Review Paper:

Exploring Diverse Precursors for Metal Sulfide Nanoparticle Synthesis: A Comprehensive Review

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Abstract

Metal complex chalcogenides and metal sulfides have been of interest in the scientific research world for their tunable chemical, optical and physical properties. A favourable synthesis method, using a single-source precursor for control purposes and the electrosynthesis method included for comparison reasons is articulated in this review. The effects of dithiocarbamates and their role in forming metal-sulfides' morphology are discussed. Based on the data collected by various microscopic and spectroscopic techniques, the chemical and physical properties of the metal-sulfides are also discussed. This review aims to provide an overview of different molecular precursors used in catalysis to produce metal sulfides with enhanced properties, through various decomposition methods either in the solution or in the vapour phase.

This review also considers several important factors such as reaction time, surfactants, precursor concentration and the type of precursor used, which can be manipulated and can play a significant role in the metal sulfides formed during decomposition.

Keywords: Precursor, Metal Sulfide Nanoparticles, Dithiocarbamates, Morphology, Surfactants.

Introduction

Scientists have been increasingly interested in nanoscale materials due to their low cost, low toxicity, adjustable transport characteristics for drug delivery, wide availability, unique properties and vast potential applications in fields such as medicine, nanotechnology, optoelectronics and biology where these materials are highly valued.[45]

Nanoparticles or nanoscale metal sulfides can exist in multiple phases like iron sulfide (several phases FeS, Fe_3S_4, Fe_7S_8, Fe_8S_9, cubic and orthorhombic FeS_2[38]) and nickel sulfide (phases α-NiS, β-NiS, NiS_2, Ni_3S_2, Ni_3S_4, Ni_7S_6 and Ni_9S_8[40]) to name a few. Identifying these phases is not always easy.

Generally metal sulfides are compounds where the sulfur anion binds to a metal, cations, or semi-metal cations to form mono-metal sulfides (M_xS_y) of several stoichiometries and a number of metal sulfides have been reported to date, SnS, TiS_2, GeS, Fe_3S_4, CoS_2, CdS and ZnS, just to name a few. Bi-metal sulfide formation also follows the same approach as mono-metal sulfides and the commonly reported ones are Cu_3SbS_4, $KFeS_2$, $ZnLn_2S_4$ and $NaCrS_2$ to mention a few. The PbS, ZnS and NaS metal sulfides have shown to be high-symmetric pyrite, sphalerite and anti-fluorite forms respectively and are important structural types.[8]

Successful application of metal sulfides to the fields as mentioned above highly depends on making alterations or manipulating the nanomaterials prepared by controlling the starting material and the environment of the reaction for the formation of nanomaterials to enhance their properties. Experimental parameters like temperature, time, surfactants, thermolysis solvents and precursor concentration have been controlled to achieve metal sulfides with ideal physical properties such as size, morphology and composition. Metal sulphides like “Nickel Sulfide” have applications in energy-based devices as catalysts and electrocatalysts.[19] They are used as anticancer agents in drug delivery,[42] and they are applied in solar cells.[41]

Semiconductor nanocrystals are incredibly small particles with unique optical and electronic properties that are dependent on their size. These nanocrystals display discrete electronic transitions, bridging the gap between molecules and crystals as shown in figure 1.[44] Since the oxidative strength of holes in the valence band and electrons in the conduction band differs greatly amongst semiconductors, their redox activity may be fine-tuned, if possible, by fine-tuning the band edges. Semiconductor nanoparticles have generated significant interest in the scientific community for their synthesis and characterization. As a result, intense research has focused on synthesizing nano-dimensional materials, particularly metal sulfides, for the past 20+ years, with various methods being investigated and developed.[48]

A variety of techniques have been utilized to synthesize metal sulfide nanoparticles including co-precipitation,[5] sonochemical, sol-gel,[31] mechanochemical, microwave irradiation, single-source precursor approach,[29] electrosynthesis, UV Irradiation,[36] microwave solvothermal,[6] chemical bath deposition,[30] and radiolytic[45] methods.

Metal Complexes: Metal complexes play a significant role in most chemical, pharmaceutical, agricultural and medicinal industries.[23] Metal complexes can enhance the efficiency of therapeutic agents by accelerating drug action through coordination with metal ions.

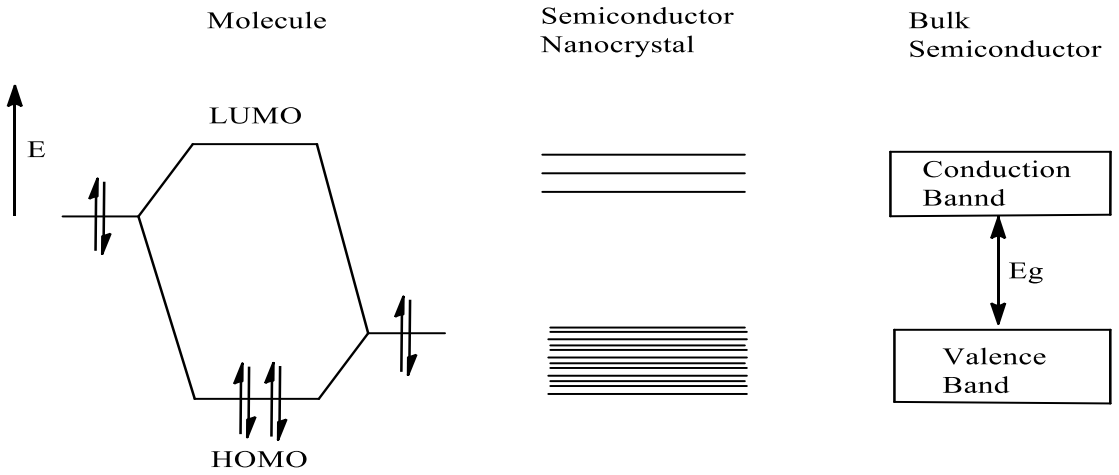


Figure 1: A diagram showing the semiconductor in transition from small molecule to bulkier crystals with regards to electronic energy.

Applying these complexes in nanomaterial synthesis results in functionalized metal nanomaterial consisting of properties such as being biocompatible, having a small size and shape dependence in controlled parameters giving versatile applications in biomedicine. Ru(II)-polypyridyl complex is a good example as it has shown to be a good theranostic tool for cancer treatment, this is due to its high luminescence and photophysical properties.[18]

Dithiocarbamate Metal Complexes: Dithiocarbamates play a vital role as materials that are extensively used in the field of coordination chemistry.[9,35] The versatile coordination ability and significant role of dithiocarbamate Schiff base ligands derived from heterocyclic compounds in various fields make their coordination chemistry of continuing interest.[22] The dithiocarbamates are versatile chelating ligands that are capable of forming stable complexes with lanthanide, actinide, main group elements and transition metals.[47] Most transition metals can form complexes with these compounds, often in multiple modes such as terminal bidentate, bridging bidentate, or monodentate.[49]

Metal dithiocarbamates are complexes that are commonly formed through the bonding of metals and sulfur. They are widely used in various applications such as in high-pressure lubricants. Zinc dithiocarbamate complexes on their own are applied in vulcanization accelerators in the rubber industry.[23] Active ingredients of pharmaceuticals, fungicides and pesticide products,[30] are applied as precursors for semiconductor nanocrystals,[3] and they show antifungal activity [10] with enhanced antimicrobial properties. The relatively same antimicrobial potential has been shown by MnS and NiS nanoparticles, inhibiting *B. subtilis* and *S. epidermidis* fungus respectively.

Metal Complexes as Single-Source Precursors: When well-defined molecular species having pre-formed metal-sulfur are heated to decomposition, either in the solution or vapour phase, organics are easily lost and nano-dimensional metal sulfides are produced. The process follows a single-source precursor method. Single-source precursors (SSPs) can be handled easily in varying laboratory settings due to being usually nonpyrophoric, less toxic and nullifying any side reactions between the chalcogenide sources and separate metals.

The morphology and size of the nanomaterial synthesized during nanoparticle synthesis can be adjusted by manipulating the external factors, such as solvent, concentration, temperature, surfactants, time etc. This is due to the single-source precursor's rate of decomposition being potentially manipulable. Two different methods can be identified for single-source precursor decomposition: chemical vapour deposition (CVD) and the solvothermal approach. The chemical vapour deposition approach relies on the precursor's volatility and is mostly applied in thin film preparation. In the Solvothermal approach, a precursor is dissolved in a hot liquid mixture of surfactants where nanocrystals are developed. This method benefits from the balance of surfactants acting as a dynamic entity throughout the development process, constantly absorbing and desorbing from the developing surface via their polar head groups and aiding in the regulation of both growth and nucleation from the produced seeds.

Due to their low cost and ability to dissolve a variety of single-source precursors, primary amines with a high boiling point like oleylamine (OA),[46] and other surfactants like hexadecylamine (HDA),[28] olive oil (OO), tri-n-octylphospine oxide (TOPO),[12] tri-n-octylphosphine (TOP),[16,43] and coconut oil (CO), are frequently used as surfactants. However, when used with dithiocarbamate precursors, they can also significantly alter the chemical makeup of the precursor.

An Overview of Several Precursors utilized for Nanoparticle Synthesis: The solvothermal approach used for synthesizing quantum dots using dithiocarbamate precursors was first reported in 1996 by Trindade et al[48]

when they heated [$Cd(S_2CNEt_2)_2$] in 4-ethylpyridine at 168 °C which resulted in CdS materials having an optical band gap of 2.63 eV.[44] Ever since then, there has been a lot of advancement for developing a variety of synthetic procedures and precursors to achieve nanoscale materials of high quality with effective applicable properties: both chemical and physical like using different surfactants as capping agents.

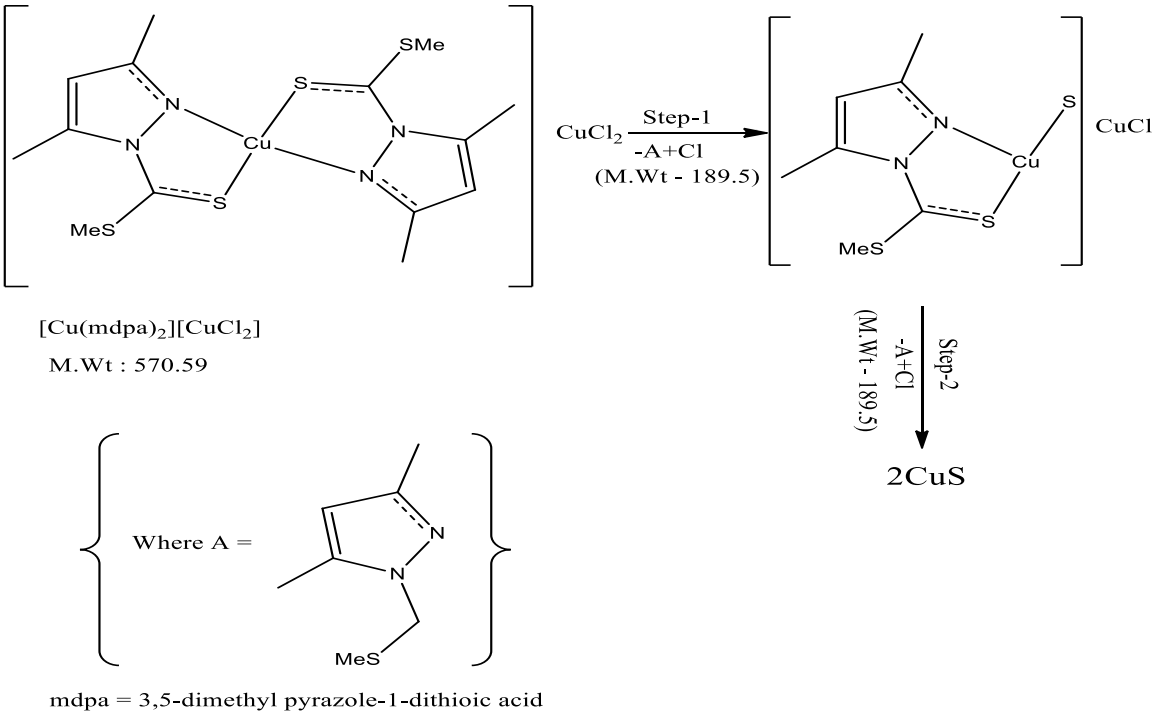
Mondal et al[25] described the production of Cu_2S as shown in scheme 1 from the decomposition of the SSP in ethylene glycol or ethylenediamine where "mdpa = 3,5-dimethyl pyrazole-1-dithioic acid". Using the solvothermal method, they mixed the complex they prepared [$Cu(mdpa)_2$][$CuCl_2$], with a solvent, either ethylene glycol (EG) or ethylenediamine (EN) in an inert atmosphere and heated for 30 minutes and 1 hour at 150 and 180 °C respectively.

Irrespective of the solvent they used, a hexagonal nanoplatelet of Cu_2S was formed. By increasing the reaction time, there was an increase in crystallinity and porosity of the Cu_2S nanocrystals. The observed large band gap of 1.8 eV and 2.4 eV for Cu_2S prepared from ethylenediamine and ethylene glycol indicated that Cu_2S is suitable for photocatalytic decomposition of poisonous and polluting substances.[25] Having observed these properties, Mondal et al[24] later reported the synthesis of p-Cu_2S thin films by the electrosynthesis method as shown in scheme 2, using the same [$Cu(mdpa)_2$][$CuCl_2$] complex as a single-source precursor to enhance photocatalytic activities.[26]

After realizing the potential photocatalytic activities of metal sulfide obtained from decomposing [$Cu(mdpa)_2$][$CuCl_2$], Mondal et al[27] reported a new single molecular precursor [$Cu(bdpa)_2$][$CuCl_2$] replacing the methyl group with a benzyl group, to synthesize hexagonal copper-deficient copper (I) sulfides. Decomposing [$Cu(bdpa)_2$][$CuCl_2$] in both chelating and non-chelating solvents such as ethylenediamine, ethylene glycol and hydrazine hydrate (HH) resulted in spherically-shaped $Cu_{1.97}S$ for EN and EG and hexagonal plate morphology of $Cu_{1.8}S$ for HH. The sulfides indicated a quantum confinement effect from the observed optical band values of 1.8-2.5 eV.[27]

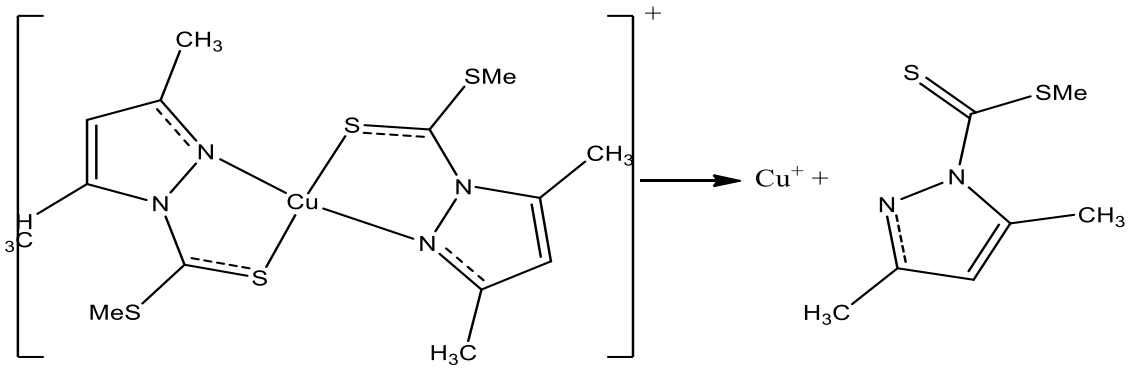
The ability of the transition metals to bind to various ligands, forming disodium salts of dithiocarbamates prepared from urea, dithiooxamide and thiourea has offered different properties. This has led to a vast number of researchers trying to explore further these properties, as coupling a different transition metal or replacing the metal of the same known complex could lead to the formation of enhanced complexes which could form nanoparticles with desirable chemical and physical properties.

Mondal et al[26] further reported two complexes, "[$Cd(mdpa)_2Cl_2$] and [$Cd(bdpa)_2Cl_2$]", this time using cadmium as the transition metal to synthesize CdS nanoparticles where mdpa is methyl ester of 3,5-dimethylpyrazole-1-dithioic acid and bdpa is benzyl ester of 3,5-dibenzylpyrazole-1-dithioic acid. Both complexes were decomposed at 150 and 180 °C with ethylenediamine and ethylene glycol as solvents, getting spherical nanoparticles from [$Cd(mdpa)_2Cl_2$] and rod shape nanoparticles from [$Cd(bdpa)_2Cl_2$] complexes.[24]

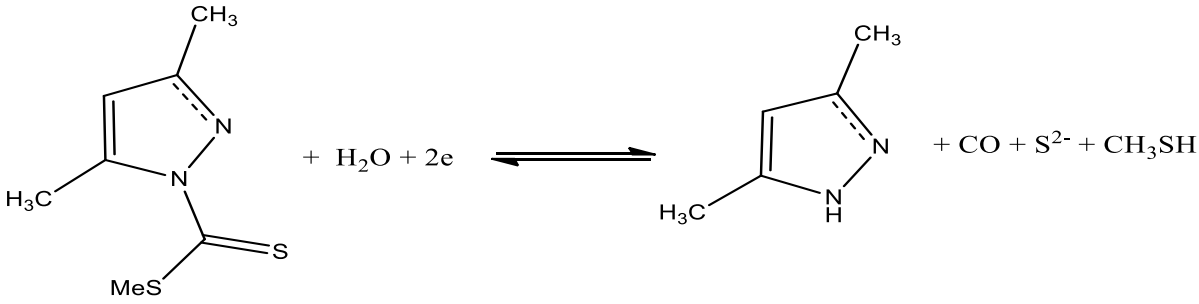


Scheme 1: A schematic presentation of the steps of decomposition of the Single-Source Precursor in the thermos gravimetric analysis.[10]

I Dissolution of complex :



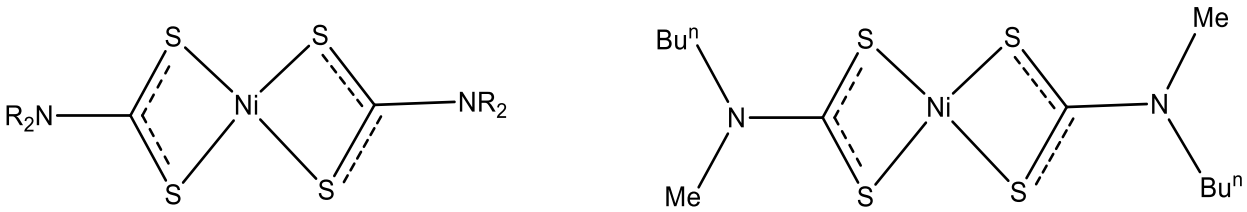
II Reduction of ligand :



III Formation of Cu_2S :

$$2Cu^{+} + S^{2-} \longrightarrow Cu_2S$$

Scheme 2: Schematic presentation of the electrochemical process.[25]



1R = Me, 2R = Et, 3R = ^{i}Bu 4

Scheme 3: Schematic presentation of dithiocarbamate complexes 1-4 used as SSP's.[33]

Varying the reaction time did not have any effect on the shape of the particles produced but resulted in increase of particle size. This demonstrated that there is a possible effect of thiol ligands as part of the reaction conditions. Where $[Cd(mdpa)_2Cl_2]$ has CH_3SH, which is a small thiol ligand that binds strongly to all planes of seed crystals producing spherical nanocrystals only, while $[Cd(bdpa)_2Cl_2]$ has $PhCH_2SH$, a bulkier thiol, preferentially binding polar facets of the nucleus, so nanoparticles grow anisotropically. It is worth noting that the formation of rod and spherically shaped nanoparticles depended on the precursor substituents present, regardless of the type of solvent utilized during the thermolysis process.[24]

Roffey et al[39] prepared and utilized nickel bis(dithiocarbamate) complexes that are square-planar as SSPs in generating NiS nanoparticles following the solvothermal method for decomposition. All complexes synthesized 1-4 shown in scheme 3 were green in colour and were not sensitive to air and moisture-stable solids. From the crystallographic studies conducted on nickel bis (dithiocarbamate) complexes, square-planar coordination

was reported which allows for solid-state packing that is efficient accounting for low solubility displayed by complex 1 where all 13 atoms are in a plane so they can pack efficiently.

Thermal gravimetric analysis (TGA) and Differential scanning calorimetry (DSC) were used to study the stability of all complexes in their solid state. The TGA of complexes 2-4 were thermally stable until 300 °C. In one sharp step, 95 % loss of their mass was observed and the melting peaks at 235 °C for complex 2, 177 °C for complex 3 and 118 °C for complex 4 were observed from the DSC graphs. However, complex 1 appeared to be different from 2-4, as it gradually loses mass from 106 to 367 °C equivalent to $S(SCNMe_2)_2$, hinting that the complex decomposes without sublimation and evaporation.

The effects of using various parameters towards the phase of the nickel nanoparticles formed were also studied. The parameters such as the surfactants (oleylamine, thiuram disulfide and tetra-iso-butyl thiuram disulfide) at the various temperatures at 150, 180, 260 and 280 °C and the precursor concentration ranging between 10-50 mM, were used to study the decomposition of the complexes.

The same differential behaviour was observed after heating the solutions to higher temperatures, 2-4 were reported to become deep brown and at around 130-140 °C, became opaque and black, with 1 doing the same only at slightly higher temperatures, being brown at lower temperatures (90 °C) and at higher temperatures (140-150 °C) becoming black. The nanoparticles were revealed to be hexagonal for all the decomposed complexes with the d-spacings of 2.95 Å and for each complex substituent, the average particle diameter varied. This demonstrates that an increase in the bulkiness of the substituent increases the average diameter of produced nanoparticles.[39]

The black crystalline phase was observed to be pure α-NiS for all decompositions 1-4 suggesting that in this oleylamine single amide exchange, varying the dithiocarbamate made no effect on the route of decomposition. For all the cases, the same product is achieved and the nickel sulfide phase produced is not affected significantly.[16] Hollingsworth et al[15] had reported further studies of complex 3 due to its easy synthesis and purification. Concentrated (5 mM) solutions were decomposed at different temperatures. At higher temperatures of 280 °C, a pure β-NiS was observed by XRD analyses, which exhibited larger average diameters compared to α-NiS nanoparticles at lower temperatures where a "square-planar nickel (II) center bound by two chelating ligands" was observed as expected.

The analysis done for different precursor concentrations (10, 20, 40 and 50 mM) to determine their effect on the synthesized α-NiS nanoparticles revealed that changing the concentration of a precursor does not significantly affect the NiS nanocrystals formed, as the morphology of the nanoparticles appeared to be roughly hexagonal for all but the average size was affected as the average nanoparticle diameter increased with an increase in precursor concentration.[15]

Copper indium diselenide ($CuInSe_2$; CIS) has a structure like that of cubic ZnS, having one of the highest thin-film solar cell efficiency of 17.7 %. This sparks interest in finding out the type of properties, a cubic ZnS or ZnS nanoparticles could offer. Recently Islam et al[17] designed zinc dithiocarbamate complexes, $[Zn(S_2CN^iBu_2)_2]$ and $[Zn(S_2CNMe_2)_2]$, aiming to understand the role they play as precursors to ZnS nanoparticles. Khalil et al[18] prepared ZnS nanoparticles by dispersing bis(diethyldithiocarbamate) zinc (II) complex in 3.0 mL of TOP injected into a hot oleylamine and the observed properties were cube-like shape with 6.5 nm size, having prominent antifungal capabilities. The synthesis of ZnS nanoparticles using the following reaction conditions: 280 °C in oleylamine and varied the precursor concentration (0.005, 0.01 and 0.02 M) and obtained a cubic phase for all concentrations with a band gap ranging at 2.94-2.88 eV and the average diameter at 4.2-4.5 nm.[1]

Over the years the need for the use of cost-effective techniques and less toxic methods while ensuring the purity and controllability of the synthesized nanoparticles, has resulted in the use of surfactants being brought to light. Surfactants help to prevent the aggregation of synthesized nanoparticles which is crucial in ensuring the stability of colloidal systems.[4] They also assist in adjusting between the solid and liquid surface/interface tensions and the dispersion stability is enhanced.

Surface-modified nanoparticles or nanostructures have broad applications. Functional nanoparticle-surfactant combinations play important roles in the structural materials, medical field, catalysis, energy conversion processes, cleaning and purification systems.[14] With these applications, Green and O'Brien[13] were amongst the first to explore the solvothermal synthesis of metal sulfides using dithiocarbamate complexes and coordinating solvents like TOP and long-chain primary amines. They prepared PbS cubes by decomposing $[Pb(S_2CNBu_2)_2]$ at 200 °C in TOP.

Gervas et al[11] reported synthesis of high-quality nickel sulfide nanoparticles using dithiocarbamate complexes bis(dipiperidinyl dithiocarbamato) nickel (II) and bis(ditetrahydroquinolinyl dithicarbamato) nickel (II) as SSPs following the solvothermal route where dodecylamine, hexadecylamine and oleylamine were used as surfactants. This group reported the use of different surfactants, temperatures and reaction times as parameters to observe any changes in the morphology of the produced sulfides.

When both complexes were thermalized in dodecylamine, the pure phase of cubic Ni_3S_4 was obtained at 190 °C and 230 °C. Both complexes in hexadecylamine at temperatures 190, 230 and 270 °C gave a pure rhombohedral phase of Ni_3S_2

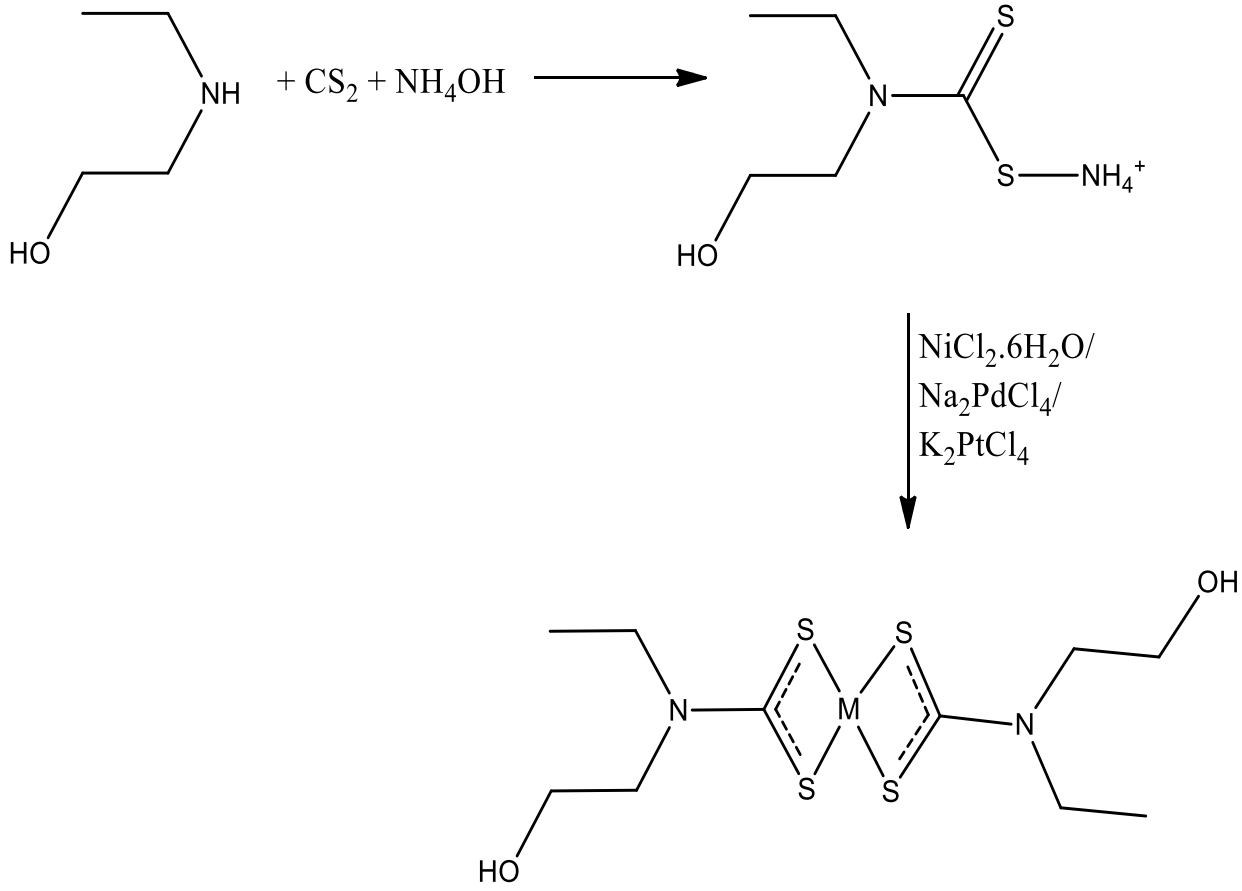
while in oleylamine, mixed phases were obtained. The X-ray diffraction peaks were in good agreement with the phases of nanoparticles obtained. Cubic Ni_3S_4, rhombohedral α-Ni_3S_2 and mixed phases when DDA, HDA and OA were used as capping agents respectively.[11]

Pullabhotla and Mabila[33], reported the preparation of SnS nanoparticles having varied morphologies, using tetra thiourea tin (II) chloride complex $[Sn(SC(NH_2)_2Cl_2]$ as the SSP. A solution of $[Sn(SC(NH_2)_2Cl_2]$ and TOP was injected into a hot HDA for 4 h at 190 °C. Samples were removed at different time intervals 30 min, 1, 2 and 4 h to see the effect of time on the formed HDA-capped SnS nanoparticles. TEM images reflected that the average sizes of the anisotropic particles were 56.15, 50.28, 44.53 and 60.46 nm for 30 min, 1, 2 and 4h respectively. The SnS nanoparticle's anisotropic growth might be a result of the large concentration of the monomer, the nature of the added precursor and a low temperature for the reaction. The particles were large and almost spherically shaped with no uniformity.

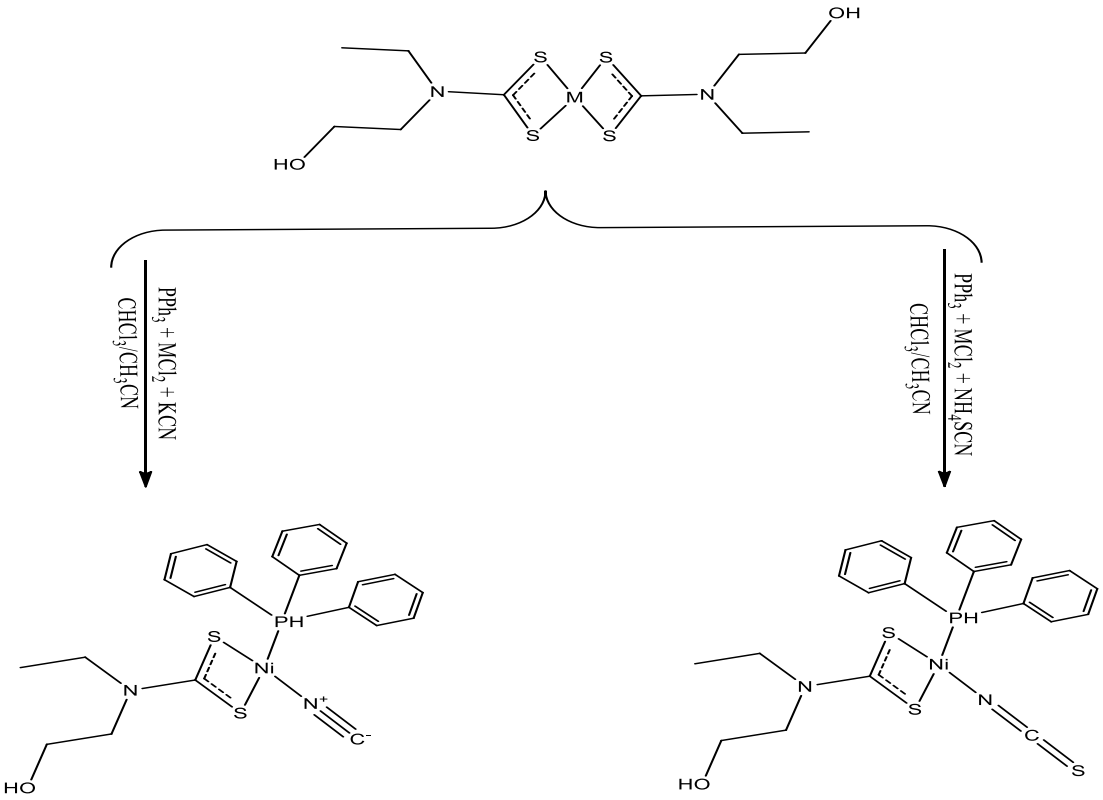
The HRTEM analysis further gave an enhanced indication of the SnS varying particle shapes. The orthorhombic SnS nanoparticles of planes (101) and (120) were assigned the interplanar distance of 0.293 and 0.360 nm of the lattice spacing. Mabila and Pullabhotla[20] reported the thermal decomposition of $[Sn(SC(NH_2)_2Cl_2]$ following a one-pot synthetic approach to avoid the use of volatile, highly toxic compounds at elevated temperatures.

During the same year 2017, Pullabhotla and Ngcobo[34] reported the use of tetramethyl thiourea lead (II) acetate complex as the single-source precursor for preparing PbS nanocrystals. They decomposed a solution of tetramethyl thiourea lead (II) acetate and TOP in hot HDA at 190 °C for 4 h which afforded PbS nanocrystals having an average of 9.97 nm sized particles. The aliquots retrieved at time intervals of 1-2 h demonstrated an increase in particle size when the thermolysis time was longer. By controlling the temperature of the reaction and the different surfactants of differing alkyl chain lengths, they were able to generate PbS nanocrystals with diameters ranging from 9.97-42.28 nm at 190 °C and 10.27-12.18 nm at 230 °C. This differed with the surfactant being used as it influenced particle growth.

The TEM images showed that after 2 h at 230 °C, the average particle size with HDA was 12.18 nm, with DDA it was 60.10 nm and with OA it was 113.05 nm, while with decylamine at 270 °C after 2 h gave rod-shaped materials having dimensions of 42.01x12.41 nm (length x breadth). This indicated the influence of capping agents having different chain lengths on the size of the particles and shape. As the chain length of capping agents increases, a decrease in the average size of particles is observed.[34]



Scheme 4: Schematic presentation of homoleptic complexes.[7]



Scheme 5: Schematic presentation of heteroleptic complexes.[7]

Homoleptic and Heteroleptic Complexes as SSP's: Bobinihi et al[7] detailed several dithiocarbamate complexes of Pt (II), Ni (II) and Pd (II) utilized as SSPs. Homoleptic complexes of these metals were synthesized (Scheme 4), first, the dithiocarbamate moiety having ethyl and ethanol groups, second. The analog of nickel being heteroleptic was also reported of type "[Ni(PPh_3)(NC)]. (PPh_3) and [NiL(PPh_3)(NCS)]", where L= 2-hydroxylethanol dithiocarbamate (Scheme 5).

Thermal decomposition studies of homoleptic [NiL_2], [PdL_2] and [PtL_2] complexes displayed in scheme 4 show 76, 61 and 50 % loss with the decomposition range at 212-258, 225-302 and 203-690 °C respectively. All metal sulfides were obtained in a single step as NiS, PdS_2 and PtS_2 respectively. Complexes displayed in scheme 5 that are heteroleptic, a single-step decomposition was observed for [NiL(PPh_3)(NC)]. (PPh_3) at 266-351 °C range with an 82 % loss. [NiL(PPh_3)(NCS)] underwent a two-step decomposition, with the first step at 204-274 °C range and step two at 280-341 °C range with 32 % and an 83 % loss respectively. Metal sulfides obtained were NiS_2 and NiS respectively with $RNCS_2Ni$ formed as an intermediate for the two-step decomposition.[7] The behaviour of both homoleptic and heteroleptic complexes with regard to their thermal decomposition steps is consistent with the work reported by Dar et al.[9]

Ternary Sulfides: The different parameters that play a significant role in the type of nanoparticles obtained, should be morphology-wise, size-wise, or even the whole make-up of a formed compound. The type of metals used have different properties from each other. Ternary compounds tend to explore this phenomenon more and the nanomaterial obtained from these compounds has electronic and optical properties, providing possible applications in electronic devices. Intending to widen the number of semiconductor nanoparticles, Akram et al[2] designed a few precursors [$Fe(S_2CNhex_2)_3$] and [$Fe((SePPh_2)_2N)_2$], after thermolysis at moderate temperatures obtained $CuFeS_2$ and $CuFeSe_2$ nanoparticles respectively. The optical band gap of both nanoparticles was observed to be decreasing for sulfides synthesized at higher temperatures.[2]

Roffey et al[38] utilized several air-stable di-isobutyl-dithiocarbamates [$M(S_2CN^1Bu_2)_n$] as SSP to form ternary sulfides of Fe-Ni, Fe-Cu and Ni-Co. First attempt to make a ternary iron-nickel sulfide was by using [$Fe(S_2CN^1Bu_2)_3$] and [$Ni(S_2CN^1Bu_2)_2$] as SSPs. Oleylamine was used as the surfactant in the decomposition of both complexes and was studied at different temperatures of 150, 180, 230, 260 and 280 °C. Both samples were heated to the desired temperature then maintained for 60 minutes to get nanoparticles which were then separated as black powders for analysis, observing mostly amorphous nanomaterials at 150 °C and approximately spherical small crystallites at 280 °C.[37] This goes to show that the crystal or nanoparticle size for ternary sulfides synthesized at higher temperatures is relatively small.

Conclusion

Precursors and synthesis techniques have been established for the synthesis of nanoparticles for several technological

applications. The different properties provided by nanoparticles arise from several components such as morphology, particle size and composition and this review has provided an overview of tuning various reaction parameters to achieve this. In this review it has been highlighted that the thiol ligands substituted in precursors display a possible effect as being part of the reaction conditions, causing shape alterations based on the bulkiness of the substituted thiol ligands. The use of different complexes was highlighted to have the same hexagonal shape to a certain extent which differ in size depending on how bulky the complex being used is. The reaction time also plays a role in the size of nanoparticles formed, as longer decomposition time results in an increase in particle size, which is in good agreement with the Ostwald ripening process.

For the surfactants used, a different trend is followed, as the chain length of the capping agent increases and the average particle size decreases. The role played by different reaction parameters has proven to play a significant role in the nanoparticles formed and their potential application across industries, being used as a medium in the medicinal industry for drug delivery. However, the type of precursor used in synthesizing nanoparticles brings several factors to the end product which could bring new innovations, hence it would be of interest to design new precursors to produce more enhanced nanoparticles.

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