Synthesis of CdS and CdMns Nanocrystals 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 and $Cd_{1-x}Mn_xS$ nanocrystals in organic phase. Aqueous $Cd(NO_3)_2$ and stearic acid in chloroform are mixed together and stirred vigorously for almost 5 hrs. Cadmium ions from the aqueous phase get transferred to the organic phase. These phase transferred cadmium ions are capped with ODT as a capping agent. It is treated with H_2S. Yellow colored stable cadmium sulphide nanocrystals are formed in the organic phase. Doping manganese with $Cd(NO_3)_2$ at different proportions, produces $Cd_{1-x}Mn_xS$ nanoparticles of different morphology.

Optical absorption spectra of both CdS and $Cd_{(1-x)}Mn_xS$ nanoparticles clearly show a well-defined exciton absorption feature around 450 nm due to quantum confinement effects.

The CdS and CdMnS nanocrystals have been characterized using UV-visible spectroscopy, TEM, FTIR, Particle Size Measurement and Photoluminiscence.

Measurements:
TEM show that the size and shape of CdS can be manipulated.

Luminiscence spectrophotometries of the samples indicate a wavelength shift in the emission spectra when Quantum dots are synthesized.

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

Keywords:
CdS Nanoparticles, Capping agent, Quantum confinement, Absorption, Doping.

(The author is doing research in nanomaterials with Dr Murali Sastry, Chief Scientist, Tata Chemicals Ltd)

Introduction:
Nanometer sized particles of metals and semiconductors are of great interest due to their interesting size dependent physical, chemical and optoelectronic properties and their potential application.

The synthesis of semiconductor nanocrystrals in a controllable manner, with their exciting size and shape dependent electronic and optical properties has been the goal of much research over the past decade[1-5] CdS nanoparticles received considerable attention having potential applications as pto electronic devices [LEDs][6], Lasers[7], electrochemical cells[8], neuro transmitters[9], etc. These exciting applications have focused attention on the synthesis size and shape control and organization of CdS nanoparticles[4,10].

A light emitting diode is a semiconductor device that emits incoherent monochromatic light when electrically biased in the forward direction. This effect is a form of electroluminescence. The color depends on the semiconducting material used can be near UV, visible or infrared. Organic CdS can act as organic LED (OLED). The CdS is the emissive material in chloroform organic phase.

One of the challenges in the synthesis of nanoparticles in colloidal form is directing the particles into different solvents providing varying physico chemical environments. Colloidal particles stabilized with suitable capping agents in volatile organic solvents are particularly attractive.

Experimental details:
Sample preparation
Chemicals
i) $Cd(NO3)_2$ - Cadmium Nitrate
ii) $C_{18}H_{36}O_2$ - Stearic acid
iii) $CHCl_3$ - Chloroform
iv) $C_{18}H_{38}S$ - Octadecane Thiol
v) $Mncl_2$ - Manganese Chloride

In a conical flask, take 50ml of 10^{-3}M $Cd(NO_3)_2$ in distilled water and adjust the pH to 8.5

In another conical flask take 50ml of 10^{-3}M Stearic acid in chloroform. Mix the two solutions together. Then stir vigorously the mixture using a magnetic stirrer for 5 hrs.

The cadmium ions from the aqueous phase get transferred to the organic phase. The mixture is poured into a separating funnel and kept for 15-20 minutes. The phase transferred cadmium in organic phase is separated.

Prepare 50ml of $5x10^{-3}$M ODT in chloroform. To equal volumes of phase transferred cadmium, add ODT. ODT behaves as a capping agent so that the cadmium ions do not agglomerate.

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

For doping with Manganese10^{-3}M solution of $Mncl_2$ in the proportion of 2%, 4%, 6%, 8%, 10% are prepared and added along with $Cd(NO_3)_2$ solution. Subsequently, the same procedure is followed.

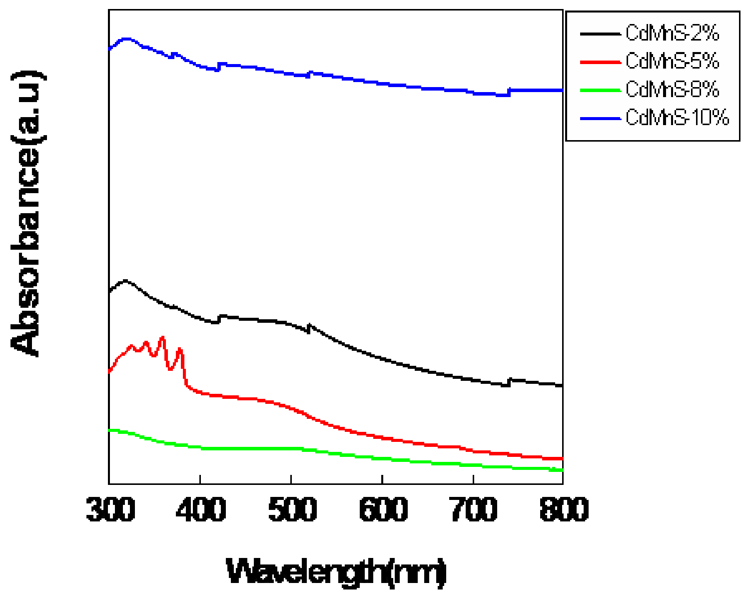
Very stable CdS and $Cd_{1-x}Mn_xS$ nanocrystals in organic phase with ODT capping agent were obtained and the sample was characterized.

Characterization:

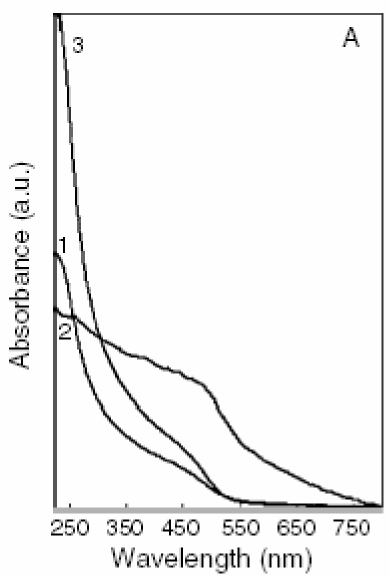
i) UV-visible spectroscopic studies were monitored on a JASCO model V-570 diode array spectrophotometer operated at a resolution of 2nm in the UV-visible region (200-800 nm)
ii) Transmission Electron Microscopy (TEM) measurements were performed on a JEOL model 1200Ex instrument operated at an accelerating voltage at 120 KV. Samples for TEM analysis were prepared by placing drops of sample on carbon coated TEM grids.
iii) Particle size measurement for the nanocrystals were done
iv) Fourier Transform Infrared Spectroscopy measurements FTIR spectra for drop coated films of CdS and $Cd_{(1-x)}Mn_xS$ nanoparticles is carried out.

Results and discussions:

Fig(1)… shows the absorption spectra of the CdS and $Cd_{(1-x)}Mn_xS$ nanoparticles in chloroform with ODT as a capping agent. The Fig(2) shows the absorption spectra of CdS in aqueous foam(Curve1) ; the Cds nanoparticlesafter centrifugation and re-dispersion (curve 2), and supernatant after centrifugation (curve 3). The same profiles indicate the same concentration and size distribution for the two CdS nanoparticles. This shows that the phase transfer process does not change the size of CdS nanoparticles.

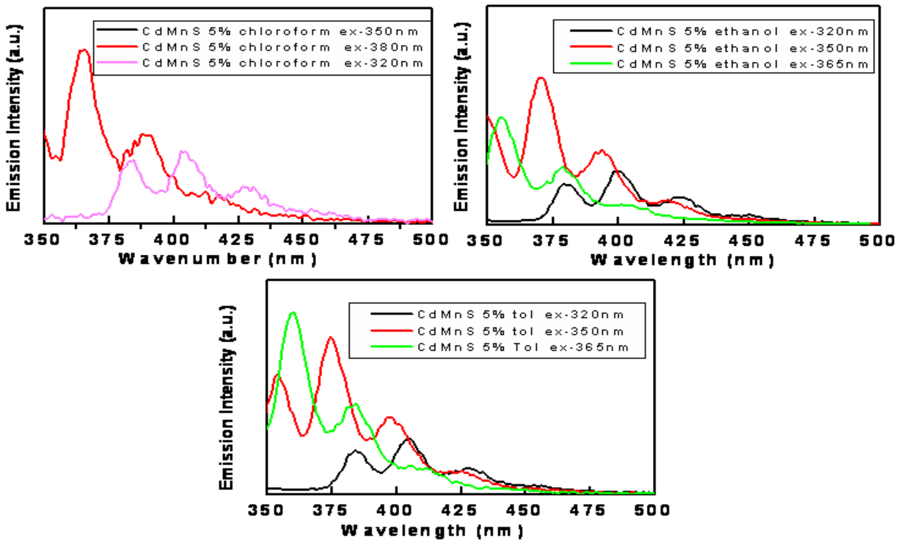


Fig(1)



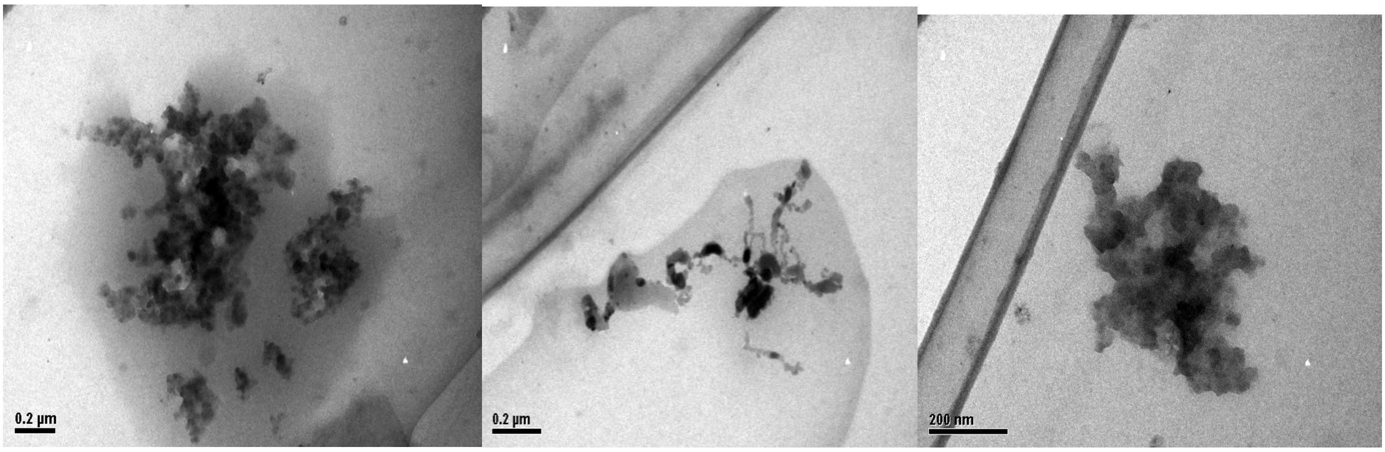
Fig(2)

The $Cd_{(1-x)}Mn_xS$ nanoparticles are centrifuged, washed and dispersed in other organic solvents like ethanol and toluene. Stable nanoparticles are obtained and their emission spectrum is shown below:



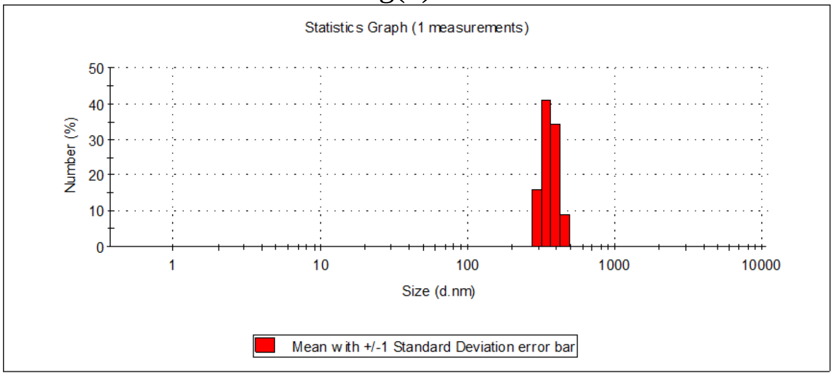
Fig(3)

The sizes and morphology of the as-prepared phase transferred CdS nanoparticles were studied by TEM and the images are shown below

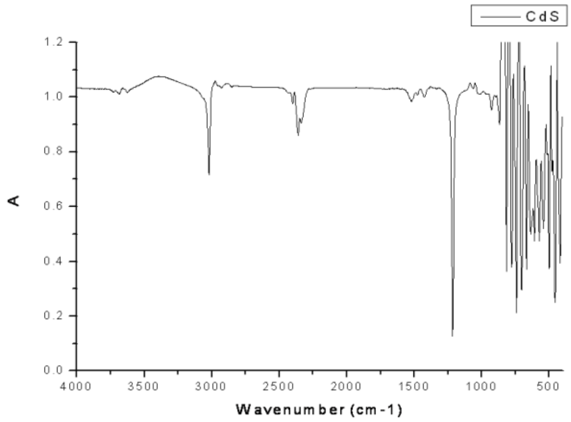


Fig(4)

It is apparent that nanoparticles have spherical and flat ribbon like morphology and their particle size distribution is shown in the fig(5)



It is observed that the size of CdS nanoparticles is in the range of 200 -500nm



Fig(6)

The FTIR absorption spectrum (fig(6)) shows absorption bands recorded in the range of 500-4000cm^{-}1. The curve shows that bond vibrational frequency is around 1200cm^{-1}.

Development of a system which allows the investigation of surface state interactions and reactions of size quantized semiconductor nanoparticles is the most significant observation in the presented study

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