

Effect of Concentration on Synthesis of Organic Passivated Cu_{2-x}S Nanoparticles from N-Pyrrolidine Dithiocarbamate Molecular Precursor

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The synthesis of copper sulfide nanocrystals from *bis*(N-pyrrolidinedithiocarbamato) Cu(II) single molecule precursors have been achieved. Fourier-transform infrared (FTIR) spectroscopy, elemental analysis and thermogravimetric analysis (TGA) were used to characterize the prepared complex. Nanomaterials were further confirmed by optical properties and X-ray diffraction (XRD) confirmed that the final TGA product was CuS. The absorption spectra of copper sulfide nanoparticles showed a parabolic curve which is a characteristic of CuS covellite structure. The formation of hexagonal CuS covellite phase was investigated by XRD pattern. The TEM images showed that nanoparticles capped with tri-*n*-octylphosphine oxide (TOPO) were better passivated than those capped with hexadecylamine.

Keywords: Dithiocarbamate complex, N-Pyrrolidine dithiocarbamate, Copper sulfide, Nanoparticles, Tri-octylphosphine oxide.

INTRODUCTION

Dithiocarbamate (DTC) compounds have gained lot of attention due to their strong coordinating capacity with various metal ions [1]. This has resulted in the wide usage of dithiocarbamate compounds in several areas such as in industry, agriculture, medicine and in analytical chemistry [2]. Dithiocarbamate ligands are normally prepared by the reaction of an amine (either primary or secondary) with carbon disulfide (CS₂) in the presence of a strong base [3-5]. In the past years, the thermolysis of the dithiocarbamate based metal complexes has proved to be the most interesting route in the synthesis of metal chalcogenide nanoparticles [6]. Their versatility in the molecular structure (high spin-low spin crossover phenomena) makes them the subjected of interest in the synthesis of metal sulfide nanoparticles [7].

Several researchers have explored the thermolysis of dithiocarbamate compounds as precursors for metal sulfide nanoparticles. Ajibade and Osuntokun thermolyzed hetero-leptic complexes in hexadecylamine [8] to obtain ZnS, CdS and HgS quantum dots. ZnS dots were obtained, while spherical and agglomerated shapes were obtained for CdS and HgS, respectively. Nirmal and co-workers used a complex of Cd with pyrrolidine dithiocarbamate Cd(pdtc)₂ to obtain CdS

nanoparticles. Thermal decomposition of the complex in hexadecylamine yielded spherical CdS nanoparticles under microwave irradiation and CdS nanorods were obtained by conventional heating method [9]. Our previous work reported the thermolysis of cyclohexylamine dithiocarbamate copper complex in hexadecylamine and tri-octyl-*n*-phosphine oxide to synthesize isotropic and anisotropic morphological CuS nanoparticles [10].

In this work *bis*(N-pyrrolidine dithiocarbamate)Cu(II) complex was used to synthesize CuS nanoparticles. The complex was thermolyzed in hexadecylamine and tri-octyl-*n*-phosphine oxide (TOPO), to obtain hexadecylamine-capped CuS nanoparticles and TOPO-capped CuS nanoparticles, respectively.

EXPERIMENTAL

Copper(II) chloride (97 %), hexadecylamine (HDA), trioctylphosphine oxide (TOPO), oleylamine, carbon disulfide, ammonium pyrrolidine dithiocarbamate (99 %), methanol, acetone and toluene were purchased from Sigma-Aldrich and used as received without any purification.

Fourier transform infrared (FT-IR) spectra were recorded from FT-IR Perkin Elmer 400 spectrometer from 4000-650

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cm⁻¹. Thermogravimetric analysis (TGA) was performed on Perkin Elmer Pyris 6 manager TGA under an inert atmosphere of dry nitrogen and at a heating rate of 10 °C/min using alumina pan as a reference. Absorption spectra of the particles were measured using Perkin Elmer Lambda 20 UV-visible spectrophotometer. Emission spectra of the particles were recorded on Perkin Elmer LS 45 PL spectrometer with a xenon lamp at room temperature. X-ray diffraction (XRD) measurements were carried out using a Bruker D8 advance diffractometer with Cu K_{\alpha} radiation (\lambda = 1.5406 Å) operated at 40 kV and 30 mA. Transmission electron microscopy (TEM) analyses were done on an LEO JEM 912 electron microscope with an acceleration voltage of 120 kV and a tungsten wire filament.

Preparation of *bis*(**N-pyrrolidine dithiocarbamate**) **Cu(II**) **complex:** The complex was prepared by dissolving 2 g of ammonium pyrrolidine dithiocarbamate in methanol (20 mL) in an ice cold environment using a two-neck flask. A solution of 1 g CuCl₂ in methanol (20 mL) was added dropwise. The turbid mixture was stirred for 15 min to ensure homogeneity. The final product was washed three times with deionized water and finally with methanol. The precipitate was then dried in an open air. The complex was obtained as a blackish-brown powder. Yield: 74 %. m.p. 283 °C. m.f. [Cu(C₅H₈NS₂)₂]; CHNS analysis (%): Calcd: C = 33.73, H = 4.53, N = 7.87, S = 36.02; Found: C = 32.39, H = 3.89, N = 8.61, S = 35.71.

Synthesis of CuS nanoparticles: An amount of 0.5 g of copper complex was weighed and dissolved in 6 mL oleylamine, while hexadecylamine was heated to 120 °C. The complex solution was injected into hot hexadecylamine. The mixture was stabilized at 120 °C for 1 h, then cooled to 70 °C. The mixture was flocculated using methanol and the flocculent was washed three times with methanol under centrifugation. The precipitate was dried at room temperature overnight.

RESULTS AND DISCUSSION

Fig. 1 shows the FTIR and TGA of ammonium pyrrolidine dithiocarbamate ligand and its Cu(II) complex. The FTIR spectra of the ligand revealed significant peaks at 1414 and 992 cm⁻¹ which were attributed to the partial double character

of (NCS_2) and (CS_2) , respectively [10,11]. The slight peak shifts in the spectrum of the complex was observed. The NCS₂ and CS_2 peaks shifted to higher frequencies of 1489 and 1004 cm⁻¹, respectively. The shift was due to a mesomeric drift of an electron cloud of the $-NCS_2$ moiety toward the metal ion [11,12]. The single peak of the CS₂ moiety indicated a bidentate type of bonding between the metal ion and the ligand. The TGA curve further confirmed the bidentate bonding since the degradation steps corresponded well with the bidentate structure. The TGA (solid line) and DTA curve (dotted line) in Fig. 1(B) gave a two-step decomposition of the complex. The first decomposition at 250 to 297 °C is due to the loss of $[C_5H_8NS_2]$ (calculated: 41.1 %, found: 41.8 %). The second decomposition which was ranging from 297 to 331 °C corresponds to the loss of [C₅H₈NS] (calculated: 32.1 %, found: 27.9 %). The final residue was found to be CuS (calculated: 23.5 %, found: 26.9 %).

The optical properties of the synthesized nanoparticles synthesized from the bis(N-pyrrolidine dithiocarbamate)Cu(II) complex are shown in Fig. 2. The absorption spectra of both hexadecylamine and TOPO-capped nanoparticles showed similar spectra, the difference being the unraveling of the surface plasmon resonance (SPR) peak in the hexadecylaminecapped nanoparticle synthesized at 6 g hexadecylamine. The unraveling of SPR peak could be due to a charge transfer process as previously reported by Kim et al. [13]. Such process was more defined when the capping agent concentration was increased. The plasmonic character of the prepared samples indicates an electron deficient copper sulfide stoichiometry [14-16]. The SPR is caused by the interaction of oscillating free electrons with light. This interaction results in an emergence of a peak in the near infrared region [14,16]. The hexadecylamine-capped nanoparticles showed the short-wavelength SPR in the range of 450-600 nm, while the TOPO-capped nanoparticles revealed a 400-600 nm range. The Tauc plot band edges gave 2.02 eV and 1.88 eV for the nanoparticles synthesized at 3 g and 6 g hexadecylamine, respectively. TOPOcapped nanoparticles gave a band edge value of 1.94 eV and 2.44 eV for particles prepared in 3 g and 6 g TOPO, respec-



Fig. 1. FTIR spectra of ammonium pyrrolidine DTC ligand (i) & *bis*(N-pyrrolidine DTC)Cu(II) complex (ii) (A) and TGA/DTA curve for complex (B)



Fig. 2. Absorption of Cu_{2-x}S nanoparticles prepared with (i) 3 g & (ii) 6 g of HDA and their Tauc plot (inset) (A) and with (i) 3 g & (ii) 6 g of TOPO & their Tauc plot (inset) (B)

tively. The absorption spectra of the hexadecylamine-capped copper sulfide nanoparticles [Fig. 2(A)] suggest an increase in particle size with an increase in capping molecule concentration, while the opposite was observed for TOPO-capped nanoparticles. The difference could be due to their different capping moieties, the $-NH_2$ group for hexadecylamine and phosphine oxide moiety (and also steric hindrance) on TOPO. The phosphine oxide moiety might bind strongly on the nanoparticle surface (thus resulting with a decrease in particle size when the capping concentration increases).

The emission spectra (Fig. 3), on the other hand, could not be compared to the absorption spectra due to SPR on the prepared nanoparticles. However, their full width at half maximum (FWHM) values shared some insight on the particle distribution of the prepared nanoparticles. The FWHM value of hexadecylamine-capped was found to be 101.6 and 114 nm for samples prepared in 3 g and 6 g hexadecylamine in Fig. 3(A), respectively. While the TOPO-capped nanoparticles gave an FWHM values of 71.2 and 102 nm for 3 g and 6 g TOPO in Fig. 3(B), respectively. These findings suggest that nanoparticles prepared in TOPO were better passivated and were narrowly distributed in comparison to the hexadecylamine capped nanoparticles.

X-ray diffraction patterns for the copper sulfide nanocrystals prepared using bis(N-pyrrolidinedithiocarbamato) Cu(II) as the precursor are shown in Fig. 4. The crystal planes revealed a pure hexagonal phase CuS covellite (JCPDS No. of 03-065-3556) which was apparent from the absorption spectra (SPR peaks indicating electron deficient copper sulfide) and the TGA analysis that gave a CuS as final residue. The



Fig. 3. Emission spectra of Cu_{2-x}S nanoparticles prepared with (i) 3 g & (ii) 6 g of HDA (A) and with (i) 3 g & (ii) 6 g of TOPO (B)



Fig. 4. XRD patterns of CuS nanoparticles synthesized in (a) (i) 3 g, (ii) 6 g HDA and (b) (i) 3 g, (ii) 6 g TOPO

(006) crystal plane was more pronounced and crystalline on the TOPO-capped nanoparticles [Fig. 4(b)] compared to the hexadecylamine-capped nanoparticles [Fig. 4(a)], suggesting a better passivation of the TOPO-capped nanoparticles. This was further confirmed by crystal size that gave 25.6 and 25.1 nm for 3 g and 6 g TOPO, respectively. The hexadecylamine crystal sizes were 35.8 and 34.4 nm for 3 g and 6 g hexadecylamine, respectively. The findings were in agreement with the PL (FWHM) values that suggested polydispersed nanoparticles on the hexadecylamine-capped nanoparticles.

Anisotropic and isotropic copper sulfide nanoparticles were obtained as shown by their TEM images in Fig. 5. A huge hexagonal shaped particles and some distorted hexagonal-like shaped particles growing on top of each other were observed in Fig. 5(a) which is a sign of agglomeration of the as-prepared particles. Fig. 5(b) showed that an increase in concentration of hexadecylamine changed the morphology of the particles, from a hexagonal shape to mixed morphologies which include sphere-like and rod-like shapes. Other than that, there was an agglomeration of particles. The anisotropic shape could be due to the oriented attachment of capping ligands on the surface of the nanoparticles that was also reported by Lee et al. [17]. These results were in agreement with the photoluminescence spectrum which gave a broader emission for the samples prepared in hexadecylamine than the ones prepared in TOPO. Unlike the hexadecylamine-capped nanoparticles, Fig. 5(c) for the TOPO-capped nanoparticles at lower concentrations gave well-dispersed nanoparticles with an average diameter of 11.1 nm. The dispersity of particles was in agreement with the photoluminescence spectra. While the particles prepared at a higher concentration of TOPO (Fig. 5(d)) gave anisotropic CuS nanoparticles, their particle shapes included hexagonal, truncated rod-like shape and circular shaped like particles. It is evident that as the capping concentration increased, the particle distribution also increase.

Conclusion

The FTIR spectroscopy showed a symmetrical CN and CS₂ peaks that are consistent with the bidentate bonding



Fig. 5. TEM images of CuS nanoparticles prepared in (a) 3 g hexadecylamine, (b) 6 g hexadecylamine, (c) 3 g TOPO and (d) 6 g TOPO

between the ligand and the metal ion. The thermal analysis revealed the degradation steps of the complex that leads to the final residue of metal sulfide. The thermolysis of this complex in the presence of TOPO and hexadecylamine gave an organically capped copper sulfide nanoparticles. The characterization of the synthesized samples confirmed that nanoparticles capped with TOPO were better passivated and smaller than the ones capped with hexadecylamine.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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