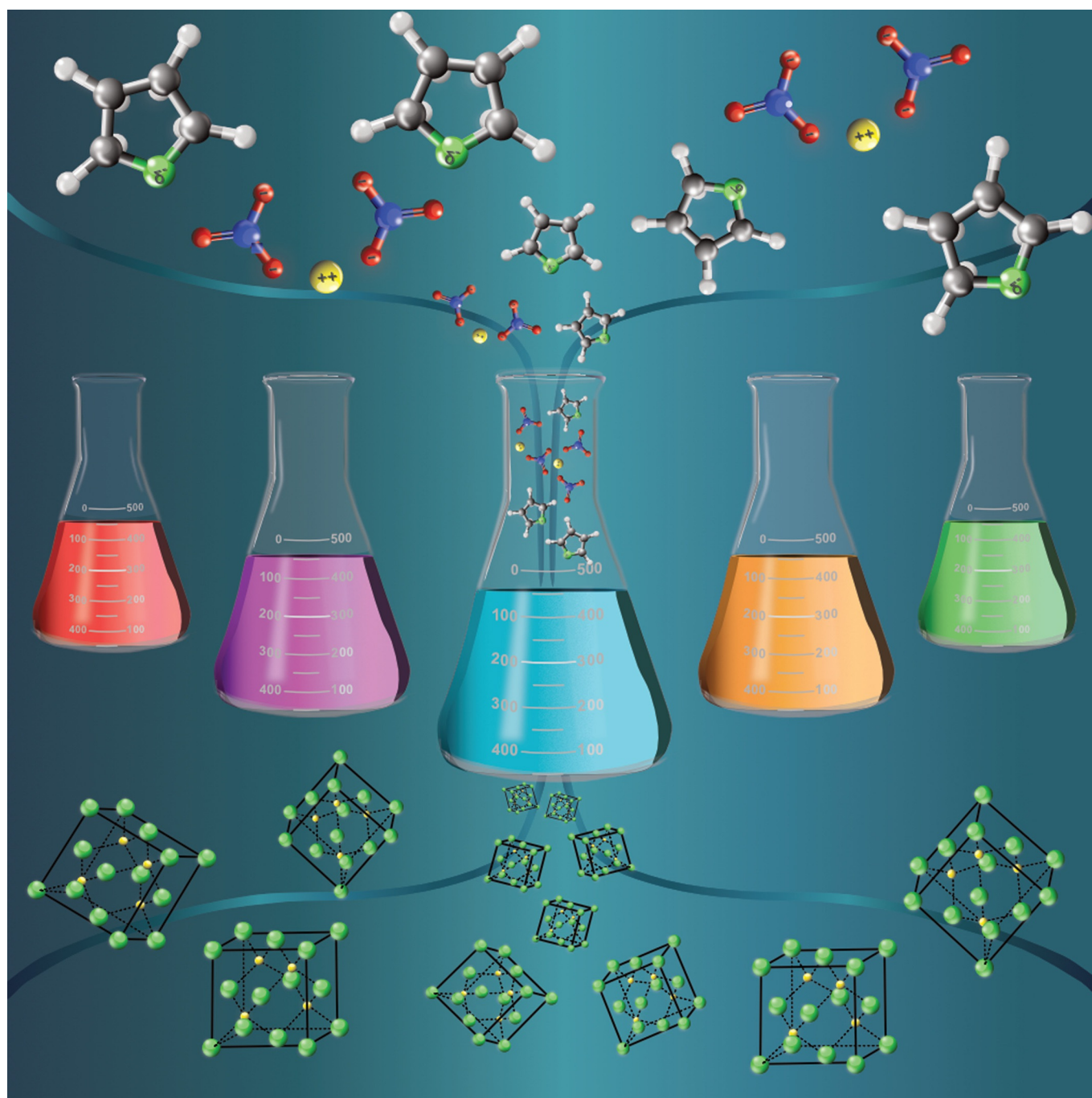


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🏆 Metal Sulfide Nanoparticles: Precursor Chemistry

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Abstract: Fascination with and the need for evermore increasing efficiency, power, or strength have been the cornerstones for developing new materials and methods for their creation. Higher solar cell conversion efficiencies, increased battery storage power, and lightweight strong materials are some that have been at the forefront of attention for these efforts. Materials created for most applications start as simple chemical compounds. A study of how these chemicals have been used in the past can be used to create new

materials and new methods of production. Herein, a class of materials that are valuable in a multitude of applications, metal sulfide nanoparticles, are examined, along with how they are being produced and how new methods can be established that will help to standardize and increase production capabilities. Precursor–solvent combinations that can be used to create metal sulfide nanoparticles in the gas phase are also explored.

1. Introduction

Increased interest in metal sulfide nanoparticles (NPs) has mainly been due to their photo- and electrochemical properties, which can rival those of metal oxide NPs. Although NPs are widely used—from catalysis to sensing applications, electronics, cosmetics, and photovoltaics, to name a few—there is still much room for large improvements in terms of the performance of the materials.


For an easy comparison, one of the most widely used metal oxide NPs are those of titanium. TiO₂ NPs contributed to a large share of the \$8.5 billion global nanomaterials market in 2019 alone.^[1] It is also a very well-known photocatalyst that has been and is still being extensively studied. Titanium dioxide has a band gap of 3.2 eV and is active below 400 nm in the UV region of the electromagnetic spectrum.^[2] This implies that it uses a rather small part of the sun's spectrum, whereas metal sulfide NP photocatalysts, such as CdS, with a band gap of 2.45 eV, possess the ability to absorb in the visible region of the spectrum of up to 520 nm.^[3] Because the band gap is the energy difference between the valence and conduction bands, this translates to the energy difference between ionization potential and electron affinity of the compound.^[4] Sulfur with a low ionization potential and higher electron affinity than those of oxygen can explain the general trend of sulfides having narrow band gaps compared with oxides. Hence, sulfides can be operational in the visible region of the electromagnetic spectrum and is an enticing alternative to traditional metal oxide photocatalysts.


The combination of metal oxide NPs and metal sulfide NPs has shown to result in properties far superior to those of the individual properties of metal oxide NPs. Mao et al. reported a comparison of the photocatalytic behavior of pure nanostructured TiO₂ and nanostructured TiO₂ modified with CdS.^[5] It is reported that the performance of nanotitania modified with CdS exceeds that of pure nanotitania. This shows that metal sulfide NPs are beneficial themselves and can also enhance the properties of existing metal oxide nanomaterials. Mittal et al. showed a ternary composite of CdS, ZnS, and TiO₂, the photoactivities of which far exceeded that of the TiO₂/CdS binary compound alone.^[6]


The combination of binary metal sulfides as cocatalysts with tertiary metal sulfides has also been studied as a photocatalyst. In a report by Nguyen et al., Zn_xCd_{1-x}S was studied for its photoelectrochemical properties, as well as the use of MoS₂ as a cocatalyst.^[7] Zn_xCd_{1-x}S itself is shown to absorb in the visible region. The absorption region also depends on the ratio of Cd and Zn present because a higher fraction of Cd moves the band gap closer to that of Cd and similarly with Zn. The loading of the MoS₂ cocatalyst also increased the rate of catalytic hydrogen generation to a rate of 0.002 mmol of H₂ generated per gram of catalyst per hour. Considering that this catalyst combination is free from noble metals, it shows that tertiary and binary metal sulfides are strong contenders as photocatalysts.

Another area in which metal sulfide NPs are appealing is electrode materials. Pushing the limits of conventional lithium-ion batteries requires new materials. Wu et al. reported producing Li₂S NPs that were coated with carbon for use in lithium–sulfur and lithium-ion batteries.^[8] The electrochemical performance for the same material was tested and shown to be stable over 100 cycles with a discharge capacity of 1200 mAh g⁻¹. Copper sulfide nanostructures are also actively being considered as viable electrode materials in lithium batteries and magnesium batteries.^[9,10] In a report by Kravchyk et al., who investigated a high-performance cathode for Mg-ion batteries, CuS was used as the working electrode.^[10] The cathode is made by casting a slurry of CuS NPs (20 nm), carbon black, polyvinylidene fluoride, and *N*-methylpyrrolidone on a tungsten current collector. They reported that the cathode exhibited a stable capacity of 300 mAh g⁻¹ after the first cycle. An all-encompassing review of metal sulfide NPs for lithium-ion batteries has been published by Xu et al.^[11] A detailed

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review of current trends in lithium sulfide batteries has been done by Yan et al.^[12]

Other areas in which metal sulfide NPs have proved to be useful are hydrogen storage, water splitting, and energy storage and conversion; extensive reviews have been written on all of these applications.^[13–15] Because the usefulness of metal sulfide NPs has become increasingly evident, herein we look at how they are created.

This review provides a wider picture of the production of metal sulfide NPs reported in the literature, more specifically at the chemical precursors used in these processes. Irrespective of the synthetic method, often the same combination of precursors are utilized. These methods can vary in process time, the requirement for post-treatment, production rates, as well as the purity and crystal structures of the products. Understanding the chemical combinations and reactions can help to tailor precursor–solvent permutations, irrespective of the choice of method.

2. Current Production Techniques

Metal sulfide NPs are currently produced in many different ways. Although many of the synthetic techniques remain unscalable, they are highly tunable.

The simplest way to synthesize metal sulfide NPs is through ball milling. NPs are obtained by grinding motion alone and additional chemical or heat treatments are dispensable. Here, a grinding medium in a cylindrical shell is rotated about the shell's axis. This technique was used by Pathak et al. to synthesize ZnS quantum dots of about 2 nm in diameter.^[16] They did so by starting with zinc acetate and sodium sulfide, which were then milled by using a steel vessel and balls with a vial rotation speed of 600 rpm. Powder samples were finally washed with methanol and then dried. They were able to produce cubic-phase ZnS, with the shortest milling time of 30 min. Similarly, Li et al. produced CuS from sulfur powder and copper metal powder by employing the same technique at a speed of 425 rpm.^[17] They required a milling time of 2 h to complete the process and obtained hexagonal CuS. This indicates that higher milling speeds reduce the time needed for the process. Moghaddam et al. also produced NPs by using the same method for binary metal sulfide NPs.^[18] They produced Cu₅FeS₄ starting with powders of copper, iron, and sulfur in the desired ratio.

Wet chemical routes are also used to produce metal sulfide NPs. The thermal decomposition of metal oleates was reported to be a scalable synthetic route for the production of metal sulfide NPs. Through this method, sulfide NPs of copper, zinc, cadmium, manganese, and lead were produced. The synthesis of the metal oleate is complex because it involves first synthesizing metal oleate complexes from metal chloride/nitrate salts. These complexes are then dissolved in a solution containing oleylamine and dodecanethiol and treated at high temperatures.^[19]

The combination of thiourea as a sulfur source along with metal salts, such as zinc nitrate (Zn(NO₃)₂), has been used to make metal sulfides. This chemistry was employed by Leng-

goro et al. to synthesize ZnS NPs through electrospray pyrolysis.^[20] Lee et al. used this chemistry to make nanocomposites, such as NiS–graphene composites, by using spray pyrolysis.^[21] The effect of varying the concentration of the sulfur source

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was also studied and shown to affect the crystal structures of the products formed. For a 1:2 molar ratio of nickel nitrate to thiourea, Ni_7S_6 , Ni_3S_4 , and Ni_3S_2 were the structures obtained, whereas for molar ratios of 1:4 and 1:8 in the spray solution, hexagonal α -NiS and cubic Ni_3S_4 crystalline phases, respectively, were obtained.

A range of hydrothermal synthetic routes for many metal sulfide NPs have also been reported. Hydrothermal synthesis is a common route to produce various nanostructures differing in chemistry and structure. This involves placing aqueous solutions of precursors in an autoclave and allowing them to react at high temperatures. CuS ,^[22] MoS_2 ,^[23] WS_2 ,^[23] and RuS_2 ^[24] NPs were all produced by hydrothermal synthesis and thiourea was used as the source of sulfur. Although there is great control over the size and composition of the nanostructures, this is still largely a process done in small batches.

The combination of a sulfur source with multiple metal sources has been implemented to create binary and tertiary metal sulfides through wet chemistry. In the work of Nguyen et al., thioacetamide was employed as the sulfur source, along with cadmium acetate and zinc acetate in ethanol to create $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ NPs.^[7] Here, the precursor–solvent solution was heated to 50 °C for 4 h, after which time the product was washed in ethanol and annealed. This method was implemented by Lee et al. to create CuInS_2 from thiourea, copper nitrate, and indium nitrate in ethylene glycol.^[25] Solution chemistry was similarly utilized in the production of tertiary metal sulfides, as reported by Ahmad et al.^[26] $\text{Cu}_2\text{ZnSnS}_4$ was synthesized from zinc acetate dihydrate, anhydrous copper chloride, and anhydrous tin chloride as metal sources. The metal sources were dissolved in oleylamine and heated to 260 °C and stirred. Elemental sulfur, which acted as the sulfur source, was mixed with oleylamine and introduced into the heated metal–solvent solution and left to react for 2 h. The produced NPs were found to be uncontaminated. Dunne et al. reported a continuous-flow hydrothermal reactor to produce metal sulfide NPs.^[27] They made use of thiourea as the source of sulfur, although various metal salts were used. Two methods of precursor feed were tested. In method I, thiourea and the metal salt solution entered the furnace at room temperature, whereas, in method II, thiourea was preheated before entering the furnace to allow decomposition into an active sulfur source (Figure 1).

Method I was found to require a temperature of at least 400 °C to break the thiourea down into an active sulfur source, whereas in method II the furnace temperature could be varied between 250 and 400 °C. This study also demonstrates how various metal precursors react with thiourea at different temperatures and how this interaction significantly varies from metal to metal. In the case of zinc, method II resulted in smaller crystalline sizes, as well as less agglomeration compared with ZnS produced by using method I. This is due to a growth-dominated particle formation in method I, in contrast to rapid nucleation and precipitation of particles in method II. Similar crystalline particle behavior was observed in the synthesis of CdS NPs. These two different mechanisms are a result of no prior breakdown or availability of reactive sulfur species, HS^- , as opposed to prior breakdown into HS^- . In their attempt to

manufacture lead sulfide, they found that, by using method I, lead sulfates are also formed in addition to lead sulfide. Method II, for which lower temperatures could be utilized, showed an absence of contamination with lead sulfate. This is a result of oxidizing conditions in method I, for which higher temperatures are used. PbS tends to become unstable under such conditions and favors the formation of sulfate; the overall Gibbs free energy of this process is $-703 \text{ kcal mol}^{-1}$.^[28] Alternatively, in the case of copper, at lower temperatures, copper(I)thiocyanate is obtained.

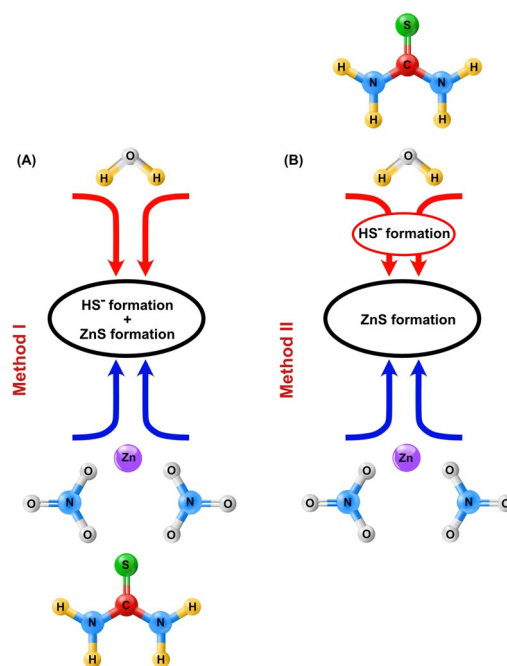


Figure 1. Two different methods of supplying the precursor feed to a continuous-flow hydrothermal reactor, as tested by Dunne et al.^[27] A) Heated deionized water is pumped separately from an unheated solution of metal salt and thiourea. Here, HS^- formation and ZnS formation takes place simultaneously. B) The sulfur source is heated alongside deionized water and the unheated metal salt solution is fed separately. The sulfur source starts to disintegrate, due to high temperature, before it comes into contact with the metal source. Hence, the formation of ZnS takes place once the two flows meet.

This is assumed to be a result of the incomplete breakdown of thiourea into an active sulfur source, such as HS^- , at 250 °C. By using method II and preheating thiourea to ensure decomposition, covellite-phase CuS without impurities was obtained. The major drawback of this process is that it suffers from the deposition of salts inside pipes and high maintenance and related energy costs limit its scale-up.

An all-encompassing review on how metal sulfides are produced, in general, has been previously done.^[29] As seen before, there are numerous methods through which metal sulfide NPs can be synthesized. The common denominator is that they all require a source of sulfur.

3. Sulfur Sources

As seen previously, there are numerous methods through which metal sulfide NPs can be synthesized. The common denominator is that they all require a source of sulfur. However, there is a lack of a comprehensive overview on which sulfur sources are preferred for the various methods of production or mechanisms of how the compounds interact to form metal sulfides.

From a pool of 100 publications on metal sulfide NPs, details of metal and sulfur sources used for the synthesis of these particles are obtained.^[5,7,10,19,21,22,25–27,30–120] Care was taken to include only studies that synthesized 0D nanomaterials (NPs) and used only a single source of sulfur for synthesis, which was commercially available at the time of writing. This is done to simplify and concentrate on the synthesis of the simplest of NPs. This includes reports on novel synthetic techniques for metal sulfide NPs for application in biology to battery electrodes. Figure 2 is created by using information on which source of sulfur these reports used to synthesize their NPs, irrespective of the synthetic method. Doped and functionalized metal sulfide NPs are also considered, along with binary and tertiary metal sulfide NPs. A further in-depth examination of the most commonly used sulfur sources was also done.

It can be seen from Figure 2 that the most commonly used source is sodium sulfide. This is easily available, but it is also easily oxidized, which, in turn, presents handling complexities. The metal salt used in conjunction with sodium sulfide is displayed in Table 1. In this manner, one can see which metal salts are more commonly employed to produce metal sulfide NPs with sodium sulfide as the sulfur source. A similar depiction is done for all other sulfur sources. As seen in Table 1, Cd and Zn sulfide NPs are the most commonly produced. Of the 43 publications utilizing sodium sulfide, 11 publications report the synthesis of doped metal sulfide NPs. Two of the studies employed an electrochemical method to produce the NPs, in which the metal source was a pure metal electrode, and hence, metal salts were unnecessary. The rest of the studies, except for five, were done by using wet chemical synthetic methods.

The two most commonly used sulfur sources, thiourea and thioacetamide, although very close in number, vary vastly in terms of pricing. Both are easily available to purchase and, at the time of writing, thiourea is about €20 for 100 g, whereas thioacetamide is about €100 for 100 g. Although both compounds contain one sulfur atom per mole, the cost per mole of sulfur is roughly €15 in thiourea and €75 in thioacetamide. Studies on thiourea followed a range of methods of preparation, which could overall be broadly described as wet chemical methods. The application of thiourea as a source of sulfur has generated various metal sulfides, the details of which are summarized in Table 1. Of these, cadmium sulfide has been the most commonly produced NPs. A clear preference for nitrate salts is also seen. In the case of thioacetamide, the copper ion is most widely used, closely followed by zinc, and acetate metal salts are the top choice. Similar to thiourea, metal sulfide

NPs synthesized by utilizing thioacetamide are all produced using wet chemical methods.

Sulfur sources and their corresponding metal sources used to produce metal sulfide NPs are summarized in Table 1. Sulfur powder, although produced in large quantities, is difficult to dissolve in most solvents at room temperature. It is also seen in the publications that all except one use high-temperature wet chemical methods to synthesize the NPs. Most of the publications highlighted herein used oleylamine as the solvent in conjunction with sulfur powder. Oleylamine is commonly used because it can dissolve a wide variety of compounds, both organic and inorganic.^[121] It is also used as a surfactant, which can control the shape and size of NPs produced by using wet chemical methods.^[122]

Sodium diethyldithiocarbamate was used as the source of sulfur to produce copper sulfide NPs, whereas zinc diethyldithiocarbamate was utilized as a single-source precursor to produce zinc sulfide NPs.^[68] Zinc diethyldithiocarbamate, as a single-source precursor, was employed in two different synthetic methods. The first method was through wet chemical synthesis. Here, zinc diethyldithiocarbamate was heated in a mixture of octylamine and toluene and the solid products were centrifuged and separated.^[79] The other method involved spray pyrolysis, in which the single-source precursor was atomized in a furnace and nitrogen was used as the carrier gas.^[113] This makes metal diethyldithiocarbamate compounds versatile because they can support the formation of metal sulfide NPs by using different synthesis techniques as well as being employed as a single-source precursor. The downside of single-source compounds is that they can be difficult to dissolve in solvents.

Tetrahydrothiophene was used as a sulfur source for a vastly different method of synthesis, flame spray pyrolysis, which makes it the only publication of the 100 considered to do so.^[120] In the literature, there is one other publication that uses the same method, but it is omitted here because it produced PbS–TiO₂ heterojunction NPs.^[123] These are the only two publications, to date, to the best of our knowledge, that use this method for the production of metal sulfide NPs, in particular.

As observed, there are a handful of sulfur sources that have been used to make metal sulfide NPs, all of which are easily commercially available and most dissolve in several solvents. Consider the examples of thiourea and tetrahydrothiophene, which have been utilized in studies as a liquid sulfur source, as seen above. These are noteworthy sulfur sources because they have been used not only in wet chemical methods, but also in gas-phase synthesis. Spray pyrolysis and flame spray pyrolysis utilize high temperatures to result in the breakdown of compounds. Pyrolysis has the potential to scale up the production of metal sulfides, similarly to that previously achieved for metal oxide NPs.^[124] Both compounds used here, tetrahydrothiophene and thiourea, contain one sulfur per molecule of the compound. A source that is has yet to be considered is, 2,2'-thiodiethanethiol, with three sulfurs per molecule of the compound. This can help in reducing the amount of sulfur source required to increase the metal to sulfur ratio obtainable in solution.

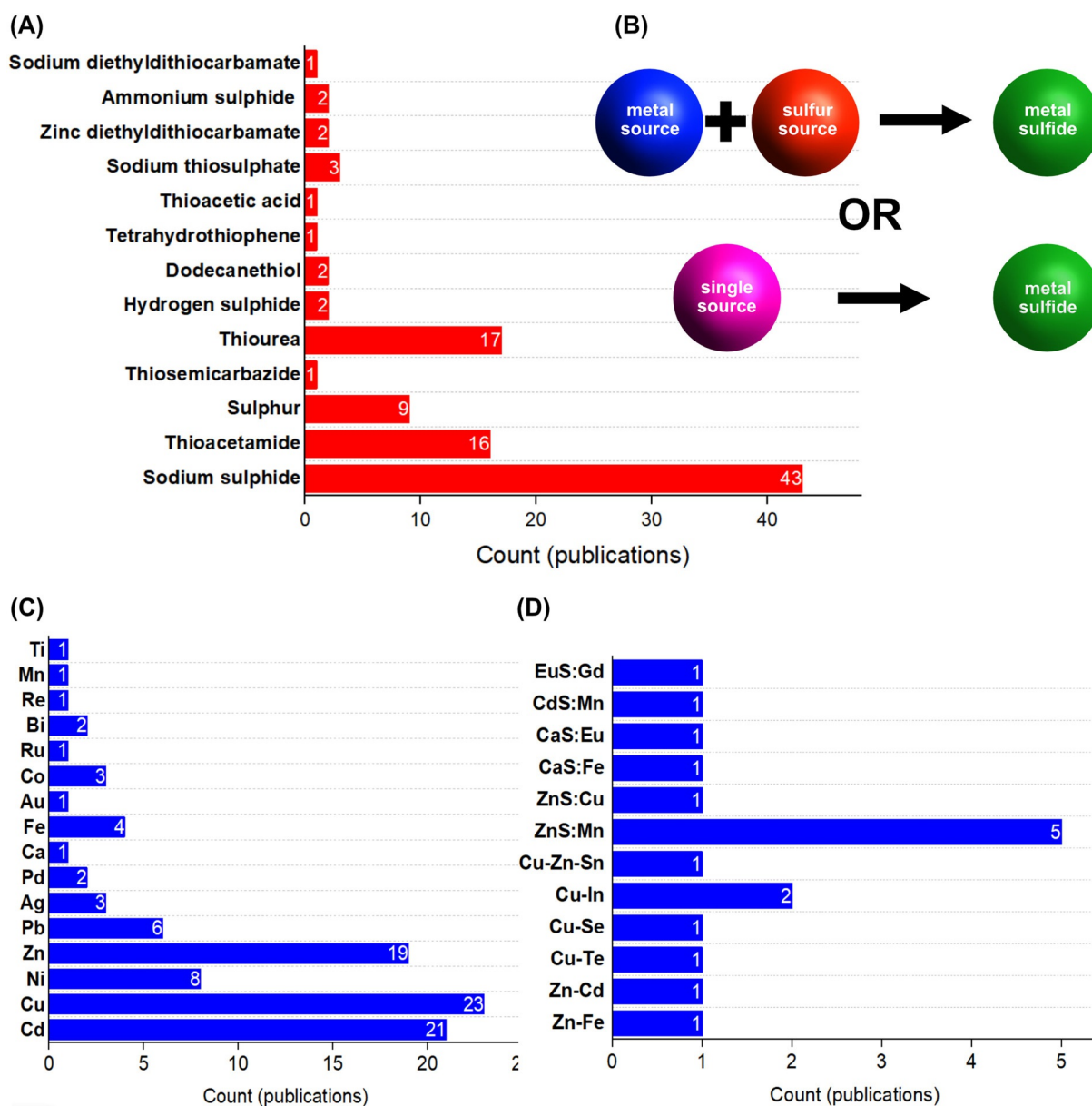


Figure 2. A) Sulfur sources reported in various publications. B) The two broadly classifiable routes to produce metal sulfide NPs, with either a specific sulfur source or a single precursor containing the desired metal as well as sulfur. Multiple metal sources can be used to create binary or tertiary metal sulfides. C) The metal cations of produced single-metal sulfide NPs (including publications with multiple-metal sulfide NPs). D) Metal cations of the produced binary, ternary, and doped metal sulfide NPs.

Sulfur sources that contain sodium—sodium sulfide and sodium diethyldithiocarbamate—to the best of our knowledge, have only been used in wet chemical synthetic routes. These compounds are more suited to liquid-phase synthesis because in the gas phase the probability of the inclusion of undesirable sodium into products increases. This is countered by using sources of sulfur such as tetrahydrothiophene, dodecanethiol, thiourea, and thioacetic acid. These sources are free from additional metal atoms in their structure, which can prevent undesirable metal impurities. The use of hydrogen sulfide as the sulfur source can be challenging because it is commonly known to be a toxic and flammable gas.

The method of synthesis commonly used with most sulfur sources, as observed in Table 1, was wet chemistry. Three of the studies used milling and two of them used spray pyrolysis for the synthesis of metal sulfide NPs. Of the studies that used milling, only two sources of sulfur were used: thioacetamide and sulfur powder. This method succeeds because repeated fracture and welding of metal and sulfur sources create surfaces that react with each other. As the product of this reaction is obtained mixed with byproducts, additional treatment would be required.^[125]

The two publications that involved spray pyrolysis have used tetrahydrothiophene and zinc diethyldithiocarbamate as their sulfur sources. These studies indicate efforts to explore

Table 1. Metal precursors used in combination with various sulfur sources in literature.

Sulfur source	Metal source	Preparation technique	NPs	Application	Ref.
sodium sulfide ^[a]	cadmium nitrate	stirring for 12 h with glucose as a capping agent	CdS	studies on dielectric properties	[30]
sodium sulfide ^[a]	copper anode	electrochemical synthesis: metal source as anode and sulfur source as part of the electrolyte ^[d]	Cu ₂ S	improving solution synthesis of Cu ₂ S	[35]
sodium sulfide ^[a]	zinc nitrate + ferrous sulfate	stirring at 293 K with methanol as solvent	Zn _{1-x} Fe _x S	studies on magnetic and electrical properties	[36]
sodium sulfide ^[a]	nickel anode	electrochemical synthesis with a steel cathode ^[d]	NiS	studies on optimizing synthesis conditions	[37]
sodium sulfide ^[a]	cadmium acetate	solution of metal source with capping agent heated, cooled down, and sulfur source stirred in	CdS	photodegradation of dyes	[38]
sodium sulfide ^[a]	cadmium chloride	sulfur source added to the metal source, sodium hydroxide, and mercaptoacetic acid solution accompanied by bubbling nitrogen	CdS	oligonucleotide label	[39]
sodium sulfide ^[a]	cadmium chloride	sulfur source added under argon, metal precursor dissolved in degassed and distilled water, and stirred	CdS	studies on size dependence of spectroscopic and electrical properties	[40]
sodium sulfide ^[a]	zinc nitrate	precursor solutions made with distilled water and then stirred for 1 h	ZnS	studies on photoluminescence emission	[41]
sodium sulfide ^[a]	cadmium acetate	sulfur source added dropwise to an ethanol solution of the metal source	CdS	studies on photoluminescence and photoconductivity	[42]
sodium sulfide ^[a]	zinc nitrate + manganese acetate	sulfur source added dropwise to a distilled water solution of metal sources	ZnS–Mn	studies on doping effects on photoluminescence	[48]
sodium sulfide ^[a]	lead nitrate	metal precursor dissolved in degassed and distilled water and sulfur source added under argon and stirred	PbS	electrochemical biosensors	[50]
sodium sulfide ^[a]	cadmium nitrate	sulfur source and additional capping agent added to solution of deionized water and metal source	CdS	studies on formation of NPs in aquatic environment	[51]
sodium sulfide ^[a]	silver nitrate	sulfur source added dropwise to a solution of metal source at 80 °C and polyvinylpyrrolidone (PVP) solution added once temperature drops to 60 °C and stirred for 3 h	Ag ₂ S	studies on properties of doped and undoped Ag ₂ S	[52]
sodium sulfide ^[a]	copper nitrate	solutions of sulfur source and metal source made with distilled water and added dropwise into polyvinyl alcohol (PVA)–distilled water solution	CuS	studies on NPs in PVA film	[54]
sodium sulfide ^[a]	cadmium perchlorate	sulfur source solution and metal source solution made separately with heptane	CdS	studies on selective photoetching properties with a surrounding silica shell	[55]
sodium sulfide ^[a]	palladium chloride	aqueous solution of metal source, sodium chloride, sodium borohydride, and sulfur sources autoclaved along with a carrier	Pd ₄ S	studies on support for NPs	[58]
sodium sulfide ^[a]	silver nitrate	metal source and sulfur source in combination with sodium citrate or sodium salt of ethylenediaminetetraacetic acid left to react for 3 d	Ag ₂ S	studies on synthesis conditions and size in colloidal solutions	[61]
sodium sulfide ^[a]	copper chloride	sulfur source stirred into metal source, cetyltrimethylammonium chloride and water for 15 min at 90 °C to obtain coated NPs	CuS	photothermal cancer therapy	[62]
sodium sulfide	zinc acetate	reaction in solution with metal and sulfur source with addition of a stabilizer	ZnS	studies on photocatalytic properties	[64]
sodium sulfide ^[a]	zinc nitrate	metal source and sulfur source added to aqueous buffer solution	ZnS	studies on precipitation in environmental conditions	[66]
sodium sulfide ^[a]	cadmium acetate	solutions of sulfur and metal source made with deionized water; one added to the other and heated	CdS	studies on interaction with ATP	[69]
sodium sulfide ^[a]	copper sulfate	aqueous solution metal source and sulfur source mixed with stabilizing agent	Cu _x S	studies on quantum effects of NPs	[71]
sodium sulfide ^[a]	zinc sulfate	metal source solution with <i>N</i> -cetyl- <i>N,N</i> -trimethyl ammonium bromide added dropwise into sulfur source	ZnS	studies on effects of capping agent on surface properties	[72]
	cadmium nitrate	metal source and sulfur source solutions in methanol added to dendrimer solution	CdS	studies on luminescence properties	[73]

Table 1. (Continued)					
Sulfur source	Metal source	Preparation technique	NPs	Application	Ref.
	cadmium nitrate	sulfur source dissolved in water and added to metal source and sodium hexameta-phosphate solution in deoxygenated water and stirred	CdS	studies on DNA on NP emission	[75]
	iron chloride/ammonium iron(II) sulfate	metal source and sulfur source solutions added to dendrimer solution	FeS	studies on NP deposition on silica gel	[76]
	ferrous sulfate	sulfur source in deionized water added to a solution of metal source in deionized water with sodium carboxymethyl cellulose	FeS	studies on soil dispersibility and removal of mercury from water	[77]
	sodium gold sulfite	aqueous solutions of metal source and sulfur source mixed for 24 h	Au ₂ S	studies on synthesis and optical properties	[80]
	cadmium chloride	metal solution is mixed with diethylene triamine solution and manganese chloride solution is added; double-distilled water used as solvent; sulfur source finally added drop-wise	CdS–Mn	studies on characteristics of Mn ²⁺ -doped cadmium sulfide NPs	[86]
	zinc acetate + manganese chloride	aqueous solutions of metal sources and sulfur source mixed with capping agents	ZnS–Mn	studies on photoluminescence emission	[87]
	cadmium sulfate	sulfur source solution added to metal source solution with acetic acid and capping agent	CdS	studies on use of bovine serum albumin as a capping agent	[89]
sodium sulfide ^[a]	cadmium nitrate	aqueous solution of metal source and sulfur source strongly stirred	CdS	studies on optical and dielectric properties	[91]
sodium sulfide ^[a]	zinc acetate	sulfur source solution was added to prepared metal source and copper acetate solution in ultrapure water and heated to 80 °C for 3 h	ZnS–Cu	photocatalysis	[97]
sodium sulfide ^[a]	zinc acetate + manganese acetate	aqueous solution of sulfur source added to solution of metal sources and stirred vigorously	ZnS–Mn	studies on photoluminescence emission	[98]
sodium sulfide ^[a]	zinc acetate	metal source and sulfur source milled together in a planetary ball mill	ZnS	studies on synthesis and optical properties	[101]
sodium sulfide ^[a]	cadmium chloride	metal source added to sulfur source, sodium hydroxide, and methanol	CdS	studies on synthesis and optical properties	[102]
sodium sulfide ^[a]	zinc chloride	sodium sulfide and mercaptoethanol was added to metal source solution	ZnS	studies on synthesis and photoluminescence properties	[104]
sodium sulfide ^[a]	zinc sulfate	aqueous solution of metal source and sulfur source mixed vigorously	ZnS	studies on structural properties	[107]
sodium sulfide ^[a]	lead nitrate	sulfur source added to metal source solution in mercaptoacetic acid and pH adjusted with sodium hydroxide	PbS	studies on NP labels for biological applications	[110]
sodium sulfide ^[a]	calcium chloride	sulfur source was added to metal source solution; absolute ethanol used as solvents for both	CaS–Fe	ferromagnetic NPs for cancer hyperthermia	[111]
sodium sulfide ^[a]	copper chloride	aqueous sulfur source solution added to a solution of metal source solution and sodium citrate	CuS	therapeutics for atherosclerosis	[112]
sodium sulfide ^[a]	unspecified calcium halide salt	sulfur source and thioglycerol solution made in ethanol, metal source solution and europium nitrate solution also made with ethanol, and sintered at high temperature	CaS–Eu	studies on fluorescent properties	[114]
sodium sulfide ^[a]	calcium chloride	sulfur source and triethanolamine solution in 2-propanol added to metal source solution in 2-propanol	CaS	studies on luminescence of capped NPs	[116]
thiourea ^[a]	nickel nitrate	metal source and sulfur source solution made by spraying solution into furnace held at 800 °C	NiS	studies on comparison of electrochemical properties of pure metal sulfide with metal sulfide-reduced graphene oxide composite	[21]
thiourea ^[a]	cobalt chloride	metal sulfur source and sulfur source solution in methanol autoclaved at 180 °C for 24 h	CoS	studies on electrochemical properties for potential application as pseudocapacitors	[22]
thiourea ^[a]	zinc nitrate, cadmium nitrate, lead nitrate, copper nitrate, iron sulfate, and bismuth nitrate	metal source solution made with deionized water (bismuth dissolved in 5% nitric acid) to which sulfur source is added and passed through a continuous-flow reactor at high temperatures	ZnS, CdS, PbS, CuS, Fe _{(1-x)S} , Bi ₂ S ₃	studies on rapid synthesis of various metal sulfides	[27]

Table 1. (Continued)					
Sulfur source	Metal source	Preparation technique	NPs	Application	Ref.
thiourea ^[a]	copper nitrate + indium nitrate	metal sources and sulfur source solution in ethylene glycol at heated	CuInS ₂	solar cells	[25]
thiourea ^[a]	cobalt dichloride	metal source, sulfur source, citric acid, and sodium chloride dissolved in deionized water and stirred	CoS	studies on incorporating NPs in a matrix for enhancement of electrochemical properties	[31]
thiourea ^[a]	cadmium sulfate	aqueous solutions of metal and sulfur source stirred for 1 h with ammonium hydroxide to adjust pH	CdS	studies on synthesis and dielectric properties	[32]
thiourea ^[a]	cadmium chloride	chemical bath deposition of aqueous solutions of metal source and sulfur source	CdS	studies on self-organization	[49]
thiourea ^[a]	ruthenium chloride	aqueous solution of metal source and sulfur source mixed and subjected to ultrasound irradiation	RuS ₂	electrode material for supercapacitors	[81]
thiourea ^[a]	copper acetate + indium acetate	metal sources, sulfur source, and octadecylamine dissolved in absolute ethanol and autoclaved at 200 °C for 16 h	CuInS ₂	studies on synthesis and mechanism of formation	[83]
thiourea ^[a]	copper acetate	metal source and sulfur source aqueous solution ultrasonicated and pH adjusted with sodium hydroxide	Cu _x S	solar cells	[88]
thiourea ^[a]	lead acetate	methanol solutions of metal source and sulfur source were treated in variations of chemical bath deposition	PdS	studies on property variation with differences in capping	[90]
thiourea ^[a]	cadmium acetate	aqueous solutions of metal source and sulfur source mixed by diffusion through eggshell membrane	CdS	studies on controlling size of produced NPs	[92]
thiourea ^[a]	lead nitrate	aqueous solution of metal source and sulfur source were strongly stirred for 24 h and triethylamine used to prevent agglomeration	PbS	studies on optical properties with capping	[93]
thiourea ^[a]	zinc nitrate	sulfur source and metal source dissolved in deionized water and autoclaved at 170 °C for 2 h	ZnS	studies on electrochemical capacitor application	[103]
thiourea ^[a]	cadmium acetate	aqueous solutions of metal source and sulfur source mixed by diffusion through eggshell membrane	CdS	studies on optical properties	[105]
thiourea ^[a]	copper nitrate	sulfur source added to metal source solution and treated with ultrasound irradiation	CuS	studies on synthesis and electrochemical properties	[118]
thiourea ^[a]	cadmium nitrate, bismuth nitrate, indium nitrate, zinc nitrate	metal source and sulfur source coordinated product pressed into pellets and combusted	NiS + NiS ₂ , CoS ₂ + CoS _{1.097} , Fe ₇ S ₈ , Cu _{1.8} S, α-ZnS	studies on synthesis by combustion in an inert environment	[119]
thioacetamide ^[a]	cadmium chloride	aqueous sulfur source added to metal source and PVP solution and sonicated	CdS	studies on capping using sonochemical synthesis	[5]
thioacetamide ^[a]	cuprous chloride	aqueous sulfur source solution added to aqueous metal source solution	CuS	studies on bioactive NP for cancer cell	[43]
thioacetamide ^[a]	cupric nitrate	aqueous solutions of metal source and sulfur source mixed with surfactant and oil	CuS	studies on producing metal sulfide NP within liquid crystal template	[47]
thioacetamide ^[a]	bismuth nitrate	sulfur source solution in ethanol added to metal source solution with diphenylthiocarbazon and tetrachlorocarbon	Bi ₂ S ₃	studies on preparation of ion-selective electrode	[56]
thioacetamide ^[a]	zinc acetate	sulfur source and metal source separately milled for 15 min and then milled together and heated ^[e]	ZnS	studies on low-temperature synthesis	[57]
thioacetamide ^[a]	copper acetate	sulfur source added to aqueous source solution with capping agent	CuS	studies on absorption of dye	[60]
thioacetamide ^[a]	nickel acetate	products of metal source and 2-hydroxyacetophenone solution in ethanol dissolved in ethylene glycol and sulfur source solution added and treated with microwave irradiation	NiS	studies on variation of synthesis conditions	[65]
thioacetamide ^[a]	nickel acetate	aqueous solution of metal source and sulfur source mixed with ammonia solution	NiS	studies on loading NP on activated carbon for dye removal	[70]
thioacetamide ^[a]	zinc acetate	ultrasonication of aqueous solution of metal source, sulfur source, and silica microspheres	ZnS	studies on surface synthesis of NPs	[78]

Table 1. (Continued)					
Sulfur source	Metal source	Preparation technique	NPs	Application	Ref.
thioacetamide ^[a]	zinc acetate + manganese nitrate	aqueous solution of both metal sources, sulfur source solution in ethanol, sodium linoleate, and linoleic acid heated to 90 °C for 10 h	ZnS–Mn	studies on photoluminescence properties	[82]
thioacetamide ^[a]	zinc acetate	metal source and sulfur source milled separately and then milled together ^[e]	ZnS	studies on synthesis technique and properties	[85]
thioacetamide ^[a]	copper acetate, nickel acetate	metal source, sulfur source, and a complexing agent were treated with ultrasound irradiation	CuS, NiS	studies on synthesis and possible formation mechanism	[95]
thioacetamide ^[a]	copper acetate	aqueous sulfur source solution and aqueous metal source solution kept at 80 °C for 24 h	CuS	studies on the effect of surfactants	[96]
thioacetamide ^[a]	cadmium acetate + zinc acetate	metal sources, sulfur source, and ethanol stirred at 50 °C for 4 h	Zn _x Cd _{1-x} S	studies on photocatalysis	[7]
thioacetamide ^[a]	copper chloride	aqueous solution of sulfur source added to aqueous solution of metal source and thio-glycolic acid pH adjusted with sodium hydroxide	CuS	studies on photothermal therapy	[108]
thioacetamide ^[a]	copper chloride	sulfur source and metal source added to ethylene glycol solution and treated with microwave irradiation	CuS	studies on synthesis and properties	[109]
sulfur powder ^[a]	copper chloride	sulfur source solution in oleylamine added to metal source solution with oleylamine, oleic acid, and octadecene mixed at high temperatures	CuS	cathode material for Mg-ion battery	[10]
sulfur powder ^[a]	cadmium chloride	sulfur source, metal source, and sodium borohydride solution in THF stirred for 3 h	CdS	studies on optical and electrical properties	[33]
sulfur powder ^[a]	copper acetylacetonate, selenium powder, tellurium powder	metal source, sulfur source, 1-dodecanethiol, and oleic acid heat treated	Cu _{2-x} S, Cu _{2-x} Se _y S _{1-y} and Cu _{2-x} Te _y S _{1-y}	studies on synthesis methods	[34]
sulfur powder ^[a]	zinc stearate	sulfur source added to metal source, tetra-cosane, and octadecene solution at high temperatures	ZnS	studies on effect of dopant on electrical properties	[63]
sulfur powder ^[a]	nickel nitrate	heated solution of oleylamine and sulfur source added to metal source and oleylamine solution with variations in ratio of sulfur and metal source	NiS, NiS ₂ , Ni ₃ S ₄ , Ni ₇ S ₆	study on single synthesis techniques for variation in phases obtained	[67]
sulfur powder ^[a]	zinc acetate + copper chloride + tin chloride	sulfur source in oleylamine added to heated metal source solution in oleylamine	Cu ₂ ZnSnS ₄	studies on synthesis and electrical properties	[26]
sulfur powder ^[a]	zinc chloride	sulfur source solution in capping agent added to metal source dissolved in capping agent	ZnS	studies on properties of NPs with capping	[99]
sulfur powder ^[a]	nickel chloride, copper acetylacetonate	sulfur source in solution added to metal source solution and capping agent and heated	Ni ₃ S ₄ , CuS and Cu _{1.8} S	studies on synthesis and structural properties	[106]
sulfur powder ^[a]	ferrocene	metal source and sulfur source ground with a mortar and pestle and heated in alumina foil ^[e]	FeS ₂	studies on solvent-free synthesis	[115]
sodium thiosulfate ^[a]	sodium perhenate	perchloric acid added to the metal source, sulfur source, and ethylene glycol solution	ReS ₂	studies on synthesis and characteristics	[59]
sodium thiosulfate ^[a]	cadmium sulfate	sulfur source, metal source, isopropyl alcohol, and sodium dodecyl sulfate aqueous solution irradiated with gamma rays	CdS	studies on synthesis and properties	[84]
sodium thiosulfate ^[a]	copper oxide + copper sulfate + copper chloride	sulfur source, metal sources, and distilled water autoclaved at high temperature	CuS	studies on synthesis from multiple sources of metal	[94]
dodecanethiol ^[b]	copper chloride, lead nitrate, manganese chloride	metal source treated with oleate source, which is added to the sulfur source, dodecanethiol, and oleylamine solution and heated	Cu ₂ S, PbS, MnS	studies on synthesis technique and reproducibility	[19]
dodecanethiol ^[b]	gadolinium acetylacetonate + europium acetylacetonate	metal sources and sulfur source solution sonicated	EuS–Gd	imaging of cells in vitro	[45]
ammonium sulfide ^[b]	lead nitrate	sulfur source solution added to metal source solution in tributylphosphate	PbS	studies on toxicity	[46]

Table 1. (Continued)					
Sulfur source	Metal source	Preparation technique	NPs	Application	Ref.
ammonium sulfide ^[b]	silver nitrate	aqueous solution of metal source, sulfur source treated in a stopped-flow reactor	Ag ₂ S	studies on real-time optical properties	[74]
hydrogen sulfide ^[c]	zinc nitrate	metal source solution with nitric acid held in a rotating packed-bed reactor and exposed to sulfur source	ZnS	studies on new synthesis techniques	[44]
hydrogen sulfide ^[c]	titanium tetraisopropoxide	sulfur solution bubbled through metal source solution in butylamine	TiS ₂	studies on new synthesis techniques	[117]
zinc diethyldithiocarbamate ^[a]	zinc diethyldithiocarbamate	precursor dissolved in octylamine and toluene and heated	ZnS	studies on synthesis from single precursor and mechanism	[79]
zinc diethyldithiocarbamate ^[a]	zinc diethyldithiocarbamate	precursor dissolved in toluene and atomized in a furnace ^[e]	ZnS	studies on synthesis in vapor phase	[113]
thioacetic acid ^[b]	copper carbonate	sulfur source solution in acetic/propionic acid added to metal source solution in acetic/propionic acid	CuS	studies on synthesis, electrical and photoluminescence properties	[100]
tetrahydrothiophene ^[b]	zinc 2-ethylhexanoate + manganese naphthenate	metal sources and sulfur source solution in tetrahydrothiophene and treated in a flame spray pyrolysis setup ^[e]	ZnS–Mn	studies on large scale production	[120]
thiosemicarbazide ^[a]	zinc acetate	metal source, sulfur source, hexamethylene-tetramine, and sodium hydroxide autoclaved	ZnS	studies on synthesis and optical properties	[53]
sodium diethyldithiocarbamate ^[a]	copper chloride	sulfur source, metal source, and oleylamine solution heated	CuS	studies on coated NPs for cancer therapy	[68]

[a] Sulfur in solid form. Most of the sulfur sources used are in the solid form, requiring dissolution in a solvent if a precursor solution is required for a chosen production technique. [b] Sulfur in liquid form. [c] Sulfur in gaseous form. Only one source, H₂S, has been used in gaseous form. [d] Prepared through electrolysis. [e] Not prepared through wet chemical methods or electrolysis, but other methods.

new paths for the production of metal sulfide NPs. Spray pyrolysis synthesis for metal sulfide NPs is yet to be widely studied. This opens up the potential for more metal sulfides to be synthesized in the gas phase.

4. Future Prospects

A reasonable way to considerably increase the production rates of metal sulfides is to consider the reactive flame spray technique (Figure 3). This method is already well established for the synthesis of metal oxide NPs and is also scalable. Direct use of this method in the production of metal sulfide NPs is challenging because oxygen is essential to support combustion. The abundance of atmospheric oxygen, compared with sulfur, supplied in this process can promote the formation of metal oxides. Also, with the electronegativity of oxygen being higher than sulfur, the abundance of oxygen plays in favor of it.

There have been two studies that have produced metal sulfide NPs of Mn²⁺-doped ZnS and PbS–TiO₂ by using flame spray pyrolysis.^[120,123] Although in both studies, which were carried out in an enclosed space, ignition of their liquid precursors was done by using a mixture of CH₄ and O₂; the total oxygen concentration was kept below 250 ppm. It is also seen in their work that the ratio of sulfur to oxygen present which determines the formation of a metal sulfide. They also show that this ratio differs from that of metal to metal and can be exploited to produce heterojunctions or doped metal sulfide NPs.

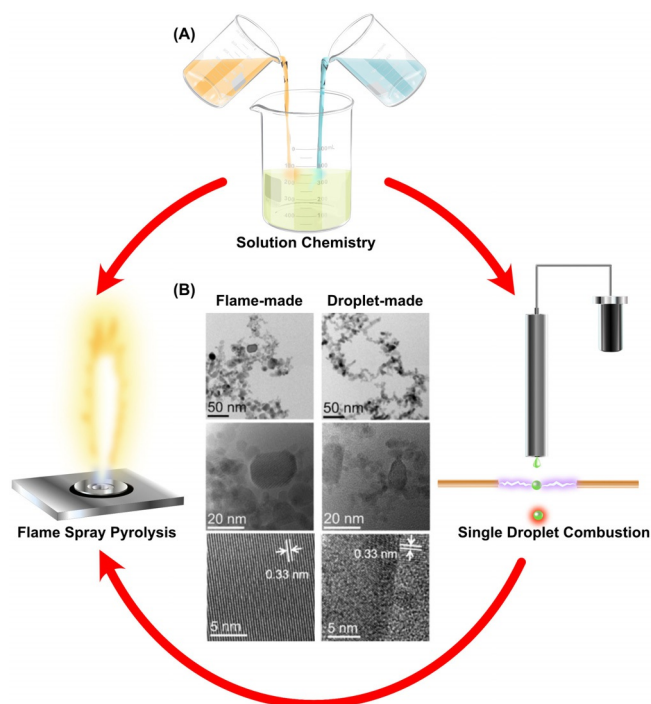


Figure 3. A) Testing a precursor–solution combination by using a single-droplet combustion setup is a cost-effective screening technique for precursor–solution combinations and an easily modifiable setup, which can be encased in a controlled atmosphere. This helps to create a fast and convenient method of studying the formation of metal sulfide NPs, which can then be transferred to the flame spray pyrolysis setup. B) The similarity in metal oxide NPs produced by using flame spray pyrolysis and single-droplet combustion.^[126] Reprinted with permission from Ref. [126].

Ellingham diagrams produced by considering the formation of metal sulfide through the interaction of metal oxide with hydrogen sulfide are shown in Figure 4. In the case of the formation of a heterojunction of PbS and TiO_2 , excluding the possibility of the formation of TiS_2 , if operating below certain conditions, is represented in Figure 4A. The ratio of sulfur to oxygen in a controlled environment is modified upon changing the amount of sulfur precursor, whether provided in liquid or gaseous forms. 2,2'-Thiodiethanethiol is the solution to a

degree of variability in sulfur. Hence, the further design of precursor–solvent systems that can work with this method of production is beneficial to make production economically viable and scalable.

To be able to achieve production that is scalable and repeatable, there is the need to further study the process of metal sulfide formation through combustion. It is also clear that atmospheric control is needed. The repeatability, output, and kinetics need to be elucidated to be able to scale up laboratory production. This is best done through single-droplet combustion studies in a controlled atmosphere. It is easy and fast to screen precursor–solvent combinations and it is cheaper because only small amounts of the precursor is needed. It is also attractive because NPs produced by using single droplets are comparable to those synthesized through flame spray pyrolysis, and hence, can easily be scaled up in the future. This has previously been shown with the production metal oxide NPs for sensors in which single-droplet combustion was used to screen for the ideal precursor–solvent system.^[126]

The choice in a controlled atmosphere in the initial stages lies between a sulfur atmosphere and an inert atmosphere, such as argon/nitrogen. Starting with combustion in an inert atmosphere provides a baseline to study the chemistry of reactions that have formally been used to create metal sulfide NPs through other processes.

The subsequent step is to study combustion reactions in a sulfur atmosphere. This is done to ensure surplus availability of sulfur atoms in the gaseous state for metal ions to interact with. To do so, the H_2S environment is provided near the combustion zone. The abovementioned reactions can be done in this atmosphere to ensure the formation of metal sulfide NPs.

H_2S is used in processes such as atomic layer deposition to create metal sulfides, owing to its volatility and reactivity. In particular, its reactivity with metal–organic precursors is of great advantage. Although the reactivity of H_2S is advantageous, it also presents numerous challenges to work with. To ensure safety, single-droplet combustion experiments will have to be housed in a containment unit to be able to study these reactions.

5. Decomposition and Gas-Phase Interactions

The decomposition of individual compounds can give an idea of the possible routes of sulfide formation in the gas phase. A simplified sketch of the process is depicted in Figure 5. Processes such as spray pyrolysis, flame spray pyrolysis, and single-droplet combustion utilize high temperatures that result in the breakdown of compounds. As observed in Figure 4, the ratio of supplied precursors to gases utilized in the process of combustion also affect the final product. In this section, the possible interactions of decomposed components leading to the formation of metal sulfide NPs are conceptualized. This is done by excluding the possibility of reactions in solution because the sulfur and metal sources can also be fed into the reactor separately to meet only in the combustion zone. It also implies that the temperatures provided should enable all reactants to decompose. Reactions in solution will also vary, de-

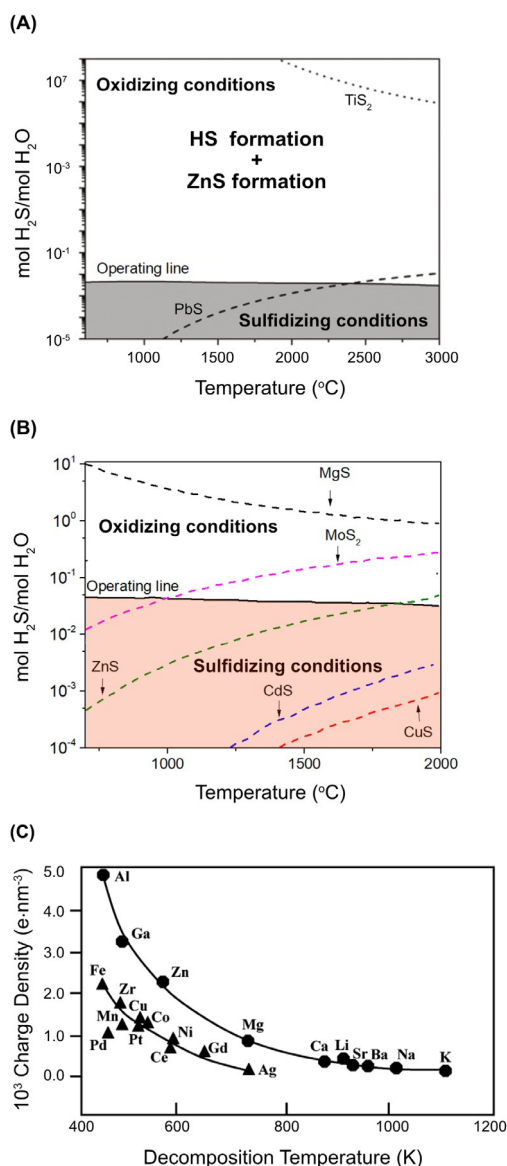


Figure 4. A) Operating below favorable conditions for the sulfidation of titanium was shown to produce a PbS– TiO_2 heterojunction structure by using flame spray pyrolysis.^[123] Adapted with permission from ref. [123]. Copyright 2012, American Chemical Society. B) Redrawn Ellingham diagram for various other metals, highlighting sulfidizing conditions.^[120] Below the operating line represents feasible metal sulfides for a given sulfur to oxygen ratio. C) The dependence of decomposition temperature on the metal cation is shown above. This dependence would imply a high probability in each system, showing variation in combustion reactions.^[131] Reprinted with permission from ref. [131]. Copyright 2003, American Chemical Society

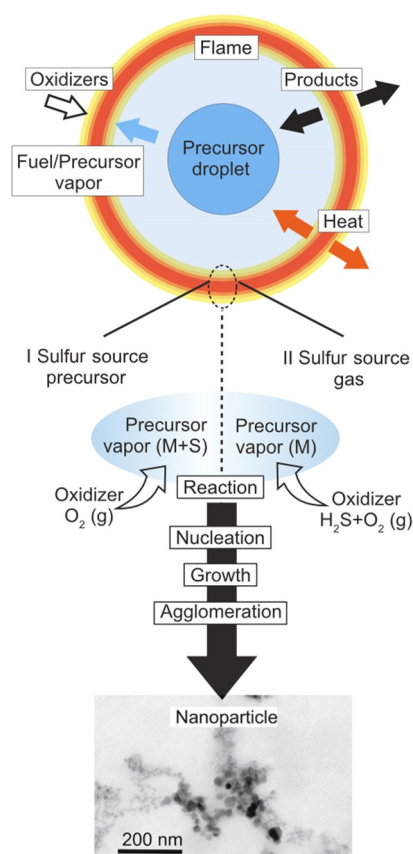


Figure 5. Simplified sketch of single-droplet combustion depicting the two (proposed) routes of NP synthesis through a gas-phase reaction: I) the precursor as the sulfur source; II) the gas contributing sulfur for the reaction. Adapted from ref. [134].

pending on the precursors and solvents used. A detailed review on possible types of interactions in solution has previously been published.^[127]

The first source of sulfur considered is thiourea. As seen previously, thiourea is a widely used source of sulfur, in conjunction with metal nitrate salts as the preferred metal source. This is seen in reports in which the interaction of thiourea with metal salts, such as zinc nitrate ($\text{Zn}(\text{NO}_3)_2$), has been used to make metal sulfides.^[20]

Studies of thiourea in the melt showed that, at temperatures in the range of 140–180 °C, the concurrence of melting of the compound and undergoing isomerism into ammonium thiocyanate could occur. Above 180 °C, the formation of the liquid phase starts, accompanied by the release of large quantities of gas-phase products. The formation of thiourea isomers below 180 °C is insignificant in high-temperature synthesis because thiourea and ammonium thiocyanate show similarities in thermal decomposition. Increasing the heating rate also pushes the degradation temperatures to higher ranges. The presence of H_2S has also been detected near the melt surface at temperatures above 185 °C.^[128]

Other studies on the decomposition of thiourea also detected the presence of NH_3 , CS_2 , thiocyanic acid (HNCS), and cyanamide (H_2NCN). However, there is an absence of H_2S detected

in gaseous decomposition products in other studies.^[129,130] Hence, the inference is that CS_2 is the reactive species contributing to the formation of metal sulfides in gas-phase processes with thiourea.

The preference of metal nitrate as the salt of choice for thiourea in wet chemical synthesis can also be applied in the gas phase. This is hypothesized by considering the disintegration of metal nitrates upon treatment at high temperatures. The first step in the decomposition of metal nitrate salts largely depends on the hydration of the salt. Unlike nonhydrated salts, hydrated salts undergo a preliminary dehydration step before decomposition. Nonetheless, metal nitrates, in general, have been shown to decompose into their oxides at high temperatures.^[131,132] The decomposition temperature of metal nitrates largely depends on the cation because it varies with the metal charge density (Figure 4C).

The reaction between the metal oxide and gaseous $\text{CS}_2/\text{H}_2\text{S}$ is known to result in the formation of metal sulfide (Figure 6). In one such study, CS_2 gas is used to produce rare-earth metal sulfides.^[133] In this study, solid samples are held in a CS_2

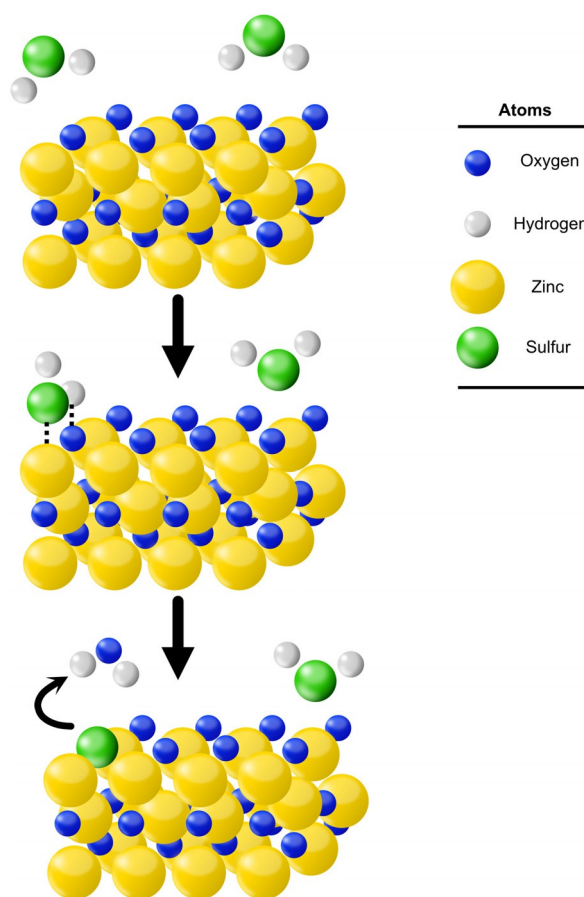


Figure 6. Schematic representation of the interaction of H_2S with ZnO at elevated temperatures. Sulfur atoms preferentially interact with the metal center. This interaction leads to the formation of ZnS islands, which lead to the formation of bulk ZnS through ion diffusion.^[139] This diffusion can be inward or outward with the movement of smaller ions through interstitial sites or larger metal atoms through vacancies.^[140] The reaction of metal oxide NPs with H_2S results in the formation of metal sulfide NPs and water.

atmosphere to produce metal sulfides and confirms the reactivity of CS_2 with metal oxides. From here, it is speculated that the reaction with evolved CS_2 and decomposed metal oxide leads to the formation of the metal sulfide in the gas phase (Figure 7).

The other sources of sulfur that can be considered for gas-phase reactions are thiophene and tetrahydrothiophene. These two compounds have been used in wet chemical methods and in methods that involve pyrolysis for the production of metal sulfide NPs. The main sulfur decomposition products of tetrahydrothiophene are CS_2 , H_2S , and thiophene.^[135] On the

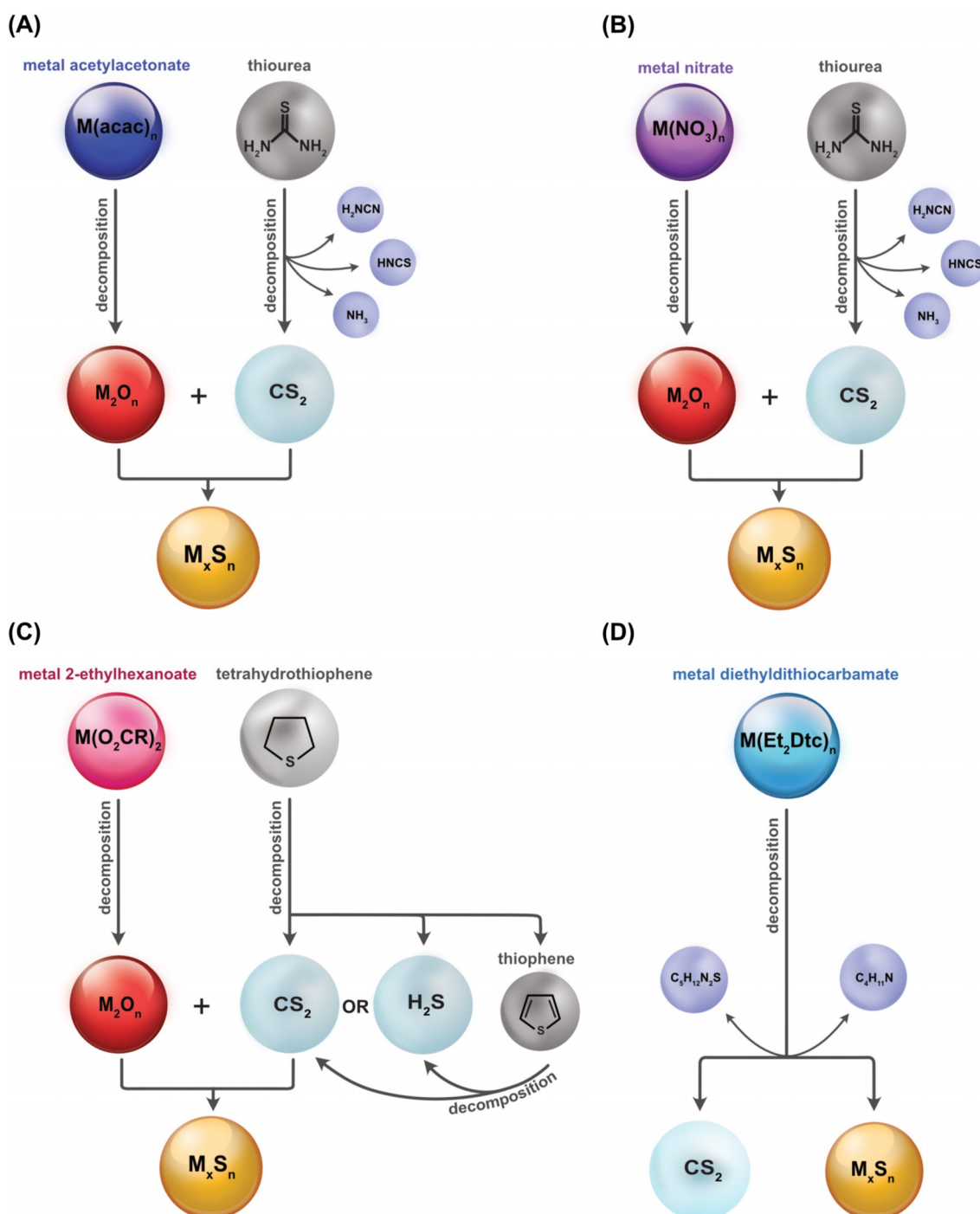


Figure 7. Possible gas-phase interactions in the decomposition of sulfur and metal sources, leading to the formation of metal sulfide NPs. A) Decomposition of metal acetylacetonate represented as previously described.^[142] B) The interaction of decomposition products of metal nitrate and thiourea.^[143] C) Decomposition of metal 2-ethylhexanoates, as described elsewhere.^[143] D) Metal diethyldithiocarbamate salt can be used as a single source of metal and sulfur. Decomposition studies of the same have been previously done.^[144] Here, only the formation of metal sulfide is shown to focus on the possible pathway that leads to its formation. Oxygen present can form different smaller organic compounds and the outcome in this combination is yet to be studied.

other hand, the main sulfur decomposition products of thiophene are CS_2 , H_2S , and elemental sulfur.^[136] This implies the existence of two reactive species, CS_2 and H_2S , that can act as a source for the formation of metal sulfides in the gas phase.

Although commonly used in wet chemical synthesis, sodium sulfide as a sulfur source is omitted here because there is the probability of incorporating undesired Na into the final products in the gas phase. Exchange reactions in solution help to exclude this problem, which is likely to be more pronounced in a gas-phase reaction.

Metal sources that can be used in combination are plenty. An appealing class of compounds are organometallics. In this class of compounds, ferrocene is stable and it retains its structure in solution. The use of ferrocene as a metal source also reduces the number of elements present in solution. In a solution in which ferrocene is combined with 2,2'-thiodiethanethiol as the sulfur source in xylene, there are only atoms of four compounds (C, H, S, and Fe) present. This helps to narrow down products/byproducts formed in the case of spray pyrolysis or flame spray pyrolysis. It also makes it simpler to study the fundamentals of the combustion process that lead to the production of metal sulfides.

Apart from the abovementioned metal sources, another consideration is the conversion of metal oxides into metal sulfides. This approach has been used to create ordered mesoporous metal sulfides in which interconnected metal oxides reacted with sulfur vapor, resulting in the formation of interconnected metal sulfide.^[137] This mechanism has been studied in depth by Rodriguez et al., who reported that H_2S dissociation on metal oxides showed preferential binding of sulfur to the metal atom.^[138] As simple as it might seem, the problem faced in solution chemistry is the dissolution or suspension of metal oxides in pyrolysis solvents.

Another class of compounds that can act as a source of metal are metal acetylacetonates. In the case of pyrolysis, the decomposition of acetylacetonate progresses with the formation of acetone and carbon dioxide. The starting temperature for the evolution of gas on the decomposition of metal acetylacetonates depends on the metal ion present. Decomposition of acetone then moves forward with methane separating from the molecule, leading to the formation of a ketene.^[141] Further dissociation of carbon dioxide formed during the decomposition of acetylacetonate largely depends on temperature and pressure. It is known that the decomposition of metal acetylacetonate results in the formation of metal oxide, as observed in Figure 7, which is then free to interact with products formed from the decomposition of the sulfur source.

Zinc diethyldithiocarbamate, which has been used as a single-source precursor in earlier studies, is also a potential candidate.^[113] Ethylhexanoate metal compounds can also be considered for use as a metal source because the disintegration of the compound leads to the formation of the metal oxide, which is free to interact with decomposed products from the sulfur source. This class of metal compounds has also been used to produce metal oxides. Tin(II) 2-ethylhexanoate was used to create SnO_2 upon decomposition in a flame spray setup and in a single-droplet setup.^[126] Flame-produced and

single-droplet-produced metal oxide NPs are shown to be similar (Figure 3B). As observed in Figure 7, the decomposition of most metal compounds leads to metal oxides. This provides a window for the formation of metal sulfides through the interaction of metal oxides with a sulfur source.

6. Summary and Outlook

The advantages, in terms of properties that can be exploited, of metal sulfide NPs are vast. The production of these particles is widely studied by using wet chemical methods, but there is a need to be able to understand the fundamentals of processes and reactions in gas-phase syntheses. This can enable higher production rates than those currently available to be established. This has been implemented in the production rates of titania, silica, and other materials by using aerosol flame technology.^[145] Gas-phase synthesis also allows for the production of metastable compounds and polymorphs. Certain precursor-solvent combinations used in liquid-phase synthesis, as observed previously, have the potential of being used in gas-phase reactions. In particular, metal nitrate salts, in combination with a sulfur source, are seen to be highly promising. Tetrahydrothiophene is the most versatile sulfur source seen here. A single-droplet combustion setup will help in the screening of sulfur sources and the required conditions faster and more cost-effectively.

Metal sulfide NPs produced in R&D and industry are almost exclusively through aqueous chemistry routes, whereas non-aqueous chemistry used in producing such particles are rare (see Table 1). Hence, focusing on the combustion screening of nonaqueous precursor-solvents with a wide variation of metal/sulfur ratios have the potential to produce pure metal sulfide NPs. In conclusion, the many advantages of metal sulfides can be better harnessed by elucidating a method to produce them that is well understood and flexible, with the potential to be scaled up. This awareness of the process should enable us to tailor metal sulfide NPs to meet the needs of required structure, composition, and even size.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: combustion · metal sulfides · nanoparticles · precursor-solvent chemistry · synthesis design

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