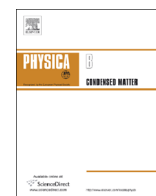




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# Morphology and thermal studies of zinc sulfide and cadmium sulfide nanoparticles in polyvinyl alcohol matrix

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## ABSTRACT

Zn(II) and Cd(II) metal complexes of 1-cyano-1-carboethoxyethylene-2,2-dithiolato- $\kappa$ S,S'-bis(N,N-dimethylthiourea- $\kappa$ S) have been synthesized and characterized with analytical and spectroscopic techniques. The complexes were thermolysed in hexadecylamine at 200 °C to prepare ZnS and CdS nanoparticles. The nanoparticles were characterized with scanning electron microscope (SEM), transmission electron microscope (TEM), and powder X-ray diffraction (p-XRD). TEM images showed spherically shaped nanoparticles, whose sizes are in the range 4.33–7.21 nm for ZnS and 4.95–7.7 nm CdS respectively and XRD confirmed cubic crystalline phases for the nanoparticles. The optical band gap energy evaluated from the absorption spectra are 2.88 eV (430 nm) and 2.81 eV (440 nm) for the ZnS and CdS nanoparticles respectively. The as-prepared metal sulfide nanoparticles were further incorporated into polyvinyl alcohol (PVA) to give ZnS/PVA and CdS/PVA composites. The polymer nanocomposites were studied to investigate their morphology and thermal properties relative to the pure PVA. XRD diffractions indicated that the crystalline phases of the nanoparticles and the sizes in PVA matrices remained unaltered. Infra-red spectra studies revealed interactions between the PVA and the metal sulfide nanoparticles and TGA studies show that the ZnS/PVA and CdS/PVA nanocomposites exhibit better thermal stability than the pure PVA.

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## 1. Introduction

The study of group II–VI semiconductor nanomaterials have received considerable attention in recent years because of their potential applications in light-emitting diodes (LEDs), electroluminescence devices and bright photostable marker for biological system [1,2]. ZnS and CdS are important members of this group of materials and they have wide band gaps of 3.65 eV (ZnS) and 2.40 eV (CdS) respectively [3]. These semiconductors nanocrystals have been extensively prepared and studied due to their size dependent optical properties relative to those of bulk materials [4,5]. Several methods have been employed for their synthesis such as colloidal [6], hydrothermal [7], laser irradiation [8], and thermolysis of single source precursors [9].

Thermolysis of metal dithiolates to give metal sulfides nanoparticles and thin films using single source precursors (SSP) have been explored in recent years [10–12]. A lot of advantages have been associated with single source precursor technique over multi-source route. Generally, SSP is a solution based procedure at moderate temperature and it circumvents the problem of air and

moisture instability of precursors (at high temperature). Syntheses are found to be easy at low temperature and risk of toxicity is minimally reduced. Being a one pot synthesis, the likelihood of pre-reaction and contamination from a one precursor molecule is reduced. Work-up methodology is simple in thermolysis of precursors due to the fact that organic and bi-products can be readily removed by filtration and centrifugation. Semiconductor polymer nanocomposite exhibits novel thermal, mechanical and optical properties for diverse applications in solar cells, multiphoton, micro stereo-lithography [13,14]. Polymer nanocomposite materials containing semiconductor nanoparticles, nanofillers, have advantages of combining multifunctional properties of both the polymer and the nanomaterials in a synergetic fashion. The interaction of the particles with the polymer matrices at molecular level along very high nanoparticle interfacial area has a great influence on the properties stated above [15,16].

Polyvinyl alcohol attracts extensive acceptance from researchers due to its availability with different molecular weights, its hydrophilicity and good film forming ability, biodegradability chemical resistance and transparency. Additionally, PVA possesses a carbon backbone that contains hydroxyl group attached, and that can be a source of hydrogen bonding which enables the formation of polymer nanocomposites [17]. Many conventional methods have been reportedly used to evaluate the spectra, morphological

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and thermal characterization of polymer nanocomposites. The role of thermal stability of polymer and composites is essential in the determination of the choice of specific applications and this property can be enhanced by incorporating appropriate fillers in the PVA polymer matrix. The hydrothermal synthesis of ZnS/PVA and CdS/PVA has been reported by Qian and his group [18]. Spherical CdS were also prepared and incorporated into PVA film via in-situ gamma irradiation induced method [19]. The proposed mechanism of formation is by surrounding CdS nanoparticles with OH bonds of the PVA chain. The same author also synthesized ZnS/PVA nanofluid through a fast clean, low cost approach. The ZnS was prepared by electrostatic force between zinc and sulfur ions using gamma irradiation technique [20].

Herein, we report a simple synthetic route for the formation of ZnS and CdS nanoparticles via the thermal decomposition of a single-source molecular precursor of Zn(II) and Cd(II) metal complexes of 1-cyano-1-carboethoxyethylene-2,2-dithiolato-κS,S'-bis(N,N-dimethylthiourea-κS). The complexes are novel, easy to synthesize unlike some other precursors that take 5–12 h to prepare [21,22]. It also gave high yield on pyrolysis. We also describe the thermal and morphological study of ZnS and CdS encapsulated in PVA matrices. For practical application, strong composite materials consisting of organic and inorganic constituents are required. Hence the choice of PVA as a stabilizing material in nanocomposite preparation is due to its significant thermo-stability, ease of processability, chemical resistance and transparency.

## 2. Experimental details

### 2.1. Material and methods

All chemical used were of analytical grade and used as purchased from Sigma-Aldrich without further purification. Powder X-ray diffraction patterns were obtained from Bruker D8 Advance equipped with a proportional counter using Cu K $\alpha$  radiation ( $\lambda=1.5405$  Å, nickel filter). TEM images were obtained from a ZEISS Libra 120 electron microscope. TGA was recorded on an SDTQ 600 thermogravimetric instrument. The infrared spectra were obtained from a Perkin Elmer Paragon 2000 FTIR spectrophotometer using the KBr disc method and UV–vis spectra were recorded on a Perkin-Elmer Lambda 25 UV–vis spectrophotometer and the photoluminescence study was recorded with Perkin-ELMER LS 45 Fluorimeter. Potassium salt of 1-cyano-1-carboethoxyethylene-2, 2-dithiolate ( $K_2ced$ ) was prepared with a slight modification of the procedure obtained from literature [23].

### 2.2. Synthesis of the mixed complexes

Methanolic solution of  $ZnCl_2$  (0.6814 g, 0.005 mol) and  $CdCl_2$  (0.916 g, 0.005 mol) were respectively refluxed with N', N' dimethylthiourea (1.042 g, 0.01 mol) in 40 mL methanol for 3 h.  $K_2ced$  (1.417 g, 0.005 mol) was dissolved in 20 mL distilled water and added to the refluxing mixtures. The colorless mixtures changed to milky yellow and yellow for  $[Zn(L_1)(L_2)_2]$  and  $[Cd(L_1)(L_2)_2]$  respectively. The reaction was further refluxed for 2 h and the products were washed with ice cold methanol, water and diethyl ether and air dried.

**$[Zn(L_1)(L_2)_2]$ :** (Yield: 1.79 g, 66%; M.p. 211–213 °C, Color; whitish yellow). Anal. calcd. for  $C_{12}H_{21}N_5O_2S_4Zn$  (460.98): C, 31.27; H, 4.59; N, 15.19; S, 27.82. Found: C, 30.79; H, 5.06; N, 15.53; S, 27.65.

*Selected IR*  $\nu$ ( $cm^{-1}$ ): 2209 (C $\equiv$ N), 1705 (C=O), 1448 (C=S<sub>2</sub>), 394 (M–S).

<sup>1</sup>H-NMR (DMSO):  $\delta$  = 3.98 (q, 2 H, -OCH<sub>2</sub>) 1.15 (t, 3 H, CH<sub>3</sub>)

<sup>13</sup>C-NMR (DMSO):  $\delta$  = 14.62 (-CH<sub>3</sub>), 58.41 (-OCH<sub>2</sub>), 90.91 (C=C), 120.88 (C $\equiv$ N), 163.92 (C=O), 206.32 (C=S)

**$[Cd(L_1)(L_2)_2]$ :** (Yield: 2.54 g, 73%; M.p. 219–221 °C, Color; yellow). Anal. calcd. for  $C_{12}H_{21}N_5O_2S_4Cd$  (508): C, 28.37; H, 4.17; N, 11.75; S, 21.51. Found: C, 28.74; H, 3.78; N, 11.90; S, 22.49.

*Selected IR*  $\nu$ ( $cm^{-1}$ ): 2209 (C $\equiv$ N), 1629 (C=O), 1473 (C=S<sub>2</sub>), 377 (M–S).

<sup>1</sup>H-NMR (DMSO):  $\delta$  = 4.01 (q, 2 H, -OCH<sub>2</sub>) 1.16 (t, 3 H, CH<sub>3</sub>)

<sup>13</sup>C-NMR (DMSO):  $\delta$  = 14.59 (-CH<sub>3</sub>), 58.91 (-OCH<sub>2</sub>), 90.58 (C=C), 121.28 (C $\equiv$ N), 165.96 (C=O), 207.72 (C=S).

### 2.3. Synthesis of HDA capped ZnS and CdS nanoparticles

In a typical experimental procedures, 0.6 g of  $[Zn(L_1)(L_2)_2]$  was dissolved in 5 mL of tri-n-octylphosphine (TOP) and injected into in a three-necked flask containing 6 g of hot HDA at 200 °C with vigorous stirring under nitrogen. An apparent 15–20 °C drop in temperature was noticed. The mixture was heated gradually and the temperature was allowed to stabilize at 200 °C. After 60 min, the obtained white material was allowed to cool to about 70 °C and methanol was added to precipitate the nanoparticles. The flocculent precipitate was isolated by centrifugation, followed by decantation of the supernatant and the dissolution of the nanoparticles in toluene. The aforementioned procedure was repeated three times to thoroughly purify the ZnS. This process was replicated with  $[Cd(L_1)(L_2)_2]$  for the preparation of CdS and the color of the product is yellow.

### 2.4. Synthesis of ZnS/PVA and CdS/PVA nanocomposite

ZnS and CdS nanoparticles were prepared following a literature procedure [24]. ZnS and CdS nanoparticles in PVA were prepared by a solution casting method [25]. 0.8 g of laboratory grade PVA (Polyvinyl alcohol) was weighed and dissolved in methanol and stirred for 2 h, followed by the addition of 3 wt% of ZnS or CdS nanoparticles dissolved in toluene and the two were added together. The resultant mixture was stirred at 60 °C for 24 h. The resultant product was poured into petri dishes to give the nanocomposites. Toluene was removed by slow evaporation over a period of 48 h in dry atmosphere. The film was then isolated and dried in vacuum at 70 °C.

## 3. Results and discussion

The synthesis of heteroleptic Zn(II) and Cd(II) complexes formed by the reaction of the respective metal salts, N', N'-dimethylthiourea (dmtu) and 1-cyano 1-carboxyethyl -2,2 ethylene dithiolate (ced) in the mole ratio of 1: 2: 1 afforded the formation of the two precursors represented by empirical formula  $[Zn(dmtu)_2ced]$  and  $[Cd(dmtu)_2ced]$ . The complexes are air stable based on the analytical and spectroscopic data. The complexes are insoluble in most common organic solvents but slightly soluble in high coordinating solvents like DMF and DMSO.

### 3.1. Spectroscopic studies of the precursor complexes

FT-IR spectra of the complexes  $[Zn(dmtu)_2ced]$  (1) and  $[Cd(dmtu)_2ced]$  (2) exhibit all the characteristics bands for CED and dimethyl thiourea. There are three characteristics bands that are typical of thiourea ligands and they are supposed to appear in frequency regions;  $\nu$ (C=S) located around 700  $cm^{-1}$ ,  $\nu$ (C–N) at around 1500  $cm^{-1}$  and the  $\nu$ (N–H) is identified around 3200  $cm^{-1}$  while the N–H bending vibration is noticeable around 1600  $cm^{-1}$  [26,27]. For the  $[Zn(dmtu)_2ced]$  and  $[Cd(dmtu)_2ced]$ , these bands are observed at; [622  $cm^{-1}$ , 1570  $cm^{-1}$ , 1613  $cm^{-1}$ , 3414  $cm^{-1}$ ] and [623, 1557, 1607  $cm^{-1}$ , 3403  $cm^{-1}$ ] respectively for the  $\nu$ (C=S),  $\nu$ (C–N), N–H bending vibrations and the  $\nu$ (N–H). It is worthy of note

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