

## Research Article

# Spectroscopical Studies on Chemically Synthesized Photoactive Nano Transition Metal Semiconductor Interfaces

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Received July 22, 2015; Accepted July 27, 2015; Published July 31, 2015

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## Abstract

This paper presents a novel method to synthesize photoactive materials. Water-dispersible transition metal doping of nanoparticles were done by integrating coordination polymer featuring acetate ligands interconnecting cadmium centers, butter of zinc and an organosulfur compound. The surfactant being the organic compound with antioxidant properties were used to further improve the stability of the nanoparticles. Basic structural, optical and spectroscopical characterizations of the synthesized materials were studied in order to make it as a potential material for photovoltaic applications. The outcome of the studies very well reveals the ability of the material as suitable candidates for photovoltaic applications. Moreover the water dispersibility of the prepared sample makes it innovative to exclude the incorporation of toxic solvents for its photovoltaic studies.

**Keywords:** Nanoparticles; Semiconductor-Metal interfaces; Aqueous chemical method; Optical studies; Photovoltaic cells

## Introduction

Semiconductor nanoparticles have numerous applications in the field of light emitting diodes [1] and photovoltaic devices [2-3] because of their size and shape dependent optical properties. Among the II-VI semiconductors CdS and ZnS is an important direct-band semiconductor with a band gap of 2.4 eV [4]. Different chemical or wet techniques for the preparation of II-VI semiconductor nanoparticles in organic and inorganic media have been already reported [5-8]. In our system we present the extremely simple and unique method of preparing CdS and ZnS nanoparticles similar to the route described in [9]. In this work we have followed chemical aqueous phase precipitation technique. This is one of the facile methods to prepare shape controllable CdS particles; this technique is simple, fast, low cost and not much time consumption to provide material with best outcomes. CdS is sulfur deficient having anion vacancies and makes it as a typical n-type material. Luminescence lifetime of CdS is long as the photogenerated electrons and holes are well separated to make charges highly localized [10-11]. In this regard II-VI semiconductors which have the ability to photogenerate multiple excitons are a promising candidate for solar cell applications [12].

## Materials and Methods

### CdS Synthesis

In the present investigation, CdS nanoparticles were prepared by chemical aqueous phase precipitation technique involving the reaction of cadmium sulphate with thioacetamide. The starting materials used for the fabrication of CdS are powders of cadmium sulfate and thioacetamide of purity better than 99.9% and water as solvent. In the typical experiment, all compounds were analytically pure and used without further purification. A series of aqueous solutions of cadmium sulfate and thioacetamide were prepared in separate flask using 100 ml distilled water. The formation of transparent liquids indicate complete dissolution of all materials in distilled water. Cadmium acetate solution was added drop wise to thioacetamide solution. The homogeneous mixing of both solutions was done under constant magnetic stirring. The initial colorless thioacetamide solution started turning to light yellow after some hours indicating formation of CdS nanoparticles to some extent. Subsequently, the colour of the solution changed to light yellow and thereafter it remains unchanged. Then the solutions were washed and centrifuged with distilled water many times to remove remnants or side products. After application of various energy sources, and washing, bright yellow precipitates of CdS nanoparticles were collected dried in oven at 70°C to collect pale yellow powders. This colloid was stable with time and did not show any observable precipitates over a long period.

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## ZnS Synthesis

The synthesis of ZnS nanoparticles was carried out by aqueous chemical method using zinc chloride and sodium sulfide as source materials. All the reagents were of analytical grade and used without further purification. The entire process was carried out in distilled water for its inherent advantages of being simple and environment friendly. All steps of the synthesis were performed at low temperature and ambient conditions. In a typical preparation, solution of 1m zinc chloride was prepared in 100 ml of deionized water and then the solution of 1M sodium sulfide was added drop wise to the solution which was kept on stirring using a magnetic stirrer at 70°C, which resulted in formation of ZnS nano colloid. The nanoparticles were collected by centrifugation at 2000 rpm for 15 minutes and further purification was made by ultrasonic bath. The resultant product was finally dried at 120°C for 2 hours.

## Zn-CdS Synthesis

The synthesis of CdS/ZnS nanoparticles was carried out by aqueous chemical method using cadmium acetate, zinc chloride and thioacetamide as source materials and ascorbic acid as capping agent. All the reagents were of analytical grade and used without further purification. The entire process was carried out in distilled water for its inherent advantages of being simple and environment friendly. All steps of the synthesis were performed at low temperature and ambient conditions. In a typical preparation, solution of 0.1 M cadmium acetate was prepared in 50 ml of deionized water along with ascorbic acid and the solution was added with zinc chloride at varying concentration, then the solution of thioacetamide of 0.2 M with varying concentrations was added drop wise to the solution which was kept on stirring using a magnetic stirrer at 70°C with varying time, which resulted in the formation of CdS/ZnS nano colloid. The nanoparticles were collected by centrifugation at 2000 rpm for 15 minutes and further purification was made by ultrasonic bath. The resultant product was finally dried at 120°C for 2 hours.

## Preparation of Zn-CdS film

CdS/ZnS film was prepared by using PVA (poly vinyl alcohol). 2g of PVA is dissolved in 20 ml of deionized water by heating at 70°C. After that 0.01 g of CdS was added and stirred well using magnetic stirrer. The resulting colloid was dried in a petri- dish.

## Characterization of Materials

The prepared samples were characterized by XRD by using X<sup>PERT</sup> PRO P Analytical powder X-ray diffractometer. The X-ray source is CuK $\alpha$  ( $\lambda=1.5405 \text{ \AA}$ ) and Ni as the filter. UV-V spectra were recorded on a UV-1800 Shimadzu spectrophotometer operated at a resolution of 1 nm. FTIR of the samples were taken BX-II (Perkin-Elmer) spectrometer. Photoluminescence (PL) measurements of solutions were recorded using HITACHI F-2500 fluorescence Spectrophotometer. Transmission electron microscopy (TEM) images were taken on a Technai G-20 TEM machine with an acceleration voltage of 200 kV.

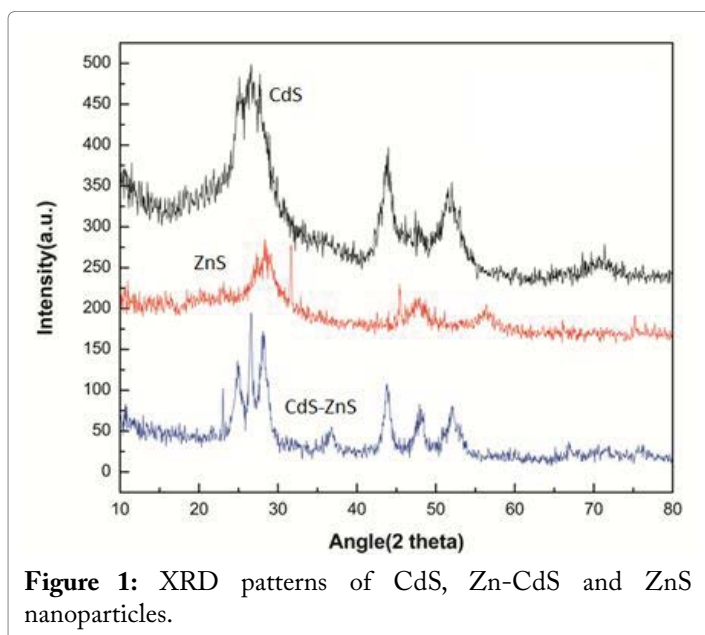
## Results and Discussion

### X-Ray Diffraction analysis (XRD)

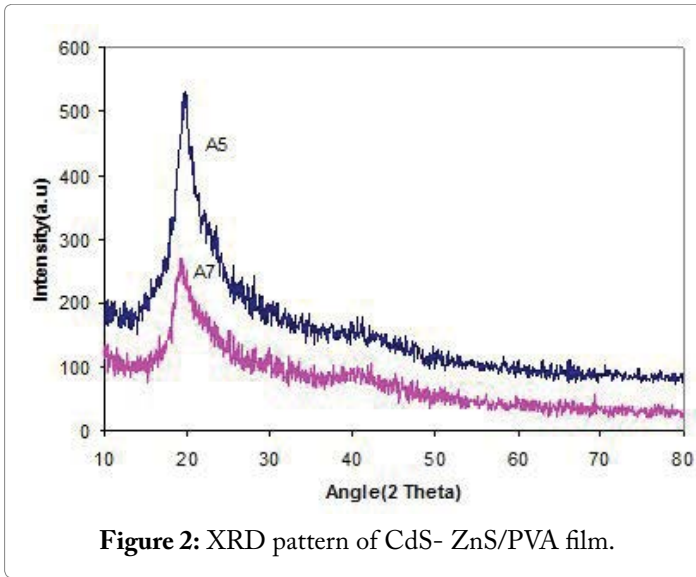
The XRD pattern of synthesized and heat treated samples of CdS, CdS-ZnS and ZnS are shown in the Figure 1. The broad peaks show the synthesized nanoparticles are Nanocrystalline. No impurity or dopant related peak has been observed in the XRD pattern. The diffraction pattern of the CdS nanoparticles shows 3 main peaks at 2 $\theta$  values 27.00°, 43.79° and 52.00° and matches with the theoretical values [JCPDS 89-0440] which corresponds to the cubic (1 1 1), (2 2 0) and (3 1 1) planes for nano-CdS. The peaks at 2 $\theta$  values 28.22°, 31.63°, 47.70° and 56.28° correspond to the rhombohedra (1 1 14), (1 0 28), (1 1 6), and (0 1 80) planes for nano-ZnS. The XRD values of the above ZnS nanoparticles are matching with their corresponding theoretical values [JCPDS 89-2426]. The peaks at 2 $\theta$  values 26.03°, 27.77°, 29.57°, 45.91° and 53.53° correspond to the hexagonal (1 1 0), (0 0 2), (1 0 1), (1 1 0), (2 0 0) planes for nano CdS-ZnS. The XRD values of the above CdS- ZnS nanoparticles are matching with their corresponding theoretical values [JCPDS 89-2943]. The broadening of the diffraction peaks is due to the finite size of the nanoparticles (Figure 2).

### Fourier transform infrared spectroscopy (FTIR)

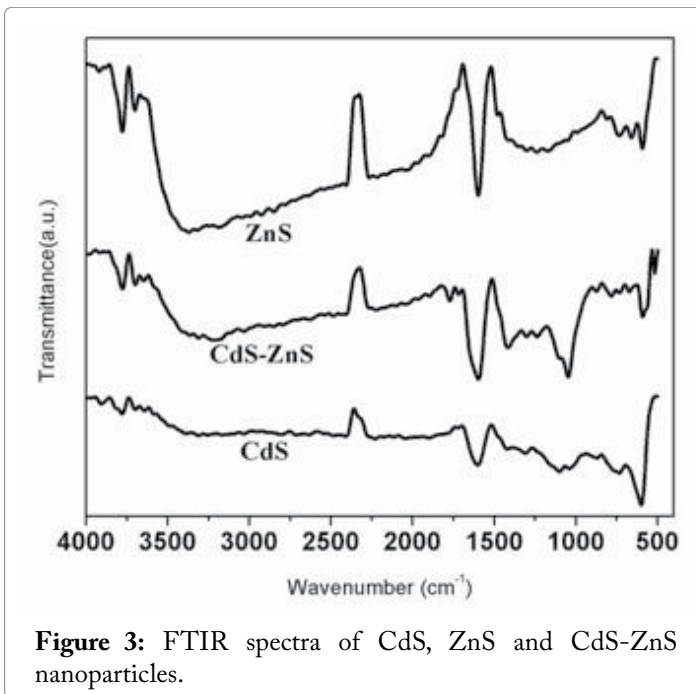
The strong absorption band at 3750 cm<sup>-1</sup> to 4116.6 cm<sup>-1</sup> is assigned to O-H stretching. The very weak absorption bands at 3666.6 cm<sup>-1</sup> – 3749.9 cm<sup>-1</sup> and 3312.5 cm<sup>-1</sup> to 3333.3 cm<sup>-1</sup> is assigned to O-H stretching vibration of water molecules, due to presence of moisture in the sample. Medium strong band positions in the range of 1375.9 cm<sup>-1</sup> – 1460.1 cm<sup>-1</sup> are possibly due to stretching vibrations of sulphate group. Traces of SO<sub>4</sub><sup>2-</sup> ion as impurity is seen as there are small absorptions appears in the range of 1089 cm<sup>-1</sup> - 1151 cm<sup>-1</sup>. There are medium to strong absorption



**Figure 1:** XRD patterns of CdS, Zn-CdS and ZnS nanoparticles.



**Figure 2:** XRD pattern of CdS- ZnS/PVA film.



**Figure 3:** FTIR spectra of CdS, ZnS and CdS-ZnS nanoparticles.

bands at 625 cm<sup>-1</sup> and 750 cm<sup>-1</sup> possibly due to Cd-S stretching. Hence the existence of above mentioned bands identify the presence of CdS and also the impurities that the samples consisted of water molecules or hydroxide ions.

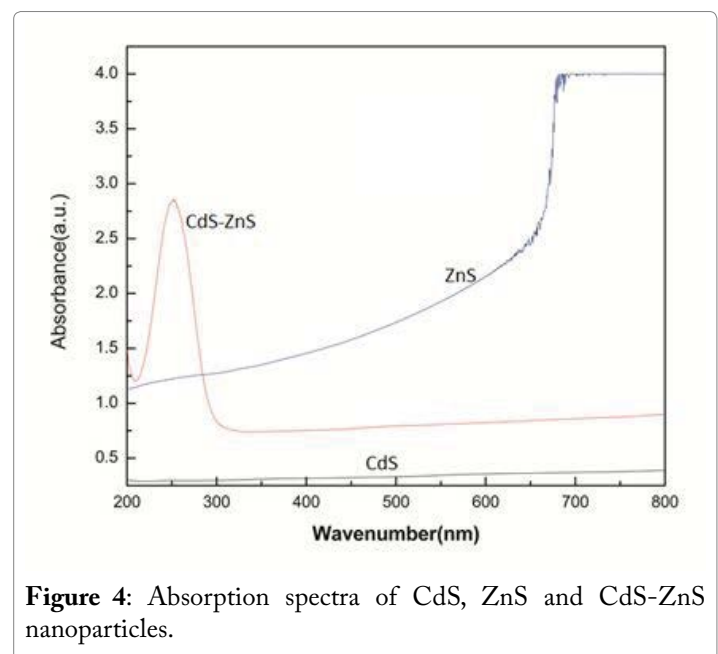
### Ultraviolet-Visible spectroscopy (UV-Vis)

Figure 4 shows the UV-Vis spectra of purified CdS nanoparticles. CdS is an II-VI semiconductor with a direct band gap of about 2.49 eV at room temperature (about 498 nm with the excitation of an exciton). The exciton Bohr diameter of CdS is about 8 nm and quantum effects are expected to appear for small particle sizes. Thus, the energy of exciton is expected to undergo a blue shift if the particle size is as a few nanometers. The CdS

particles with band edge energies smaller than 2.49 eV had smaller size than that of bulk materials. That is, the band edge wavelengths showed a blue shift from 498 nm. The samples had the band edge energies larger than 2.49 eV. This phenomenon reveals that we have synthesized CdS particles in the Nano scale. It exhibits the absorption edge of ZnS nanoparticles at 325 nm (3.8 eV), which is slightly blue shifted from that of bulk ZnS (340 nm,  $E_g = 3.65$  eV). This closeness of the absorption peak to the bulk ZnS crystals are attributed to the near band-edge free excitons. The broadening of the absorption spectrum could be due to the quantum confinement of the nanoparticles (Figure 4).

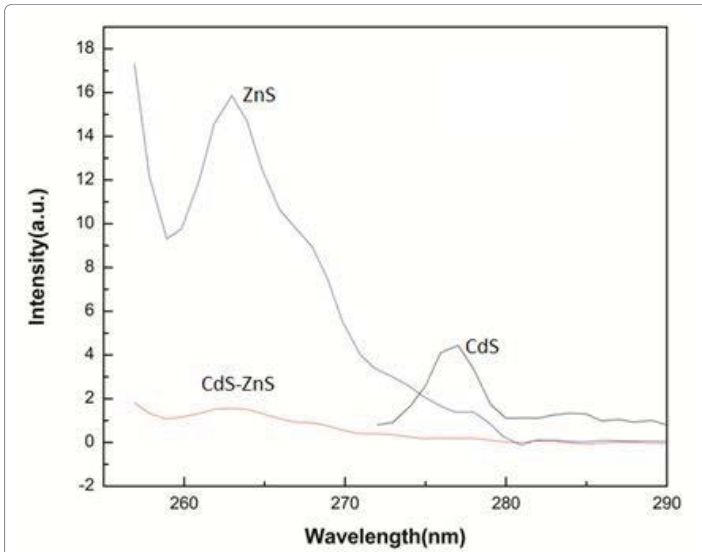
### Photoluminescence studies

The intense PL emission spectra of n-CdS, n-CdS-ZnS and n-ZnS have been shown in Figure 5 and Figure 6 respectively. However, the broad deep-trap emission overwhelms the near-band emission due to the high density of the deep-trap state and the high ratio of surface atoms in CdS nanocrystals. The near-band emission is red-shifted with increasing reaction time; indicate that the sizes of CdS nanocrystals increase through the reaction time. Furthermore, the broadening of the near-band emission peak with increasing reaction time implies widening of the crystal size distribution. The deep-trap emission is also red-shifted with increasing reaction time. The broadening of band emission reveals the broad size distribution of nanoparticles. A preliminary photoluminescence measurement on CdS and ZnS nanoparticles shows the excitation wavelength was 277nm and 264 nm for CdS and ZnS respectively. In the case of CdS, the PL spectrum shows a broad emission peak at 478nm. A similar emission peak at 490 nm was detected for CdS-ZnS nanoparticles with the excitation of 263 nm. Due to the broad nature of the peak, it is difficult to state clearly that a blue shift is detected, but the broader peak may be indicative of size quantization. Similar to CdS, a broader emission

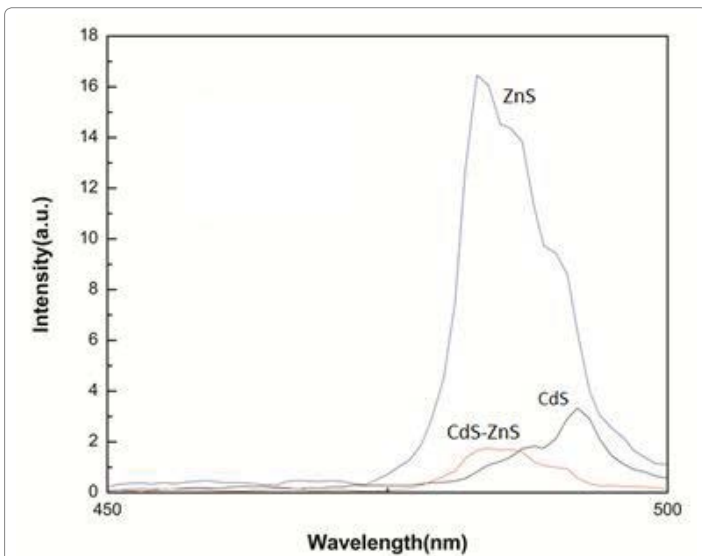


**Figure 4:** Absorption spectra of CdS, ZnS and CdS-ZnS nanoparticles.





**Figure 5:** Photoluminescence spectra of CdS, ZnS and CdS-ZnS nanoparticles.

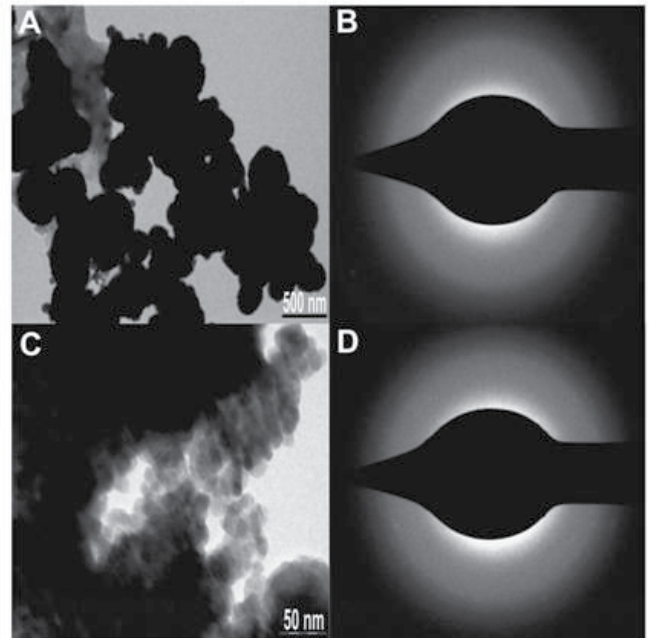


**Figure 6:** Excitation spectra of CdS, ZnS and CdS-ZnS nanoparticles.

peak centered at 463 nm was observed in the PL spectrum of n-ZnS. Usually for semiconductor nanocrystals, two emission peaks can be observed, the exciton and the trapped luminescence. The exciton emission peak is sharp and the trapped emission is broad. The emission bands showed in the spectra can be attributed to band gap emission and the strong band gap emission demonstrates the highly crystalline nature of the as-synthesized particles.

#### Transmission electron microscope (TEM) analysis

The morphology of prepared nanoparticles was studied by TEM. Figure 7 shows the typical image for CdS, CdS-ZnS nanoparticles.



**Figure 7:** TEM images and SAED pattern of the as-prepared samples of CdS (A, B) and CdS-ZnS (C, D) nanoparticles.

In this, the shape of the nanoparticles are close to spherical and some aggregation is observed. The TEM observations for the as-prepared CdS, CdS-ZnS nanoparticles are recorded. It is apparent that CdS-ZnS nanoparticles are spherical. A more careful analysis reveals that the particles are held together by a porous irregular network.

#### Conclusion

In this work, we have employed a very simple and cost effective method of preparing water dispersible CdS, CdS - ZnS and ZnS nanoparticles. By this aqueous chemical method, nanoparticles in the range of 15-20 nm are synthesized with varying concentrations of ascorbic acid. The nanostructures of the prepared nanoparticles have been confirmed using XRD, UV-VIS absorption and TEM analysis. The UV-VIS spectra of heat treated CdS nanoparticles reveal a flat type, similar to bulk CdS compounds. UV spectra of ZnS revealed that the absorption band was blue shifted from the bulk. The presence of organic content and presence of chemical functional groups in the samples of CdS nanoparticles was also identified in the FTIR analysis. There are medium to strong absorption bands at  $625\text{ cm}^{-1}$  to  $750\text{ cm}^{-1}$  possibly due to Cd-S stretching. The absorption bands at  $586.7\text{ cm}^{-1}$  to  $649.07\text{ cm}^{-1}$  indicates Zn-S stretching. Hence, confirms the presence of CdS, ZnS and CdS-ZnS nanoparticles.

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