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THE EFFECT OF TEMPERATURE AND PRECURSOR CONCENTRATION ON THE SYNTHESIS OF COBALT SULPHIDE NANOPARTICLES USING COBALT DIETHYLDITHIOCARBAMATE COMPLEX

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Cobalt sulphide generally exist in various phases with different compositions including Co_4S_3, Co_9S_8, CoS, Co_{1-xS}, Co_3S_4, Co_2S_3 and CoS_2. $Co_{1-x}S$ nanoparticles were synthesized by thermolysis of cobalt(II) diethyldithiocarbamate complex $Co[(CH_3CH_2)_2NCS_2]_2$ in the presence of hexadecylamine (HDA) stabilizing agent. The effect of precursor concentration and temperature on the size and shape nanoparticles were investigated by varying concentration of the complex (1.0, 0.5, 0.25 and 0.125 g) and temperature (80, 145 and 210 °C). The XRD patterns showed that $Co_{1-x}S$ nanoparticles are in a hexagonal phase. The TEM images showed that the nanoparticles are spherical in shape with the size of 2 to 16 nm. It was observed that as the precursor concentration was decreased, the nanoparticles size decreased and became mono-dispersed. With the increase in temperature, the nanoparticles size also increased. There was no effect of both temperature and precursor concentrations that was observed on the shape of the nanoparticles.

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Keywords: Cobalt sulphide, Dithiocarbamate complex, Temperature, Concentration

1. Introduction

Nanomaterials are known to display enhanced optical, chemical and magnetic properties which are different from their bulk counter parts [1]. Cobalt sulphide is a II-VI semiconductor material. Semiconductor materials have found applications in various fields such as solar energy absorbers [2], ultra high-density magnetic recording [3], anode for lithium ion batteries [4], catalysts for hydrodesulphurization and dehydrodearomatization [5]. Cobalt sulfide exist in several phases and stoichiometric compositions which includes Co_4S_3, Co_9S_8, CoS, $Co_{1-x}S$, Co_3S_4, Co_2S_3 and CoS_2 [6]. Due to easy reduction of cobalt ion and easily oxidation of sulfide ion which results in the difficulty in controlling the stoichiometry of cobalt sulfide, cobalt sulphide has been reported as the most challenging metal chalcogenides to prepare [7].

Cobalt sulfide nanoparticles have been prepared using various methods such as hydrothemal [7], solvothermal methods [8], microwave-assisted techniques and thermolysis of a single-source precursors [9]. Single-source precursor is more apealing than conventional methods wich uses dual sources, the reason is thatit uses a single molecule that contains all the elements and the already templated metal-chalcogen bond that is required in the final product. This minimise the chances of incoporating impurities. It also involves the use of complexes which are themal stable, air stable and moisture insensitive [10]. The driving force in nanoparticles preparation is the need of nanoparticles with the desired properties and the potential application. The reaction conditions such as temperature, precursor concentration, extraction time and the capping reagents plays a major contribution in nanoparticles preperation interms of size and shape control. This work presents the preparation of $Co_{1-x}S$ nanoparticles by thermolysis of N,N`-diethyl-dithiocabarmate cobalt(II) complexes and the effect of precursor concentration and temperature on the size and shape of $Co_{1-x}S$ nanoparticles.

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2. Experimental

2.1. Materials

Cobalt chloride hexahydrate (≥ 98%), sodium diethyldithiocarbamate (98%), methanol (99.5%), hexadecylamine (HDA) (90%), trioctylphosphine (TOP) (90%), toluene (99.5%) were purchased from Sigma Aldrich. These chemicals were used without any further purification.

2.2. Synthesis of the cobalt diethyldithiocarbamate complex [$Co((CH_3CH_2)_2NCS_2)_2$]

A solution of $CoCl_2{\cdot}6H_2O$(aq) (1.00 g, 4.21 mmol) in distilled water (15 ml) was added into a solution of $NaS_2CN(C_2H_5)_2$(aq) (1.90 g, 8.43 mmol) in distilled water (15 ml). The mixture was then stirred for an hour at room temperature. The resulted green precipitate was filtered, washed with excess distilled water and dried in open air environment. Percentage yield 82 %, m.p. 258 - 261°C. Anal Calc. for $C_{10}H_{20}N_2S_4Co$ (355.479): C, 33.79; H, 5.67; N, 7.88. Found: C, 32.31, H, 5.63; N, 7.19. IR spectra ν(cm^{-1}): 2974(m), 2931(m), 2874(w),1744(m), 1570(w), 1458(s), 1447(s), 1378(m), 1367(m), 1294(w), 1266(s), 1214(s), 1149(s), 1134(s), 1078(s), 100(m), 914(m), 852(m), 786(m), 518.61(s), 486.70(s).

2.3. Synthesis of the cobalt sulphide nanoparticles

In a typical synthesis, a mass of the complex (0.125 - 1.0 g) was dissolved into 5 ml TOP. The solution was injected into 5.0 g of hot HDA at (80 - 210 °C). It was then refluxed, purged with nitrogen and allowed to stabilize at a desired temperature with constant stirring and heated for an hour. The solution was then cooled to 70 °C and an excess of methanol was added. The formed precipitate was separated by a centrifuge, washed with methanol three times and allowed to dry.

To investigate the effect of precursor concentration, different masses of the complexes (1.0, 0.5, 0.25 and 0.125 g) were used while temperature was maintained at 145 °C. For the investigation of the effect of temperature, various temperatures (80, 145, and 210 °C) were used while the mass of the complex was kept constant at 0.25 g. Other parameters kept constant were extraction time at 1 hour and capping molecule at 5.0 g of HDA.

2.4. Characterization

Infrared spectra were recorded using FT-IR Perkin Elmer 400 spectrometer at a range of 650 to 4000 cm^{-1}. The thermogravimetric analysis was performed using Perkin Elmer Pyris 6 TGA. The samples were decomposed at a temperature range of 30 to 800 °C under an inert atmosphere of dry nitrogen and at a heating rate of 10 °C min^{-1}. Elemental analyses (C, H, N) were performed on a Thermo Scientific Flash 2000 CHNS-O analyzer fitted with auto sampler. Absorption spectra of the nanoparticles were measured using Perkin Elmer Lambda 25 UV-VIS spectrophotometer in the spectral range of 190-900 nm. The samples were placed in a quartz cuvettes (1 cm path length) with toluene as the solvent. Powder X-ray diffraction patterns of the samples were recorded using a Shimadzu xrd 700 x-ray diffract meter diffractometer with Cu Kα radiation (λ=1.54 Å) at 40 kV and 40 mA. The samples were mounted flat and scanned between 5° and 90° in a step size of 0.05° with a count rate of 9 s. Transmission electron microscope (TEM) analysis was performed using HITACHI JEOL 100S operated at 80 kV. All samples were deposited on carbon-coated copper grids and allowed to dry.

3. Results and discussions

The bidentate ligand of diethyl-dithiocarbamate ligand was used in the synthesis of cobalt complex. The formed complex was confirmed by a combination of FT-IR spectra and elemental analysis. Thermal gravimetric analysis (TGA) was performed in the complex in order to understand the reactions involved in the decomposition pathway and thermal behaviour of the complex. Figure 1 shows the thermogram of the cobalt diethyldithiocarbamate complex. The TGA curve shows that the decomposition proceeds in two stages. The first decomposition stage accompanied by a weight loss of 2% occurs at 71 °C, can be associated with moisture. The second intense decomposition stage accompanied by a weight loss of 71.08% occurs at 390 °C, is associated with the breaking off of the ligand moiety. This resulted to the residue of 24.41 %, which is in good agreement with theoretical percentage of 25.59 % of CoS within the complex. No further weight loss was observed above 390 °C which indicate high stability of the cobalt sulphide.

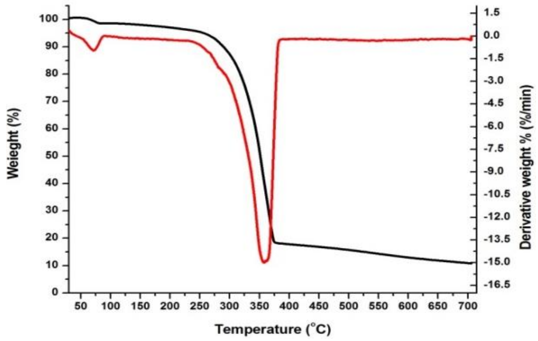

Fig. 1. The TGA and Derivative thermograph of the complex.

3.1. Effect of precursor concentration

The concentration of the precursor has a major influence on both size and shape of the nanoparticles. It has a profound effect on the size as high concentration favours larger nanoparticle size [1]. The effect of concentration on shape is quite complex, but it has been reported that chemical potential of nanoparticles is related to the formation of different size and shape [10]. The chemical potential of the reaction is mainly determined by the by monomer concentration at fixed temperature. The effect of precursor concentration was studied by varying concentration of the complex (1.0 g, 0.5 g, 0.25g and 0.125 g): 5g of HDA capping agent. These masses of the complex were chosen since the mass ratio between the complex and capping agent is very critical for effective capping as well as for the yield of the nanoparticles production.

The FT-IR spectra was used to characterize non-bound hexadecylamine and bounded hexadecylamine to the surface of cobalt sulphide nanoparticles. The vibrational frequency of hexadecylamine bound to cobalt sulphide nanoparticles were observed to shift as compared to non-bound hexadecylamine. Fig. 2(a-e) show the FT-IR spectra of hexadecylamine and hexadecylamine capped cobalt sulphide nanoparticles prepared by varying the concentration of the complex. The hexadecylamine (primary amine) is characterized by N-H stretching frequencies at 3334 cm^{-1}, 3228 cm^{-1} and 3174 cm^{-1}. The hexadecylamine bounded to cobalt sulphide nanoparticles show similar stretching frequencies at 3311 cm^{-1}, 3250 cm^{-1} and 3075 cm^{-1}, which is down shifted by 23 cm^{-1}, 8 cm^{-1}, and 99 cm^{-1} from the non-bounded hexadecylamine. The change in stretching frequency is associated with the N-H functional group being used in bounding with cobalt sulphide. Another region of interest is NH_2 scissoring, the N-H bend of non-bound hexadecylamine frequency was observed at 1608 cm^{-1}. The similar N-H bend of bounded hexadecylamine was observed at 1570 cm^{-1}, a down shift of 38 cm^{-1}. The final region of interest is C-N stretching, the non-bound hexadecylamine show a C-N stretching frequency at 1112 cm^{-1}. However, the stretching frequency of C-N in hexadecylamine capped cobalt sulphide nanoparticles showed a stretching frequency at 1143 cm^{-1} up shifted from non-bound hexadecylamine.

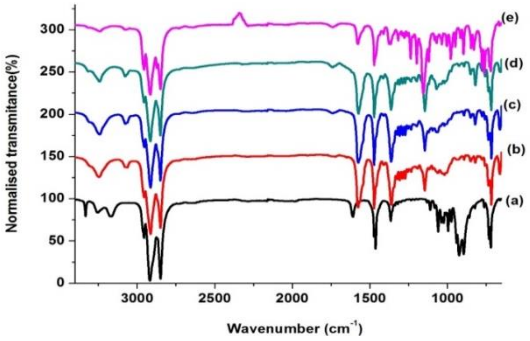

Fig. 2. The FT-IR spectra of cobalt sulphide nanoparticles prepared at 145 °C for 60 minutes, with 5.0 g HDA using various amount of complex: (a) HDA (b) 1.0 g, (c) 0.5 g, (d) 0.25 g and (e) 0.125 g.

Thermogravimetric analysis was used to characterize cobalt sulphide nanoparticles capped with hexadecylamine. The TGA curves of non-bound hexadecylamine and hexadecylamine capped cobalt sulphide nanoparticles prepared at various amount of complex are presented in figure 3(a-e). The TGA thermogram of non-bound hexadecylamine show single decomposition between 164 °C and 278 °C, without any residue. However, all the hexadecylamine capped cobalt sulphide nanoparticles show similar decomposition. They show one step decomposition between 215 °C and 450 °C, with a final residue of about 1.3 %. The residue can be associated with cobalt sulphide nanoparticles.

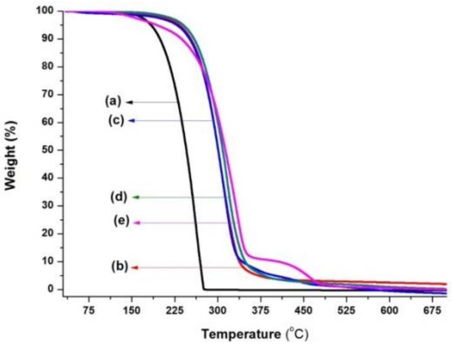

Fig. 3. The TGA thermograph of cobalt sulphide nanoparticles prepared at 145 °C for 60 minutes, with 5.0 g HDA using various amount of complex: (a) HDA alone (b) 1.0 g, (c) 0.5 g, (d) 0.25 g and (e) 0.125 g.

Fig. 4 (a-d) (black) shows the absorption spectra of HDA-capped cobalt sulphide nanoparticles prepared at different precursor concentrations of the complex. Nanoparticles prepared with 1.0 g of the precursor showed two absorption peaks at 415 and 335 nm, and a band edge of 535nm (Figure 4(a)). When the concentration of the precursor was decreased to 0.5 g, two absorption peaks were observed at 410 and 330 nm and a band edge at 515 nm. This is associated with particles being smaller than the one observed at 1.0 g (Figure 4(b)). When the concentration was further decreased to 0.25 g, the absorption peaks were observed at 360 and 260 nm, with a band edge at 435 nm (Figure 4(c)), remarkable decrease in particles with concentration. When the concentration was further decreased to 0.125 g, two major absorption peaks were observed at 355 and 240 nm, and a band edge at 410 nm. All precursor concentrations showed a blue shift from the bulk cobalt sulphide (1127.27 nm) [8], which signifies that the formed particles size are small in size than their bulk counterparts. The photoluminescence spectra are also shown in Figure 4(a-d) (red). The corresponding emission peaks are found at 577, 485, 415, and 420 nm (Figure 4(a-d, respectively). All the emission peaks were red shifted from their absorption peaks due to a Stoke shift. Furthermore, the nanoparticles prepared at 1 g, 0.5, 0.25 g (Figure 4(a- c) gave broad emission peaks which is associated with polydispersed cobalt sulphide nanoparticles, whereas lower concentration (0.125 g) gave narrow emission band signifying monodispersity.

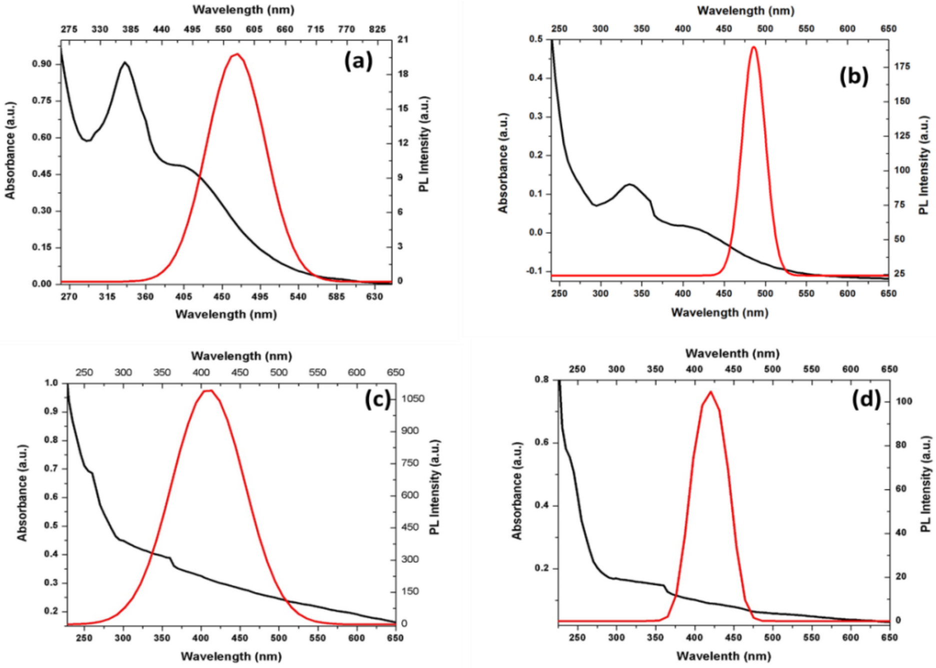

Fig. 4. The absorption spectra of cobalt sulphide nanoparticles prepared at 145 °C for 60 minutes, with 5.0 g HDA using (a) 1.0 g, (b) 0.5 g, (c) 0.25 g and (d) 0.125 g of the complex.

Fig. 5 (a-d) shows the XRD patterns of the HDA capped cobalt sulphide nanoparticle prepared by varying concentration of the complex. The diffraction patterns are well defined, characterized by (100), (102), (200) and (202) reflection of hexagonal $Co_{1-x}S$ nanoparticles (JCPDS No.042-0826). There is no peak due impurity that was observed which suggests that pure $Co_{1-x}S$ was obtained by thermalizing of the cobalt complex. The XRD showed similar patterns for all precursor concentrations which confirm that the concentration variation of the complex has no effect on the stoichiometry and phase of the prepared cobalt sulphide nanoparticles.

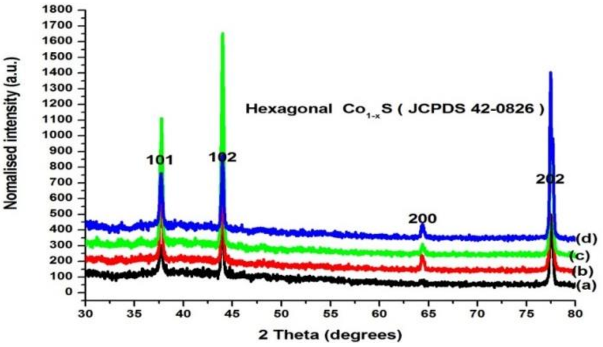

Fig. 5. The XRD patterns of cobalt sulphide nanoparticles prepared at 145 °C for 60 minutes, with 5.0 g HDA using (a) 1.0 g, (b) 0.5 g, (c) 0.25 g and (d) 0.125 g of the complex.

The TEM images of HDA capped cobalt sulphide nanoparticles prepared with various precursor concentrations of the complex are shown in Fig. 6(a-d). The TEM results showed that all the prepared cobalt sulphide nanoparticles in different concentrations are spherical in shape and they decreased in size as the concentration of the precursor decreases. The high precursor concentration (1.0 g) (Figure 6(a)), gave agglomerated nanoparticles forming small islands with average size of 11.26 ± 2.09 nm. The histogram confirmed that the nanoparticles are poly-dispersed. As the concentration of the precursor was decreased to 0.5 g (Figure 6(b)), the nanoparticle average size also decreased to 10.63 ± 2.57 nm, without any agglomeration and they became mono-dispersed. As the concentration was further decreased to 0.25 g, the average nanoparticle size further decreased to 7.51 ± 1.73 nm, and was also monodispersed. The nanoparticles prepared at lower concentration 0.125 g (Figure 6(d)), the average nanoparticle size was 4.14 ± 1.91 nm and were monodispersed.

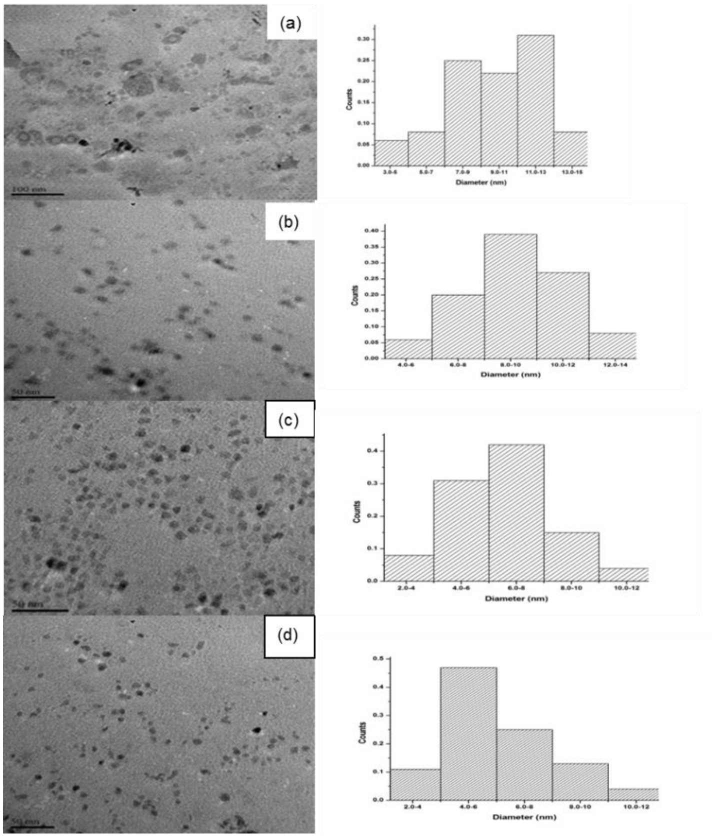

Fig. 6. TEM images of cobalt sulphide nanoparticles prepared at 145 °C for 60 minutes, with 5.0 g of HDA using (a) 1.0 g, (b) 0.5 g, (c) 0.25, and (d) 0.125 g of the complex

3.2. Effect of temperature

Temperature is one of the major factors that contribute significantly on size, shape and phase of the nanoparticle. The temperature reaction has a profound effect on the size of nanoparticles as higher temperature favours larger particle size. The shape of nanoparticles is also affected by temperature as result of competition between kinetic and thermodynamic regime during particle growth. The effect of temperature was studied by varying temperature of the reaction (80 °C, 145 °C and 210 °C). These temperatures were chosen since the HDA melts between 43-45 °C, has a flash point of 140 °C and a boiling point of 330 °C. At 80 °C and below, the complex decomposes slowly since HDA will not be hot enough to completely decompose it within one hour at this temperature. At temperature above 210 °C, the HDA form fumes as it evaporates and thus decreases in volume.

The FT-IR spectra was used to characterize hexadecylamine capped cobalt sulphide nanoparticles prepared by varying the temperature of the reaction. The FT-IR spectra of non-bounded hexadecylamine was compared with hexadecylamine bounded to cobalt sulphide nanoparticles. Figure 7(a-d) show FTIR spectra of non-bounded hexadecylamine and cobalt sulphide nanoparticles capped with hexadecylamine prepared by varying the temperature. Similar feature of the vibration frequency as outline in the effect of concentration section were observed, except for cobalt sulphide nanoparticles prepared at 80 °C. The FTIR spectra did not show any frequencies associated to N-H stretching, this could be due to the fact that at this temperature hexadecylamine could not bound to the complex used to prepare nanoparticles. At this temperature, hexadecylamine could not decompose the complex because the temperature is very low for this complex to be decomposed and hexadecylamine is not hot enough as it`s melting point is between 45 °C and 50 °C. After reaction all the hexadecylamine could have been washed out by methanol since there no interaction between it and complex. The colour of the precipitates was green, which is similar to the colour of the complex. This confirms that the cobalt sulphide nanoparticles could not be formed at this temperature.

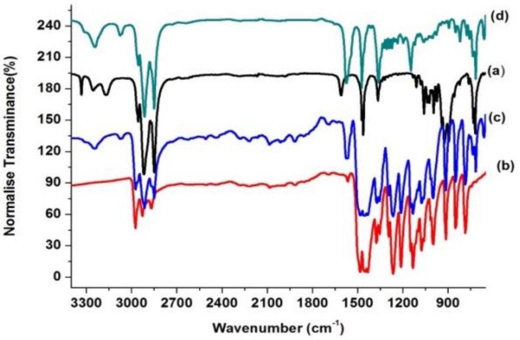

Fig. 7. The FT-IR spectra of cobalt sulphide nanoparticles prepared by using 0.25 g of complex, with 5 g HDA, 60 minutes at different temperature: (a) HDA, (b) 80, (c) 145, (d) 210 °C.

The thermogravimetric analysis was performed hexadecylamine capped cobalt sulphide nanoparticles. The TGA curved of non-bounded hexadecylamine and hexadecylamine capped cobalt sulphide nanoparticles were presented in figure 8 (a-d). The TGA curve of non-bounded hexadecylamine show one step decomposition between 164 °C and 278 °C, with no residue similar observation in effect of concentration were observed. The hexadecylamine capped cobalt sulphide nanoparticles showed similar properties as one outline in the effect of concentration. These nanoparticles showed single decomposition between 215 °C and 450 °C, with a final residue of 1.3 %. However, further small decomposition was observed beyond 450 °C until final residue reached zero. For particles prepare at 80 °C, the decomposition similar to the complex were observed. The TGA thermogram show single step decomposition between 275 °C and 375 °C, more stable than compared with cobalt sulphide prepared at 145 °C and 210 °C. The residue was observed at about 20 %. This is associated to undecomposed cobalt complex.

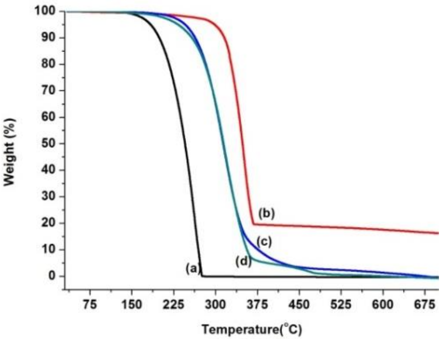

Fig. 8. The TGA thermograph of cobalt sulphide nanoparticles prepared by using 0.25 g of complex, with 5 g HDA, 60 minutes at different temperature: (a) HDA, (b) 80, (c) 145, (d) 210 °C.

The absorption spectra of HDA capped cobalt sulphide nanoparticles prepared at different reaction temperature as presented in Figure 9(a-c) (black). The spectra for cobalt sulphide nanoparticles prepared at 80 °C show three absorption peaks at 390, 360, and 320 nm (Figure 9(a)). The corresponding band edge was estimated to be at 450 nm. When the temperature was further increased to 145 °C, the absorption peaks were observed at 360 and 260 nm, with a band edge at 435 nm (Figure 9(b)). This decrease in cobalt sulphide nanoparticles as the temperature was increase is due to HDA being not hot enough to decompose all the complex at 80 °C and lower temperature. However, as the temperature was increased to 210 °C, the spectra show two major absorption bands at 360 and 260 nm with the band edge estimated at 460 nm. This can be associated with an increase in cobalt sulphide nanoparticle size as temperature was increase from 145 °C to 210 °C. All the prepared nanoparticles showed a blue shifted band gap from the bulk band gap of cobalt sulphide (1127.27 nm) [8]. This is due to the formation of smaller particles size of the prepared nanoparticles. The corresponding photoluminescence were shown in (Figure 9(a-c)) (red). The emission peaks for the nanoparticles were observed at 455, 415, and 450 nm (Figure 9(a-c) respectively).

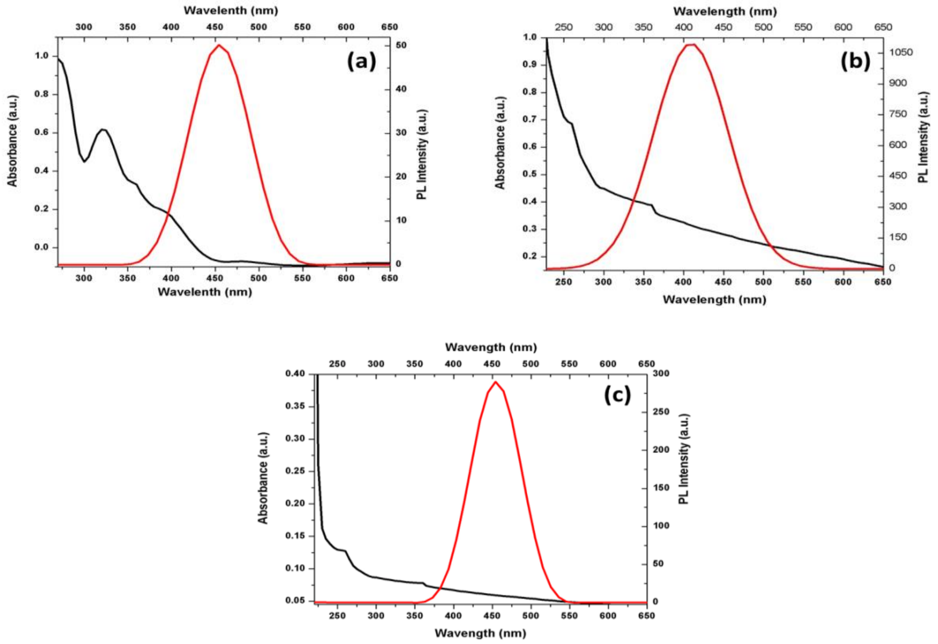

Fig. 9. The absorption and emission spectra of cobalt sulphide nanoparticles prepared by using 0.25 g of complex, with 5 g HDA, 60 minutes at different temperature: (a) 80 , (b) 145, (c) 210 °C.

The X-ray diffraction patterns of HDA capped cobalt sulphide nanoparticles prepared at various temperatures are shown in Fig. 10. The XRD of the cobalt sulphide nanoparticles prepared at various temperatures exhibit diffraction pattern at (100), (102), (200) and (202), which are associated with hexagonal $Co_{1-x}S$ structure. These results are similar to those obtained using various precursor concentrations.

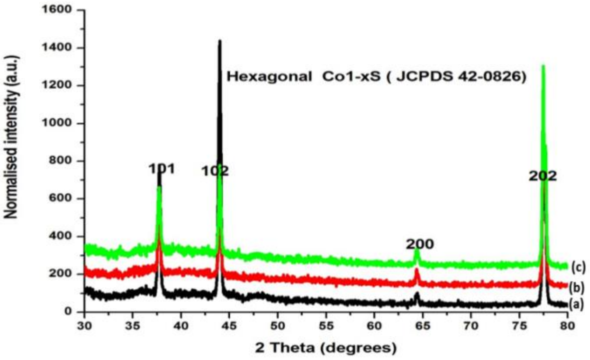

Fig. 10. TEM images of cobalt sulphide prepared by using 0.25 g of complex, with 5 g HDA, for 60 minutes at different temperatures (a) 80, (b) 145, (c) 210 °C.

Fig. 11 (a-c) represent the TEM images for HDA capped cobalt sulphide nanoparticles prepared at various temperatures. The results showed that all the prepared cobalt sulphide nanoparticles are spherical in shape. The nanoparticles prepared at 80 °C were agglomerated due to the capping molecule, HDA not being hot enough to decompose the precursor at this temperature as it melt between 45 to 50 °C, which then resulted in agglomeration on nanoparticles. As the temperature was increased to 145 °C, mono-dispersed nanoparticles with an average size of 3.40 ± 1.03 nm were obtained. This was the best temperature for the preparation of the nanoparticles using diethyldithiocarbamatecobalt (II) complex. As the temperature was further increased to 210 °C, the mono-dispersed nanoparticles with an average size of 9.26 ± 2.08 nm were obtained.

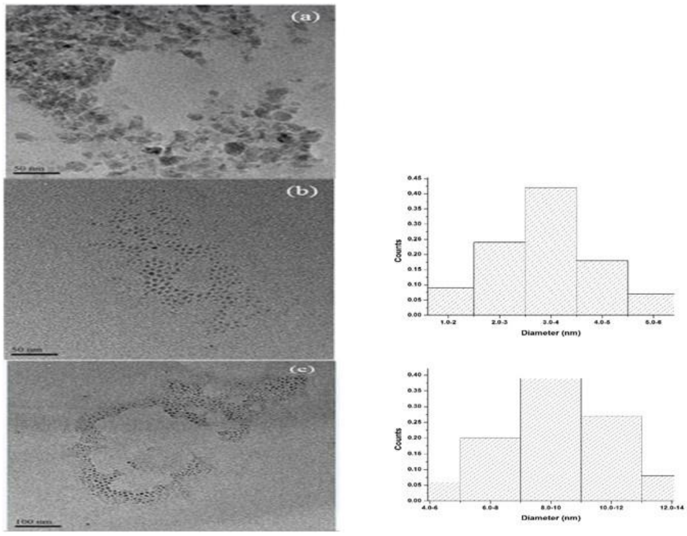

Fig. 11. TEM images and histograms of HDA capped cobalt sulphide nanoparticles prepared using 0.25 g of the complex at different temperatures: (a) 80, (b) 145 and (c) 210 °C.

4. Conclusions

HDA capped cobalt sulphide nanoparticles were successfully prepared using a single source precursor by varying the amount of the complex and temperature. The TEM and XRD results showed that the nanoparticles are spherically shaped with a hexagonal phase.

Precursor concentration showed an effect on the size of nanoparticles, as the size decreased with a decrease in precursor concentration. Both temperature and precursor concentration showed no effect on the shape and phase of the prepared nanoparticles.

Acknowledgements

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