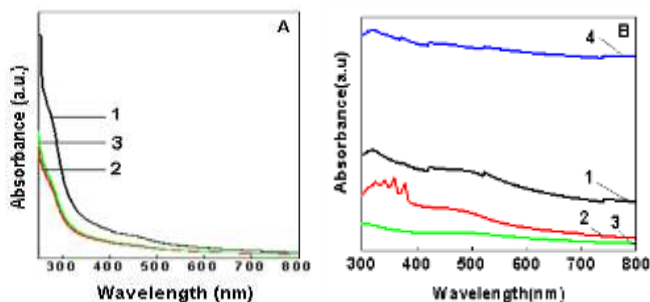


Fig.1(A) UV-visible absorption spectra of CdS nanoparticles with different levels of capping agent (ODT) in concentration of 0.005M (1), 0.006M (2) and 0.007M (3).

Fig.1(B) UV-visible absorption spectra of alloyed $Cd_{(1-x)}Mn_xS$ nanoparticles (1-2% Mn, 2-5% Mn, 3-8% Mn, 4-10% Mn)

Fig. 1(A) shows the UV-visible absorption spectrum of CdS nanoparticles at room temperature with different levels of capping agent (octa decane thiol) in the concentration of 0.005M (curve1), 0.006M (curve2) and 0.007 M (curve3). Subsequently the stability of the nanoparticles was optimized at 0.005 M concentration of ODT.

The preparation produces CdS quantum dots whose structures, composition and electronic structure are well characterized [19]. The absorption is attributed to CdS nanoparticles. The yellow colour of these solutions indicates the formation of CdS nanoparticles. The characteristic excitonic peak centred around 440 nm clearly reveals the quantum confinement effect arising due to small size of as formed CdS nanoparticles. The absorption band blue shifts with decreasing size due to quantum size effects. The absorption spectrum of CdS: Mn nanocrystals are typical for quantum sized semiconductor nanoparticles with a blue shift of the absorption edge relative to the bulk. The low concentrations of Mn^{2+} ions do not influence the position of the band gap of CdS [20]. The manganese emission in nanocrystals is the result of energy transfer from

semiconductor nanocrystal to the manganese ions. On creating the doping of Mn ions, the wavelength was found to shift towards the higher wavelength and the variation in the band gap suggests that there is direct energy transfer between the excited states and the 3d levels of the Mn^{2+} ions that are coupled by energy transfer processes [21]. A strong absorption peak at 320nm is assigned to the optical transition of the first excitonic state of the $Cd_{1-x}Mn_xS$ nanoparticles and its rather narrow shape is an evidence of very small size dispersed particles [22-23].

Room temperature fluorescence spectra (excitation at 350nm) for the samples of CdS, 5% manganese doped $Cd_{1-x}Mn_xS$ with chloroform solvents are studied and shown in fig 2(A) & 2(B).

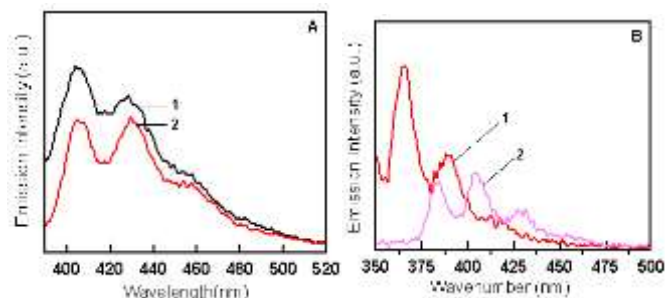


Fig.2(A) Fluorescence emission spectra recorded from ODT capped CdS nanoparticles in chloroform with excitation wavelength of 350nm (1) and 380nm (2).

Fig.2(B) Fluorescence emission spectra of ODT capped $Cd_{0.95}Mn_{0.05}S$ nanoparticles in chloroform with excitation wavelengths 350nm and 380nm (1) and 320nm (2).

In figure 2(A) the excitation wavelength for curve 1 is 350 nm and for curve 2 the excitation wavelength is 380 nm. Fluorescence emission spectra of CdS nanoparticles are studied with chloroform as solvent. Figure 2(B) illustrates the fluorescence spectra of $Cd_{0.95}Mn_{0.05}S$ nanoparticles with chloroform as the organic solvent. Curve 1 refers to the spectra for excitation wavelength 350 nm and 380 nm. Curve 2 refers to the fluorescence spectra for excitation wavelength of 320 nm.

The characteristic emission observed for the phase transferred CdS nanoparticles lies in the visible region of 400 nm – 520 nm. The peak is centred at 405 nm corresponds to the bandgap or near band gap emission resulting from recombination of electron hole pairs. The broader emission band at 427 nm is assigned to the charge carrier recombination from electrons trapped at the surface defects. The deep trap emission occurring at 430 nm allows the trapping of electrons and holes at the surface trap sites nonradiatively and gives low energy trap emission usually with low quantum yield.

Similarly, the fluorescence measurements on $Cd_{(1-x)}Mn_xS$ nanocrystals in organic phase suggests clear enhancement in the band edge emission characteristic compared to the undoped CdS nanoparticles as shown in fig. 2(B). The characteristic emission observed for phase transferred 5% Mn doped CdS nanoparticles lie in the visible range of 350 nm to 500 nm.

$\text{Cd}_{0.95}\text{Mn}_{0.05}\text{S}$ with chloroform as solvent exhibits a broad feature at 365 nm. A significant shift in the peak position is observed in the spectra of $\text{Cd}_{(1-x)}\text{Mn}_x\text{S}$. The cause for this blue shift in the emission spectra is thought to be an indication that the quantum confinement length is primarily defined by particle width and its difference between the widths of the various particles. The surface state saturation is modified by particle-surfactant interaction. It can be inferred that the quenching of the fluorescence can be altered by changing the cadmium concentration.

FTIR measurements have been made in the wave number range 1000 cm^{-1} and 4000 cm^{-1} . Fig. 3(A) illustrates the FTIR measurements of undoped CdS (curve 1), 5% manganese doped cadmium sulphide (curve 2).

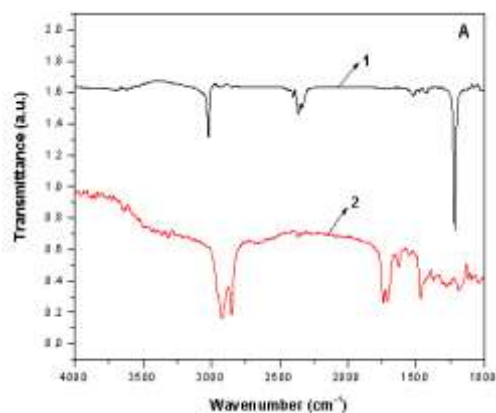


Fig. 3(A) FTIR spectra recorded from drop coated film on Si(111) wafer of CdS nanoparticles (1) and 5% Mn doped CdS nanocrystals (2).

CdS particles showed characteristic absorptions in the symmetric stretching band in the range of $2900\text{--}3000\text{ cm}^{-1}$ associated with C-H stretching. Strong band positions $1200\text{--}1300\text{ cm}^{-1}$ are possibly due to stretching vibrations of the sulphate group.

Figure 4 shows the TEM micrographs recorded at different magnifications from as prepared phase transferred CdS nanoparticles in chloroform.

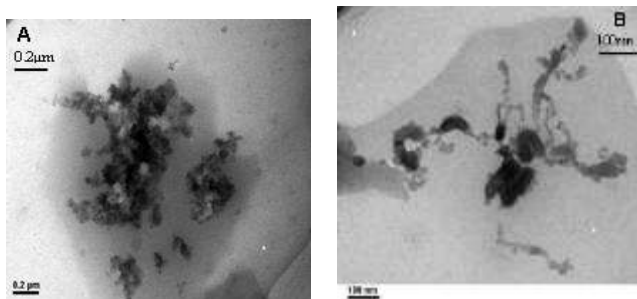


Fig. 4 TEM micrographs recorded at different magnifications from a drop coated film of ODT capped CdS nanoparticles.

Ribbon like CdS nanostructures capped with ODT is clearly seen in Fig. 4(B). This strongly suggests the strong surface binding of the ODT molecules with CdS nanoparticles thus restricting their aggregation. Fig. 4 (A) shows spherical nanoparticles under assembly into superstructures of variable morphology that were found to be uniformly distributed. The

CdS nanoparticles were observed to form monolayers of honey comb like structure. Thus the morphology of the CdS nanoparticles synthesized varies from spherical to flat, ribbon like structures and plate like structures. They indicate the polycrystalline nature of the semiconductor nanoparticles.

IV. CONCLUSIONS

Cadmium sulphide nanoparticles exhibit photoluminescent properties. The nanocrystals can be synthesized in organic phase at room temperature using a simple chemical route. The increase of the dopant concentration results in the enhancement of the luminescence yellow orange emission. UV-vis absorption and the fluorescent spectra are consistent with narrow size distribution and excellent particle quality. LEDs are luminescent devices that are composed of semiconductor materials that are capable of emitting light and these advanced materials synthesized in organic phase can be used for having very high quantum efficiency in LEDs

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