

Synthesis and characterization of reproducible stoichiometry of cobalt sulfide nanoparticles using sulphur containing single-source precursors.

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Abstract

Cobalt sulphide nanoparticles are one of the most complex and challenging particles to synthesize due to strongly reducibility of the cobalt ion and the oxidizable nature of the sulphide ion. Cobalt sulphide therefore exist in various phases with different compositions including Co_4S_3 , Co_9S_8 , CoS , Co_{1-x}S , Co_3S_4 , Co_2S_3 and CoS_2 . Herein, we describe the synthesis of Co_xS_y nanoparticles; furthermore we interrogate the influence of the reaction conditions on the structure and optical properties of the nanoparticles. Co_xS_y nanoparticles were synthesized by thermolysis of N, N, N', N'-tetramethylthiuram disulphide cobalt (II) complex in the presence of stabilizing agent, hexadecylamine (HDA). The advantage of this method is that the bond between the cobalt and sulphur atoms already exist, therefore decomposition of the complex at write conditions will result in the formation of Co_xS_y nanoparticles. The cobalt sulfide nanoparticles were prepared by varying concentration (1.0, 0.5, 0.1 and 0.05 g) of the $\text{CoCl}_2[(\text{CH}_3)_2\text{NCS}_2\text{S}_2\text{CN}(\text{CH}_3)_2]_2$ complex at a temperature of 130 °C. The effect of temperature was also investigated by varying the temperature (80, 130, 200 and 250 °C). The nanoparticles were characterised by a combination of absorption spectroscopy, photoluminescence (PL), X-ray diffractometry (XRD) and transmission electron microscopy (TEM).

Keywords: Cobalt sulphide nanoparticles, concentration, temperature, single-source precursor

Introduction

Transition-metal semiconductor has shown to be one of the most active research areas.¹ Because of their particular optical, electronic, magnetic and chemical properties, these materials have been widely applied in many fields such as solid-state secondary lithium battery cathodes, industrial catalysts, solar energy conversion, and fluorescence devices.¹⁻³ In this study cobalt sulfide was synthesized using a single source precursor route. Single source precursors are molecules that contain all the elements required in the final material. These precursors were designed such that there is bond between metal and sulphur atoms, and including stoichiometry. The advantages of using a single source precursor route are that they reduce the chances of impurities in the final product, they minimize the synthetic time and they prevent the competition of functional groups from the surfactant.⁴ In addition to that, these organometallic precursors are moisture-insensitive, air-stable, less toxic, and easy to synthesize and handle.⁵⁻⁷ Semiconductor nanocrystals are synthesized from the precursor by controlled thermal decomposition in the presence of a stabilizing surfactant. Cobalt sulfides form a group of II-IV semiconductor materials with considerable potential application in electronic devices.⁶ They are one of the most complex metal sulfides systems, with a number of phases and different composition. Cobalt sulfide include phases such as Co_4S_3 , Co_9S_8 , CoS , Co_{1-x}S , Co_3S_4 , Co_2S_3 and CoS_2 . The diversity in the stoichiometry poses some challenge in controlling the morphologies of small-(particle).

Experimental section

Synthesis of complex: Cobalt(II) chloride tetramethylthiuramdisulfide complex was synthesized from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ salts (4.25 mmol) which were dissolved in hot methanol (50 ml). This solution was added into the solution of tetramethylthiuram disulfide (prepared by dissolving tetramethylthiuramdisulfide (8.41 mmol) in hot methanol (50 ml)). The mixture of these solutions was heated to reflux with constant stirring for 60 minutes. The formed precipitates were filtered, washed with excess methanol and dried in open air environment. $\text{C}_{12}\text{H}_{24}\text{N}_4\text{Cl}_2\text{S}_8\text{Co}$ (610.7166): Anal Calc. C, 23.42; H, 3.96; N, 9.17; S, 42.00. Found: C, 22.97; H, 3.71; N, 8.12; S, 44.21. IR ν (cm^{-1}): 2922.74(m), 2853.61(m), 1927.80(m), 1698.80(w), 1500.35(s), 1375.87(s), 1237.79(s), 1142.53(s), 1044.90(s), 971.54(s), 955.85(w), 896.21(w), 848.38(m), 792.64(w). ^1H NMR (CDCl_3) δ : 3.101(s, 3H).

Synthesis of nanoparticles: Cobalt sulfide nanoparticles were synthesized at various concentrations of complex and temperature in about 5.0 g HDA. Different masses of the complex, (1.0, 0.5, 0.1 and 0.05 g) were dissolved into trioctylphosphine (TOP) (5 ml) separately. Each solution was injected into hot hexadecylamine (HDA) (5.0 g) which was heated and maintained at temperature of 130 °C under nitrogen atmosphere. This reaction was maintained at this temperature with constant stirring for 30 minutes. Then, the solution was cooled to 70 °C and an excess of methanol was added. The precipitate formed were isolated by centrifugation, washed with methanol three times to remove some of the capping agent and dried in open air environment.

Characterization techniques: Several analytical techniques were used to characterize the as prepared materials. **Elemental analysis**, Powder X-ray diffractometry (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), Fourier-Transform Infrared spectra (FT-IR), UV-visible spectroscopy (UV) and Photoluminescence (PL)

Results and discussion

The complex was prepared in a mole ratio of 1:2 between the cobalt salt and the ligand, tetramethylthiuram disulfide to produce a six coordinate with the binding to the metal through sulphide. A combination of elemental analysis, and spectroscopic technique confirms the formation of the complex. Thermogravimetric analysis curve of complex shows that the has precursor decompose into two steps between 655 °C – 826 °C and 1027 °C – 1225 °C. The observed residue was 92.85 % resulting from the loss of organic moiety from the ligand. The observed final residue was 20.47 %, which is in good agreement with the theoretical 20.15 % of CoS. Cobalt sulfide is known to have an optical band gap of 1078.26 nm with a cubic structure. The absorption spectra of cobalt sulfide nanoparticles prepared at different concentrations of complex are shown in Figure 1(I). Cobalt sulfide nanoparticles prepared at high concentration (Figure 1a and 1b) show two major absorption peaks, a hump at 418 nm and a maximum peak at 329 nm. The spectra results for the particles prepared at low concentration (Figure 1c and d), reveals two peaks at 329 and 415 nm. The band edges of these particles are blue shifted from the bulk. Table 1 clearly shows that as concentration of the precursor decreases, the band edge also decreases. These results indicates that the size of the nanoparticles decrease with concentration of the precursor.

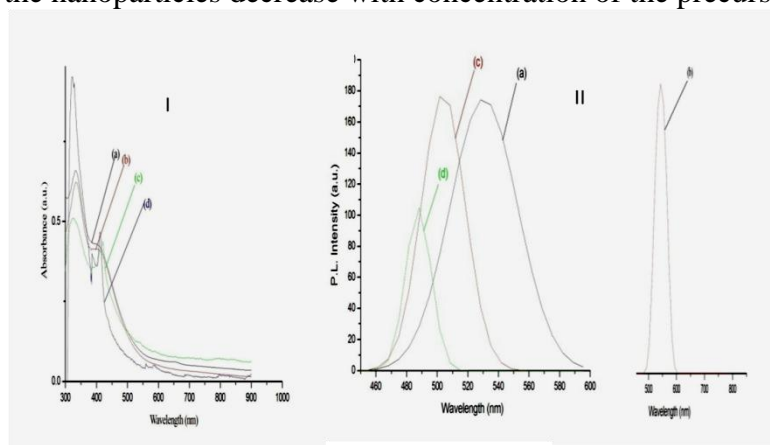


Figure 1: The absorption (I) and emission (II) spectra of cobalt sulfide nanoparticles prepared at 130 °C, 30 minutes and various amount of the complex in 5.0 g HDA (a) 1.0 g, (b) 0.5 g, (c) 0.1 g, (d) 0.05 g.

Table 1: Absorption band edges and emission maxima of the cobalt sulphide nanoparticles prepared at 130 °C and 30 minutes using various amount of precursor in HDA.

Amount of precursor (g)	Absorption band edge (nm)	Emission maximum (nm)
1.0	543	565
0.5	524	547
0.1	486	506
0.05	459	483

The emission spectra of the samples prepared at various concentrations are given in Figure 1(II). The emission maximum of the samples is red shifted from their respective band edges of the absorption spectra. The emission peaks have a narrow shape which indicates the monodispersity and good passivation of particles. The emission maximum shift to lower wavelength as the concentration of the precursor is decreased. Figure 2 shows the XRD patterns of the nanoparticles prepared at various concentration of precursor. Figure 2(a-d) shows four predominant peaks due to Co₃S₄ face-centered cubic with 2θ values 15.19, 27.82,

38.45 and 65.02. The two predominant peaks, 15.19 and 27.82 are indexed to 100 and 311 planes for cubic Co_3S_4 .

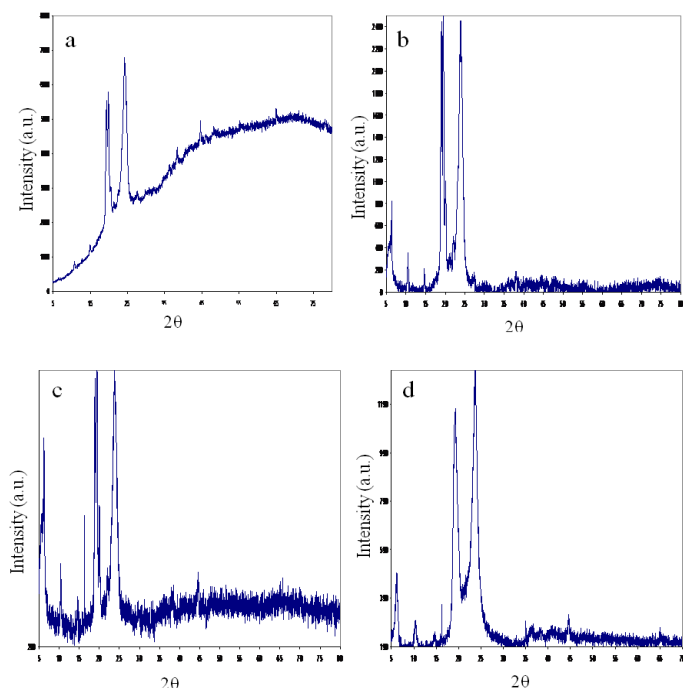


Figure 2: XRD pattern of cobalt sulfide prepared at 130 °C for 30 minutes and various amount of the complex in 5.0 g HDA (a) 1.0 g, (b) 0.5 g, (c) 0.1 g, (d) 0.05 g.

The crystallites sizes of selected cobalt sulfide nanoparticles were estimated using Scherer equation.

$$d = 0.9 \lambda / B \cos \theta_B \quad (1)$$

In this equation, d represents the crystalline size (nm); λ is the X-ray wavelength; B is the width at half maximum of the diffraction peak at θ_B ; θ_B is the diffraction angle. The average crystalline size for samples were determined to give an average values of 30.34 nm(1.0 g), 28.65 nm(0.5 g), 26.78 nm(0.1 g) and 23.94 nm(0.05 g). The TEM images of the compound prepared at various concentrations are given in Figure 3(a-d). The TEM of these nanoparticles show an increased in particle sizes as the concentration of complexes were increased. At concentration of 1.0 g (Figure 3(a)) show spherical particles and decreased to 0.5, 0.1 and 0.05 g gave mixture of spheres and rod shaped particles with the lowest concentration with irregular growth. The particle size trend conforms with the decrease from the highest to the lowest concentration promoted by the amount of precursor provided in the nucleation and growth of particles.

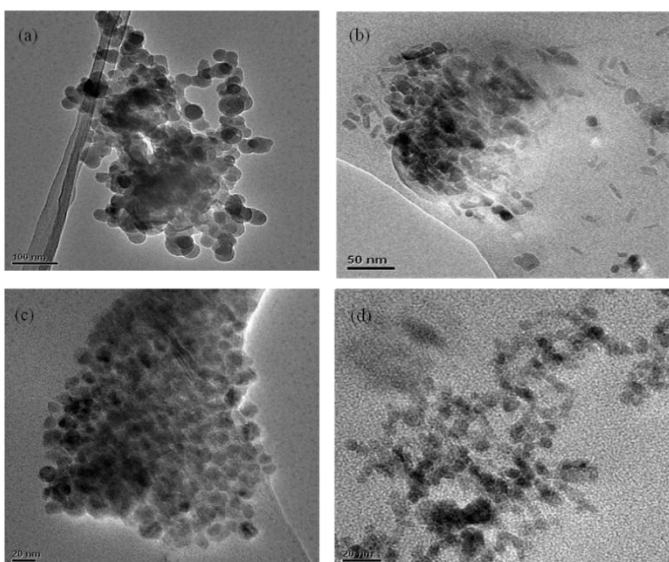


Figure 3: TEM images of cobalt sulfide prepared at 130 °C for 30 minutes and various amount of the complex in 5.0 g HDA (a) 1.0 g, (b) 0.5 g, (c) 0.1 g, (d) 0.05 g.

Conclusion: The cobalt sulfide nanoparticles were successfully prepared by single source precursor method. The particle size was found to decrease with concentration of the complex. The shapes of the particles were found to be dominated by spheres at high concentration, rods and spheres at lower concentration. XRD patterns also proved that no change in formation of the stoichiometry of cobalt sulphide which indicate that concentration have little or no effect on the stoichiometry.

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