



Synthesis and Characterization of Zn(II), Cd(II) and Hg(II) Complexes of Diethyl Thiourea and 1-Ethoxycarbonyl-1-ethylenecarbonyl-2,2-dithiolate and Their Use to Prepare Metal Sulfides Nanoparticles

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Zn(II), Cd(II) and Hg(II) mixed complexes of ligand diethylthiourea as primary ligand and 1-ethoxycarbonyl-1-ethylenecarbonyl-2,2-dithiolate as secondary ligand were synthesized and characterized by elemental and spectroscopic techniques. The complexes were used as precursors to prepare metal sulfide nanoparticles. The optical and structural properties of the nanoparticles were studied by UV-visible, photoluminescence, XRD and SEM. The absorption spectra of the nanoparticles show peaks which are blue shifted relative to their bulk molecules due to quantum confinement effects. The XRD diffraction patterns shows that ZnS and CdS nanoparticles are in cubic phase while the HgS nanoparticles are in metacinnabar crystalline phase. The nanoparticles sizes obtained from the TEM ranges from 2-11 nm.

Keywords: Dithiolates, Alkylthiourea, Group 12 complexes, Nanoparticles, Metal sulfides.

INTRODUCTION

Physical and chemical properties of materials deviate from the bulk with reduction of size to nanometer range. Among different classes of materials, nanostructured semiconductors have been studied due to their novel properties and practical applications¹⁻⁵. Their unique chemical and optical properties are due to their size dependent emissions^{6,7}. Bawendi and co-workers⁸ pioneered the use of organometallic compounds for controlled synthesis of semiconductor nanoparticles, but the hazardous nature of the starting materials call for the need for a safer synthetic routes. This led to the development of single source precursor route for the synthesis of semiconductor nanoparticles. This method avoids the use of volatile and hazardous compounds at high temperatures and lead to nanoparticles with homogeneous distribution of metal ions at molecular level⁹⁻¹¹.

The single source precursor method has been widely used to prepare group II-VI semiconductor nanoparticles¹²⁻¹⁴. In this study, we report the synthesis and spectroscopic characterization of Zn(II), Cd(II) and Hg(II) complexes of diethylthiourea with 1-ethoxycarbonyl-1-ethylenecarbonyl-2,2-dithiolate (ecda) and their use as single source precursors to prepared hexadecylamine capped ZnS, CdS and HgS nanoparticles. The metal sulfides nanoparticles were characterized by scanning electron microscopy (SEM), X-ray dispersive spectroscopy (EDX), transmission electron microscopy (TEM), UV-visible and X-ray diffraction (XRD). The choice of hexadecylamine

as a preferred capping agent in this work arose from the fact that it is an effective capping agent with good selectivity¹⁵. It decreases the growth rate, size of nanoparticles and improves the photoluminescence quantum efficiency by effectively passivating the surface defects while behaving as nonradioactive relaxing centre¹⁶.

EXPERIMENTAL

All chemicals and reagents were used as received without further purifications. Potassium salt of 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate ($K_2\text{ecda}$) was prepared according to literature procedure¹⁷. The FTIR was done as KBr discs on a Perkin Elmer Paragon 2000 FTIR spectrophotometer in the range 4000-370 cm^{-1} . The ^1H NMR and ^{13}C NMR was carried out using 400 MHz and 101 MHz Bruker NMR spectrophotometers respectively. The optical properties of the metal sulfide nanoparticles were recorded using Perkin Elmer Lambda 25 spectrophotometer in toluene from 800-200 cm^{-1} . The photoluminescence measurement of the nanoparticles was done using a Perkin Elmer LS 45 Fluorimeter. Scanning electron microscope (SEM) was done using JOEL JSM-6390 LVSEM at a rating voltage of 15-20 kV at different magnifications as indicated on the SEM images. Energy dispersive spectra were processed using energy dispersive X-ray analysis (EDX) attached to a Jeol, JSM-6390 LV SEM with Noran System Six software. Powder X-ray diffraction patterns of the nanoparticles were recorded on a Bruker D8 Advanced, equipped with a

proportional counter using $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$, nickel filter). The transmission electron microscopy (TEM) images were obtained using a ZEISS Libra 120 electron microscope operated at 120 kV.

Preparation of complexes: About 40 mL methanolic solution containing 0.005 mol of the corresponding metal salts (ZnCl_2 , 0.681 g; CdCl_2 , 0.917 g; HgCl_2 , 1.357 g) was added to diethylthiourea (detu) (0.01 mol, 1.042 g) in 30 mL methanol. The mixture was refluxed for 4 h followed by the addition of K_2ecda (0.005 mol, 1.417 g) in 30 mL methanol. Each of the mixture was refluxed further for 8 h, filtered and dissolved in acetone. The product was washed with methanol, diethylether and dried over CaCl_2 .

[Zn(detu)₂ecda]: Yield: 1.42 g (54.9 %), m.p. 227-229 °C. $^1\text{H NMR}$ (DMSO) $\delta = 2.78$ (s, 3H -NH-CH₃), 1.16 (t, 3H -OCH₂CH₃), 3.97 (q, 2H, -OCH₂). $^{13}\text{C NMR}$ (DMSO) $\delta = 206.23$ (C=S), 163.87 (C=O), 120.76 (C≡N), 90.84 (C=C), 58.32 (-OCH₂) and 14.53 (-CH₃). Selected IR (KBr, ν_{max} , cm^{-1}): 2200 (C≡N), 1462 (C=S₂), 373 (M-S), 1681 (C=O). Anal. calcd. for $\text{C}_{16}\text{H}_{29}\text{N}_5\text{O}_2\text{S}_4\text{Zn}$ (517.06): C, 37.17; H, 5.65; N, 13.54; S, 24.80. Found: C, 37.31; H, 5.70; N, 13.63; S, 24.55.

[Cd(detu)₂ecda]: Yield: 2.0 g (77.3 %), m.p. 231-233 °C. $^1\text{H NMR}$ (DMSO) $\delta = 1.16$ (t, 3H -OCH₂CH₃), 3.99 (q, 2H, -OCH₂). $^{13}\text{C NMR}$ (DMSO) $\delta = 208.15$ (C=S), 121.57 (C≡N), 90.25 (C=C), 58.49 (-OCH₂) and 14.57 (-CH₃). Selected IR (KBr, ν_{max} , cm^{-1}): 2206 (C≡N), 1463 (C=S₂), 372 (M-S), 1651 (C=O). Anal. calcd. for $\text{C}_{16}\text{H}_{29}\text{N}_5\text{O}_2\text{S}_4\text{Cd}$ (564.09): C, 34.07; H, 5.18; N, 12.42; S, 22.73. Found: C, 34.11; 4.92; N, 12.90; S, 22.81.

[Hg(detu)₂ecda]: Yield: 2.1 g (64.0 %), m.p. 344-346 °C. $^1\text{H NMR}$ (DMSO) $\delta = 1.13$ (t, 3H -OCH₂CH₃). $^{13}\text{C NMR}$ (DMSO) $\delta = \text{NA}$. (Not available due to insolubility problem) Selected IR (KBr, ν_{max} , cm^{-1}): 2188 (C≡N), 1458 (C=S₂), 375 (M-S), 1458 (C=S₂), 1651 (C=O). Anal. calcd. for $\text{C}_{16}\text{H}_{29}\text{N}_5\text{O}_2\text{S}_4\text{Hg}$ (652.27): C, 29.46; H, 4.48; N, 10.74; S, 19.66. Found: C, 29.87; H, 4.81; N, 10.52; S, 19.51.

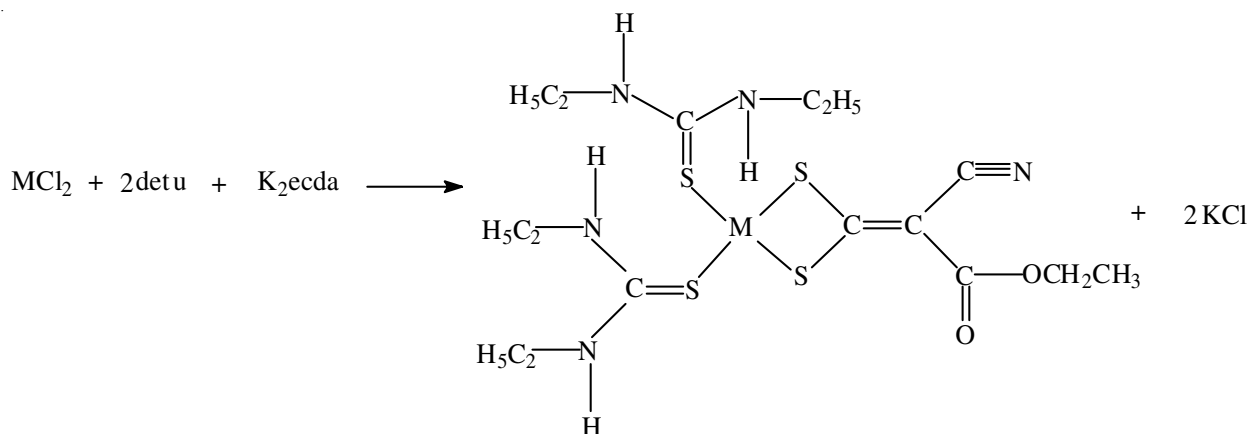
Synthesis of ZnS, CdS and HgS nanoparticles: Synthesis of the metal sulfide nanoparticles, chemically passivated with hexadecylamine was carried out as follows. In a typical experiment, 0.7 g of the respective complex was dissolved in 15 mL tri-*n*-octylphosphine oxide and injected into 7.5 g of hot hexadecylamine at 120 °C. A subsequent decrease in temperature of 20-30 °C was observed. The solution heated to 120 °C

and stirred for 1 h at this steady temperature after which the solution was cool to about 70 °C and large amount of methanol was added and centrifuge to remove excess hexadecylamine. The as-synthesized flocculent precipitate was separated and redispersed in toluene. The solvent was then removed by evaporation under reduced pressure to give hexadecylamine-capped ZnS, CdS and HgS nanoparticles. The particles were again washed with methanol and redispersed in toluene for spectroscopic measurements.

RESULTS AND DISCUSSION

All the metal complexes are formulated as four coordinate $[\text{M}(\text{detu})_2\text{ecda}]$ (where M = Zn, Cd and Hg) consisting of two molecules of monodentate diethylthiourea and one molecule of bidentate chelating ligand. The complexes were characterized with elemental analysis, FTIR, $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectroscopy. The two diethylthiourea molecules acts as monodentate ligands while, 1-ethoxycarbonyl-1-ethylene-2,2-dithiolate (ecda), acts as a bidentate chelating ligand through the sulfur atoms. Formation of the complexes can be represented as shown in **Scheme-I**. The three complexes are insoluble in common organic solvents although they are sparingly soluble in coordinating solvents such as DMF and DMSO.

Infrared spectra studies of metal complexes: The IR spectra of the free ligands and the metal complexes were compared and assigned on careful comparison. Relevant IR spectra for the ligands and the complexes are shown Table-1. The N-H stretching vibrations that occur at 3219 cm^{-1} in the diethylthiourea shifted to about 3275 cm^{-1} in the complexes. The shifts are attributed to hydrogen bonding in the complexes. The most important vibrational modes of the 1-ethoxycarbonyl-1-ethylenecyano-2,2-dithiolate ligands are: 2161 cm^{-1} due to $\nu(\text{C}\equiv\text{N})$; 1681 cm^{-1} due to $\nu(\text{C}=\text{O})$; 1360 cm^{-1} due to $\nu(\text{C}=\text{CS}_2)$ and 1160 cm^{-1} due to $\nu(\text{C}-\text{S})$ ^{18,19}. These were observed in the metal complexes at 2200, 1681, 1462 and 1193 cm^{-1} for $[\text{Zn}(\text{detu})_2\text{ecda}]$; 2206, 1651, 1463 and 1176 cm^{-1} for $[\text{Cd}(\text{detu})_2\text{ecda}]$ and 2188, 1656, 1458, 1191 cm^{-1} for $[\text{Hg}(\text{detu})_2\text{ecda}]$ characteristic of ecda complexes in a bidentate chelating mode²⁰. The stretching vibrations due to $\nu(\text{C}=\text{S})$ that appear at 794 cm^{-1} in the free diethylthiourea shifted to about 670 cm^{-1} in the metal complexes. The red shifting of the $\nu(\text{C}=\text{S})$ bond of the free ligand confirm that diethylthiourea is coordinated to the metal ions *via* the sulfur with a reduction



Scheme-I: Synthesis of $[\text{M}(\text{detu})_2(\text{ecda})]$, M= Zn, Cd and Hg

TABLE-1
KEY IR SPECTRAL BANDS (cm⁻¹) OF METAL COMPLEXES

Complexes	$\nu(\text{N-H})$	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C=O})$	$\nu(\text{C=S}_2)$	$\nu(\text{C-S})$	$\nu(\text{C=S})$	$\nu(\text{M-S})$
[Zn(detu) ₂ ecda]	–	2200	1681	1462	1193	670	373
[Cd(detu) ₂ ecda]	3275	2206	1651	1463	1176	666	372
[Hg(detu) ₂ ecda]	3362	2188	1656	1458	1191	669	375

of π -electron density of the $\nu(\text{C=S})$ bond^{18,19}. The complexes show medium to weak $\nu(\text{M-S})$ stretching vibrations between 420 and 250cm⁻¹. The $\nu(\text{M-S})$ was observed at 373, 372 and 375 cm⁻¹ in [Zn(detu)₂ecda], [Cd(detu)₂ecda] and [Hg(detu)₂ecda] respectively and this confirms the coordination of the ions to the sulfur atoms²⁰.

NMR spectra of the metal complexes: The ¹H NMR of [Zn(detu)₂ecda] show sharp well resolved signals at δ 7.29 which can be assigned to the NH proton of the thiourea group. The peak at δ 2.78 can be assigned to CH₃-(NH)₂. The quartet at δ 3.97 ppm can be assigned to OCH₂ and peak at δ 1.16 ppm can be ascribed to CH₃ of the ester group. The ¹³C NMR spectra of this metal complex show peaks at C-S (206.23), C=O (163.87), C \equiv N (120.76), C=O (90.84), -OCH₂ (58.32) and CH₃ (δ 14.53 ppm) of the ecda²⁻ carbon group.

The ¹H NMR of [Cd(detu)₂ecda] show two triplet peaks at δ 1.16 and 1.05 ppm which were assigned to the CH₃ groups. There is also a quartet peak at δ 3.99 ppm which is due to the CH₂ of the OCH₂ of the ecda²⁻ group. The ¹³C NMR spectra of the complex show signals for C-S (208.15), C=O (163.85), C \equiv N (121.57), C=O (90.25), -OCH₂ (58.49) and CH₃ (δ 14.57 ppm) for the carbons of ecda²⁻ and thiourea group. The downfield shift observed for the protons. The ¹H NMR of [(Hg(detu)₂ecda)] could not be assign due to poor solubility.

Synthesis of the nanoparticles: The synthesis of the precursor complexes were designed to allow for direct bonding between the sulfur donor atoms and the metal ions. This is an important condition in precursor molecules since it is expected that upon thermolysis, the relatively stronger bond between the metal and sulfur (M-S) would remain while the organic part of the molecule (being held by weaker bond) is broken off. In all the complexes, respective metal sulfides remained as the final product upon their thermal decomposition. The thermolysis of the precursor complexes were carried out at 120 °C to allow decomposition and appreciable growth under 1h. The choice of capping agent, hexadecylamine (HDA), is necessitated by its property. It has a great coverage of the coordinately unsaturated metal at the surface due to its high electron-donating ability and high capping density as a result of its small stereo chemical interference^{21,22}.

Optical properties of metal sulfides nanoparticles: The optical spectra of the ZnS, CdS and HgS nanoparticles are shown in Fig. 1. UV-visible measurements at an excitation wavelength of 250 nm for ZnS nanoparticles show an absorption peak with a broad to close band edge emission at 287 nm (4.32 eV).

This peak exhibited a blue shift of about 53 nm compared to the bulk 340 nm (3.65 eV)²³. The photoluminescence emission maximum for the ZnS nanoparticles appeared at 331 nm (3.74 eV) compared to the bulk and this is due to quantum confinement of the ZnS nanoparticles²⁴. The electronic

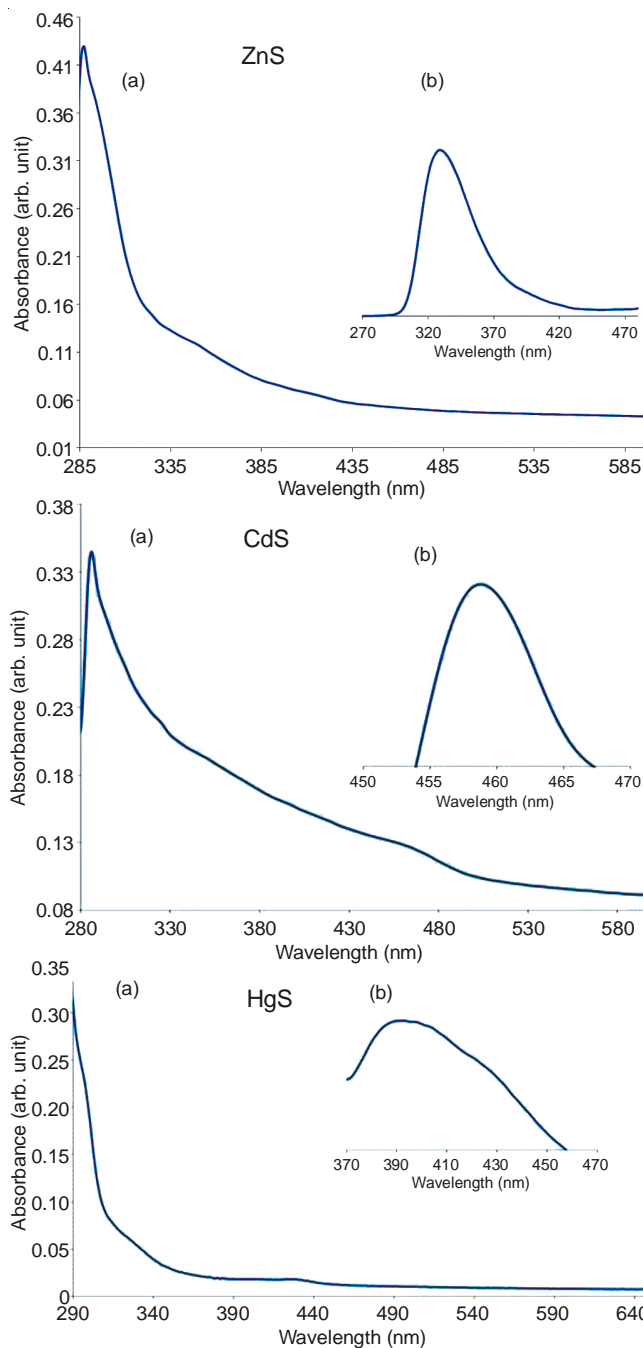


Fig. 1. Absorption and emission spectra of the nanoparticles

spectrum of CdS nanoparticles shows quantum size effect which is characteristics of nanodispersed semiconductors nanoparticles. The band edge of the bulk CdS is 515 nm (2.14 eV)²⁵ and the synthesized CdS shows a blue shift in the absorption edge to 467 nm (2.65 eV). The photoluminescence spectrum shows an emission maximum at around 458 nm which is also a significant blue shift from the band edge of the

bulk (515 nm) as shown in Fig. 1. The optical property of HgS nanoparticles shows the presence of excitonic feature at 430 nm (2.88 eV) with a typical tailing of the absorption band and an emission maximum at 390 nm (3.17 eV) as compared to the bulk HgS which occur at 620 nm (2.0 eV)²⁵. This showed quantum confinement with a significant blue shift from the band edge compared with the bulk.

X-ray diffraction studies: Typical XRD patterns of the as-prepared hexadecylamine capped ZnS, CdS and HgS nanoparticles are shown in Fig. 2. There are three reflections at (1 1 1) (2 2 0) and (3 1 1) planes, in the XRD diffractogram of hexadecylamine capped ZnS nanoparticles, indicating the zinc blende structure (cubic, β -ZnS)^{26,27}. The broadening of the three diffraction peaks is also observed and this suggests that the dimension of the ZnS nanoparticles is very small. The average size as estimated from the XRD is 9.9 nm. The XRD pattern of the hexadecylamine capped CdS shows three main reflection patterns at (1 1 1), (2 2 0) and (3 1 1) which can be indexed to 2θ values of 26.87°, 44.48° and 52.54°.

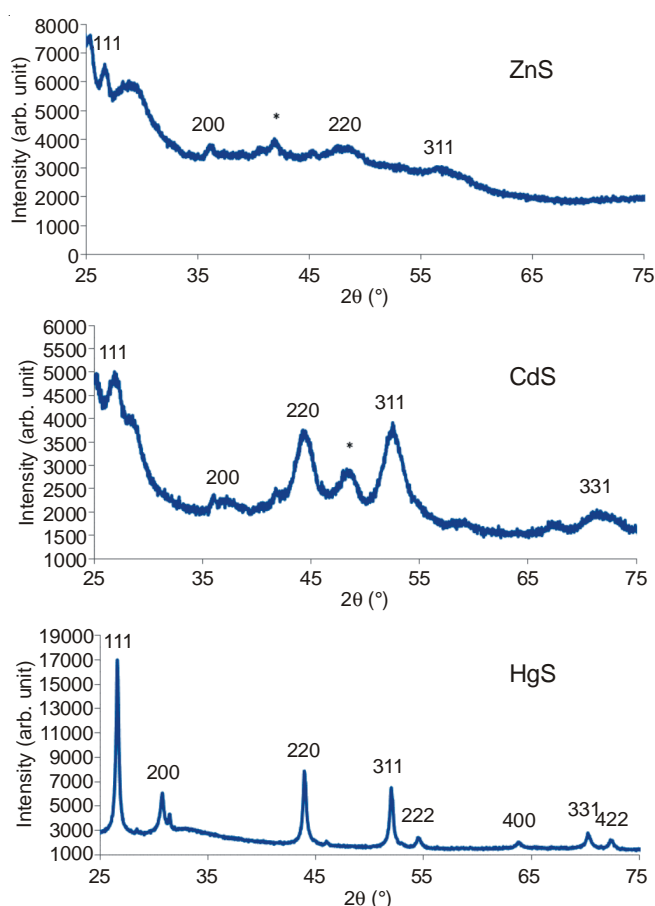


Fig. 2. XRD diffractogram of hexadecylamine capped ZnS, CdS and HgS nanoparticles

The CdS nanoparticles were indexed to JCPDS file card no 10-454, identified as β -CdS cubic crystal system²⁷. The mean crystallite size for CdS was estimated to be 7.7 nm. The broadening of the peaks may be ascribed to the small particle size of the nanocrystals. HgS nanoparticles has peaks at diffraction angles 26.59°, 30.81°, 43.98°, 51.99°, 54.61°, 63.81°, 70.42° and 72.52° that corresponds to the Miller indices (111) (200) (220), (311), (222), (400), (331) and (422) respectively.

These are comparable to the planes of HgS metacinnabar system (JCPDS 00-006-0261)²⁸. Surface passivation is shown by the elongation in the XRD patterns and the relative broadening of the peaks confirmed the small crystallites sizes.

Transmission electron microscopy: The TEM image of ZnS nanoparticles (Fig. 3) shows that smaller particles aggregate into secondary particles because of higher surface energy. The particles size ranges between 2.69–4.66 nm and appear to be dot shaped. The CdS nanoparticles appear spherical and uniformly monodispersed (Fig. 3). The CdS nanoparticles are in the range 4.88–7.68 nm. The HgS nanoparticles appear to be spherical with some agglomeration. The HgS nanoparticles crystallite sizes are in the range 8.34–11.10 nm. It is hard to determine the exact dimension of HgS particles by only observing the TEM image because the extremely small particles aggregate to secondary particles²⁹.

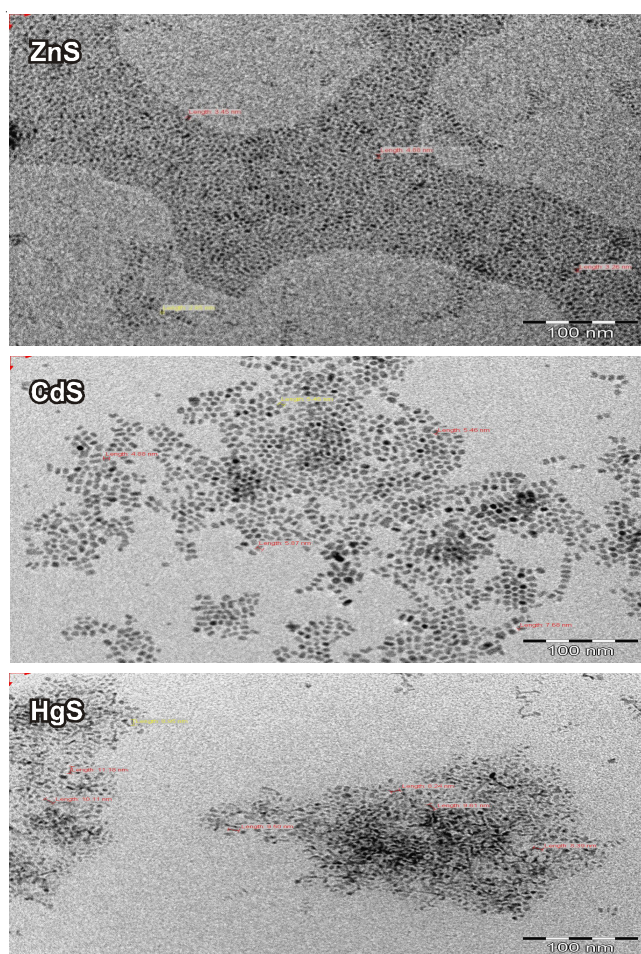


Fig. 3. TEM images of the ZnS, CdS and HgS nanoparticles

Scanning electron microscopy: All the three samples of ZnS, CdS and HgS are respectively subjected to scanning electron microscopy analysis and it was revealed that the shapes of the particles are irregular. The ZnS nanoparticles at lower magnification showed a rough surface which appeared to be smooth at higher magnification as shown in Fig. 4. A good growth environment of the nanoparticles can be revealed by the similarity and uniformity of the spheres and this also indicate good crystallinity of the sphere from other aspect³⁰.

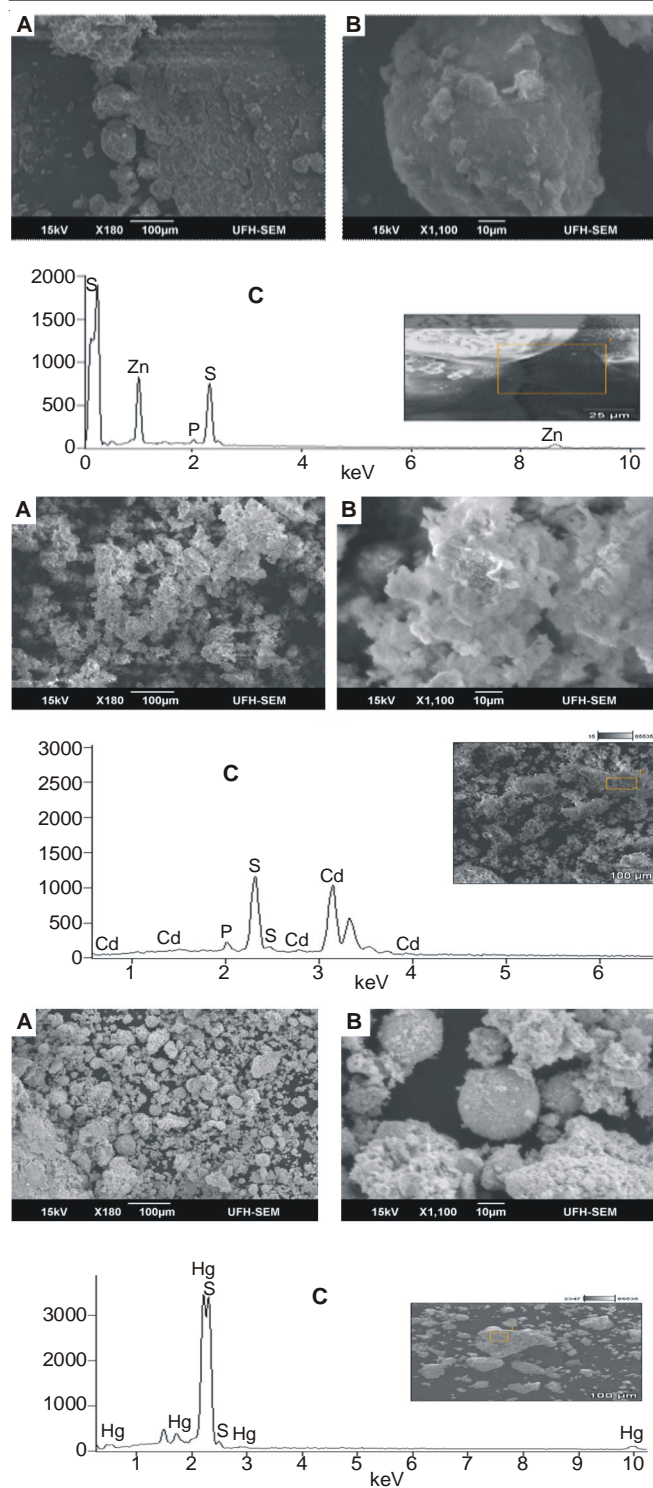


Fig. 4. SEM micrographs of ZnS, CdS and HgS at (A) low magnification, (B) high magnification (C) EDX spectra of the these samples

At higher magnification the large particles were observed to be aggregates of the nanoparticles as seen in the SEM images of ZnS and CdS and HgS nanoparticles (Fig. 4). The energy dispersive X-ray analysis measurement was used to confirm the chemical composition in atomic percentage of the elements. The EDX of the nanoparticles; ZnS, CdS and HgS showed peaks of Zn and S, Cd and S, Hg and S respectively with the appearance of phosphorus peaks in ZnS and CdS as the only noticeable contaminant from tri-*n*-octyl phosphine in which

the precursor metal complexes were injected prior to the injection into hot hexadecylamine.

Conclusion

Zn(II), Cd(II) and Hg(II) complexes of mixed diethylthiourea and ecda have been synthesized and characterized. The complexes were thermolyzed in hexadecylamine to give hexadecylamine capped ZnS, CdS and HgS nanoparticles. The optical properties of the nanoparticles showed absorption peaks with broad to close band emissions that are blue shifted compared to bulk materials which can be ascribed to quantum confinement effects. The XRD diffraction patterns of the nanoparticles show that the ZnS and CdS are in cubic crystalline phase S while HgS nanoparticles are in metacinnabar crystalline phase.

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