



Advances in the fabrication of inorganic sulfides for functional materials: A comprehensive review

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Abstract

This review provides a comprehensive overview of current fabrication techniques for inorganic sulfide structures, with particular emphasis on their synthesis, structural control, and application potential. Inorganic sulfides, especially transition metal sulfides, exhibit unique electronic, optical, and catalytic properties, rendering them highly attractive for applications in semiconductors, optoelectronics, and energy conversion. Various synthesis methods are discussed, including chemical vapor deposition, atomic layer deposition, hydrothermal processing, spray pyrolysis, electrodeposition, and physical vapor deposition. Their operational principles, advantages, limitations, and impacts on material properties are systematically analyzed. A comparative discussion highlights how synthesis conditions influence morphology, crystallinity, and functional performance. Furthermore, the review surveys the application landscape of sulfide nanostructures, focusing on photovoltaics, sensors, catalysis, and energy storage systems. It is concluded that although several fabrication methods have reached industrial relevance, challenges related to scalability, environmental sustainability, and process reproducibility remain. Emerging strategies, such as the integration of machine learning and green chemistry principles, offer promising avenues for optimizing sulfide material synthesis. This work thus serves as a valuable resource for materials scientists and engineers seeking to advance the design and production of next-generation sulfide-based technologies.

Keywords

advanced (nano)materials, inorganic sulfides structures, transition metal sulfides, sulfide nanostructure fabrication and application.

1. INTRODUCTION

Sulfur is the fifth most abundant element on Earth and plays a vital role in human life, from the formation of amino acids, through the chemical industry, to advanced semiconductor structures. Inorganic sulfide materials have attracted increasing attention in recent decades due to their compelling physico-chemical properties and broad applicability in nanotechnology, optoelectronics, and energy-related fields. The intrinsic characteristics of sulfide-based compounds, particularly transition metal sulfides (TMS) (Schmidt et al., 2020), render them promising candidates for applications ranging from catalysis and sensors to next-generation semiconductors and nanodevices (Ajiboye and Onwudiwe, 2021; Liu et al., 2024). Among these properties, tunable band gaps, high electrical conductivity, excellent thermal and chemical stability, and strong light-matter interactions (Rahman et al., 2024) position inorganic sulfides at the forefront of materials engineering (Wold and Dwight, 1993). With the ongoing miniaturization of electronic and photonic devices, the development of nanoscale inorganic sulfide structures has become a crucial area of research. Nanoscale forms, including nanowires, nanorods,

quantum dots, and two-dimensional layers such as MoS₂ and WS₂, have demonstrated enhanced electronic and optical behavior owing to quantum confinement and surface-dominated effects, thereby expanding their functional potential within semiconductor and nanomaterials engineering (Chhowalla et al., 2013; Wang et al., 2012).

From an engineering perspective, the fabrication of inorganic sulfide structures is pivotal in determining their performance in real-world applications. As the synthesis method directly influences structural morphology, crystallinity, defect density, and phase purity, a comprehensive understanding of fabrication techniques is essential. Traditional and modern fabrication approaches, including hydrothermal synthesis (Shi et al. 2013), chemical vapor deposition (Rogalski et al., 2003), sol-gel processes (Almeida and Xu, 2018), atomic layer deposition (Zaidi et al., 2022), and physical vapor deposition, offer a range of control parameters for tailoring nanoscale structures to achieve optimal functionalities. These methods have been continually refined to enhance reproducibility, scalability, and compatibility with existing industrial fabrication lines, particularly within the semiconductor manufacturing sector (Shinde and Rout, 2021). Innovations in both bottom-up



and top-down fabrication methodologies have further enabled precise control over nanostructure assembly and integration into functional devices (Abid et al., 2022; Lee et al., 2012).

This review aims to provide a comprehensive analysis of the diverse fabrication techniques employed in the synthesis of inorganic sulfide structures. Particular attention is given to the correlation between fabrication methods and resulting material properties, scalability for industrial application, and the potential for integrating these materials into multifunctional electronic systems. The discussion on the relationships between synthesis, structure, and properties is intended to guide materials scientists and engineers in advancing next-generation sulfide-based technologies.

2. INORGANIC SULFIDE PROPERTIES

Historically, inorganic sulfides were primarily considered from a geological perspective as sources of valuable metals. These minerals have long been significant in economic geology, providing essential raw materials for numerous industries. However, this perception has evolved, and these compounds have garnered growing attention across other scientific disciplines. In-depth studies of inorganic transition metal sulfides have revealed a wide range of physical, chemical, electrical, and optical properties, making them highly valuable for diverse industrial and scientific applications. Their unique characteristics arise from their crystal structures, bonding nature, and electron configurations.

However, natural sulfide deposits often contain impurities of up to several percent, which precludes their use in advanced technologies – particularly when ores are contaminated with toxic elements such as arsenic, cadmium, or mercury (Vaughan and Corkhill, 2017). For this reason, synthetic routes are typically preferred over classical ore extraction in precision-demanding applications such as semiconductors. This need has driven the development of more sophisticated methods for sulfide synthesis, enabling precise control over composition and crystallographic structure. Recent interest has increasingly focused on nanomaterials based on multinary sulfides, which offer properties not achievable with simple monosulfides (Chen et al., 2017). Notably, certain properties can be tailored during the synthesis stage. For example, sphalerite (ZnS) is diamagnetic and an electrical insulator. However, substituting zinc with iron (Zn, FeS) induces paramagnetic behavior, while further substitution with copper (CuFeS₂) leads to antiferromagnetic and semiconducting properties (Vaughan, 2005).

One of the most notable features of inorganic sulfides is their tunable electronic properties. Many transition metal sulfides – such as CuS, ZnS, CdS, TiS₂, SnS, SnS₂, Bi₂S₃, MoS₂, and NiS – exhibit semiconducting behavior with layer-dependent band gaps, making them attractive for nanoelectronics and optoelectronic applications, including photovoltaics, electroluminescent devices, transistors, and photosensors (Kanade et

al., 2021), as well as solar cells and lasers. These materials are most commonly employed in the form of thin films or nanoparticles. Their specific applications are closely tied to the size of their energy band gaps. For instance, ZnS is suitable for UV light absorption, NiS nanoparticles have been utilized as IR detectors, and Bi₂S₃ and SnS possess ideal band gaps for solar absorption, rendering them highly appropriate for solar energy conversion devices (Ebrahimi et al., 2019; Güler and Kurtuluş, 2006; Pejova and Grozdanov, 2006; Vattikuti et al., 2018).

3. OVERVIEW OF FABRICATION METHODS FOR SULFIDE STRUCTURES

Without a doubt, the structure of a material plays a crucial role in determining its application potential. A particular group of materials, known as layered transition metal sulfides (LTMS) (Wold and Dwight, 1993), has received considerable attention. In recent years, fabrication methods for heterostructures – such as monolayers, bilayers, multilayers, quantum dots (0D), nanowires (1D), nanosheets (2D), nanoflowers/crystals (3D), and nanoparticles – have attracted significant interest due to their unique and tunable properties (Abid et al., 2022). The fabrication of semiconductor materials remains highly demanding; thus, precise control over morphology, thickness, and surface area is critical to achieving the desired properties of on-demand materials for novel device architectures. It is well known that the know-how surrounding the fabrication of sulfide monolayers is protected by numerous patents held by various companies (Chianelli et al., 2006; Thorp et al., 1977). To meet these demanding requirements, a range of sophisticated synthetic techniques has been developed. However, only a limited number of these methods have been successfully implemented at the industrial scale, while many others remain confined to laboratory research (Koteeswara Reddy et al., 2015; Norton et al., 2021).

In the fabrication of nanomaterials, two main approaches can be distinguished: top-down and bottom-up. The top-down approach involves breaking down bulk materials into nanoscale particles through physical or mechanical methods. In contrast, the bottom-up approach relies on chemical reactions to assemble nanostructures from atoms or molecules. Each of these approaches offers distinct advantages and limitations that significantly influence the resulting particle morphology, size distribution, physicochemical properties, and ultimate application potential (Abid et al., 2022).

In general, fabrication methods can be categorized into chemical and physical approaches. The chemical route involves reactions between precursors occurring in either the liquid or gaseous phase. In contrast, physical methods rely on the evaporation of the target material, followed by its deposition onto a substrate (Koteeswara Reddy et al., 2015; Parsons and Alotaibi, 2023; Shinde and Rout, 2021). Both approaches

allow for controlled crystal growth processes, enabling the precise tuning of structural and morphological properties. A general overview of the fabrication methods for sulfide structures is presented in Fig. 1.

3.1. Chemical vapor deposition

Chemical vapor deposition (CVD) is one of the most common, versatile, and effective techniques for synthesizing high-quality inorganic metal sulfides in the form of layered structures. Fundamentally, it involves chemical reactions between precursors in the gas phase and on a heated substrate, leading to the formation of a solid thin film of the desired material (Shinde and Rout, 2021). Typically, CVD is a complex, multi-step process comprising a sequence of gas-phase and surface reactions, as well as adsorption and surface diffusion phenomena. The two principal steps involve the evaporation of reactants, followed by reactive sputtering, during which atomic or molecular species adsorb onto the substrate surface (Curtis et al., 2024).

In the context of sulfide synthesis, metal oxide, metal-organic, or halide precursors are commonly utilized alongside a sulfur source such as H_2S , CS_2 , or elemental sulfur. The process

is generally conducted in a controlled inert atmosphere at elevated temperatures, typically ranging from 300 – 800 °C, depending on the thermal stability and reactivity of the precursors (Rogalski et al., 2003). Unwanted volatile by-products are removed with the aid of a vacuum pump.

This technique is particularly advantageous for producing large-area, uniform, crystalline sulfide layers with precise control over thickness, composition, and morphology. These characteristics can be finely tuned by adjusting key process parameters, including carrier gas flow rate, precursor stoichiometry, growth temperature, substrate type, cooling rate, partial pressure in the reaction chamber, and chamber geometry. Each of these factors directly influences crystal growth, thereby impacting the structural, compositional, and functional properties of the resulting nanostructures. Therefore, the precise optimization of these variables is essential for the reproducible fabrication of high-quality materials. Crystal growth mechanisms are predominantly governed by three key aspects: thermodynamics, kinetics, and hydrodynamics of the system.

The CVD method has been successfully employed for the synthesis of FeS , SnS , SnS_2 , ZnS , WS_2 , MoS_2 , and Bi_2S_3 thin films, which are essential for applications in electron-

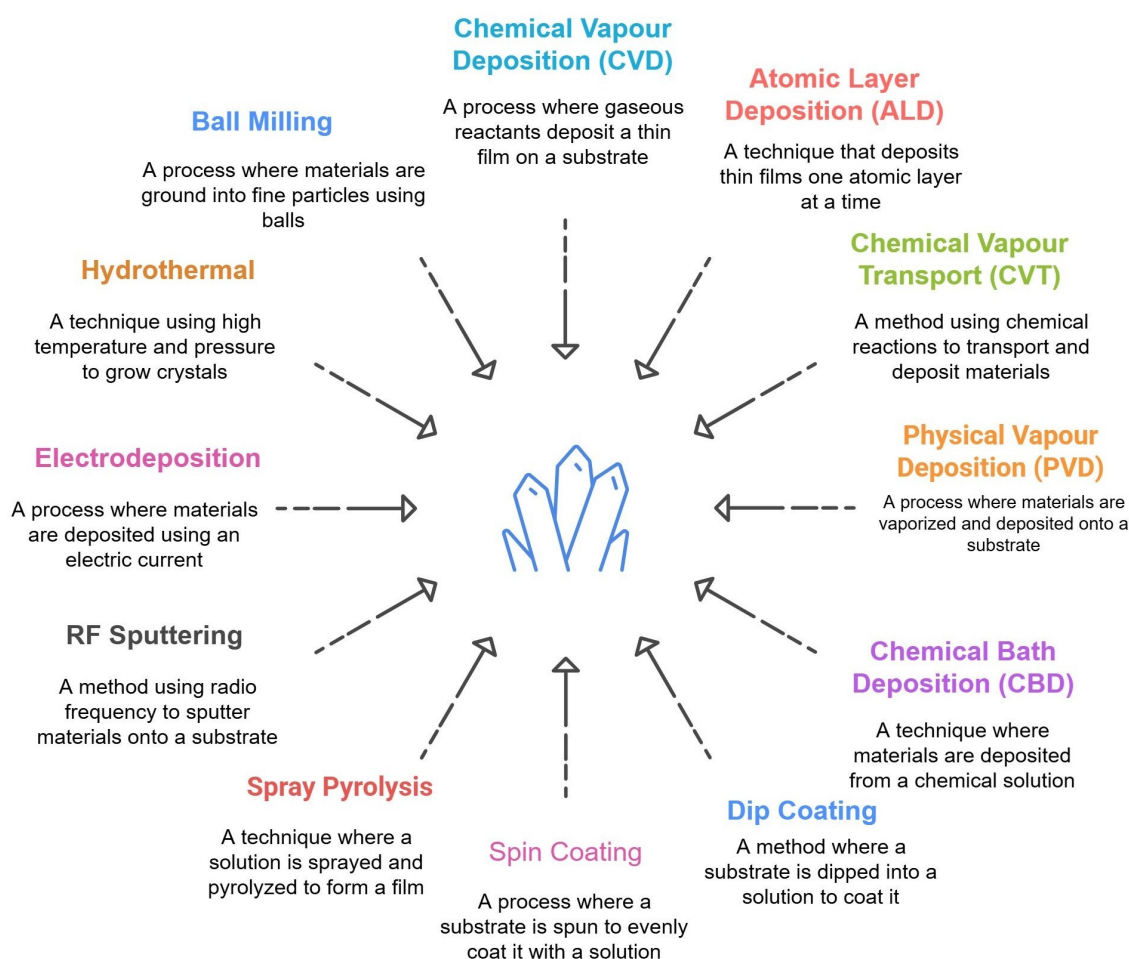


Figure 1. Schematic overview of fabrication methods for inorganic sulfide structures.

ics, optoelectronics, and energy-related technologies (Carmalt et al., 2003). Moreover, this technique enables the fabrication of vertically aligned or layered nanostructures, which is particularly important for two-dimensional transition metal dichalcogenides, such as MoS₂ and WS₂.

Despite its many advantages, several limitations of the CVD technique should also be noted. These include the high cost of equipment, the complexity of multiple process control parameters, the generation of toxic by-products, and restrictions on the choice of substrate materials due to the high processing temperatures. Nevertheless, CVD remains a critical bottom-up approach for the scalable production of high-performance sulfide materials, underpinning numerous advancements in modern nanotechnology applications (Ajiboye and Onwudiwe, 2021; Koteeswara Reddy et al., 2015).

3.2. Atomic layer deposition

Atomic layer deposition (ALD) constitutes a highly promising method for the fabrication of finely structured sulfide materials. This technique has gained prominence as a powerful approach to producing high-quality inorganic sulfide thin films and nanostructures (Mahuli and Sarkar, 2015). Originally developed for oxide materials, ALD has been adapted to accommodate a broad spectrum of chalcogenides, including metal sulfides, owing to its exceptional atomic-scale control over film thickness, stoichiometry, and uniformity (Shinde and Rout, 2021).

The ALD process is fundamentally based on sequential, self-limiting surface reactions between gaseous precursors and the substrate (Witkowski et al., 2022). Typically, the process proceeds through a four-step cyclic sequence: (i) exposure of the substrate to the metal precursor, (ii) purge with an inert gas, (iii) exposure to the sulfur precursor, and (iv) a second purge. Each cycle results in the deposition of a sub-monolayer of the target material, with the overall film thickness being precisely controlled by the number of deposition cycles. The self-limiting nature of chemisorption in each step ensures conformal coating, even on substrates with complex geometries, such as high-aspect-ratio structures and porous surfaces.

In the synthesis of metal sulfides via ALD, commonly employed metal precursors include chlorides or alkylamides, while hydrogen sulfide or various organosulfur compounds serve as sulfur sources. For instance, co-deposition of copper and tin sulfides using Cu(acac)₂, SnCl₄, and H₂S has enabled the fabrication of Cu₂SnS₃ and Cu₃SnS₄ thin films – materials of particular relevance to optoelectronic applications. The selection of precursors and optimization of process parameters such as deposition temperature, chamber pressure, and pulse duration are critical, as they directly influence film quality and composition. The process must be conducted within a temperature window that prevents premature thermal decomposition of the precursors while simultaneously facilitating the intended surface reactions.

One of the key advantages of ALD in sulfide layer fabrication is its ability to produce uniform films on both planar and three-dimensional nanostructured substrates. This has been successfully demonstrated for materials such as ZnS, MoS₂, FeS₂, as well as for more complex compounds like Cu₂SnS₃ and Cu₃SnS₄. Moreover, ALD supports the synthesis of ultra-thin, two-dimensional (2D) chalcogenide materials. In contrast to physical deposition techniques, ALD enables controlled nucleation and growth starting from the first monolayer – a critical requirement for the fabrication of 2D materials characterized by strong in-plane covalent bonding and weak interlayer van der Waals interactions (Basuvalingam et al., 2019). These properties are harnessed in the development of semiconducting 2D materials such as MoS₂, WS₂ (Aspiotis et al., 2023), and VS₂ (Zazpe et al., 2024), with applications in electronics, catalysis, and energy storage (Zaidi et al., 2022).

Despite its many advantages, ALD is not without limitations. The most significant drawback is the relatively slow crystal growth rate which is inherent consequence of the sequential nature of the deposition cycles. This may hinder its scalability for high-throughput manufacturing. Additionally, the requirement for volatile and thermally stable precursors constrains the range of compatible materials. Nevertheless, ongoing advances in precursor chemistry and reactor design continue to mitigate these limitations (Ajiboye and Onwudiwe, 2021; Jones and Hitchman, 2008).

3.3. Chemical vapor transport

Chemical vapor transport (CVT) is a thermally activated bottom-up synthesis method widely utilized for the production of high-purity, crystalline inorganic materials, particularly transition metal chalcogenides such as sulfides. This technique is especially advantageous for the growth of single crystals, nanostructured materials, and layered compounds, offering precise control over stoichiometry, morphology, and crystallographic phase (Schmidt et al., 2013). Its importance has grown in response to the increasing demand for high-quality materials for optoelectronic, catalytic, and energy-related applications.

In a typical CVT process, a sealed quartz ampoule is charged with a mixture of solid precursors and a transport agent. The ampoule is then subjected to a controlled temperature gradient within a dual-zone furnace: the source materials are placed in the hot zone, while the product crystallizes in the cooler zone. Within the hot zone, the metal and sulfur components react with the transport agent to form volatile intermediates. These gaseous species migrate to the cold zone, where they decompose, leading to the deposition of the desired sulfide product (Shinde and Rout, 2021). This transport mechanism is inherently cyclic, with the transport agent being regenerated during the reverse reaction, enabling continuous mass transfer. A general view of the CVT system is shown in Fig. 2. A well-known example of this mechanism is the synthesis of SnS₂ using iodine as the transport agent. At

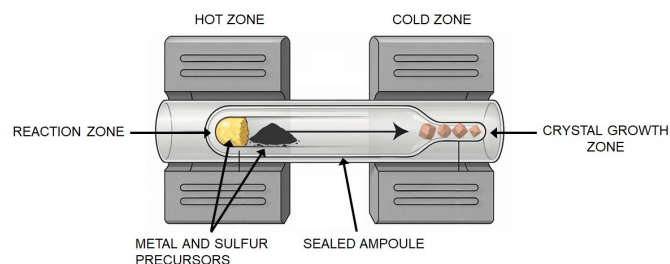
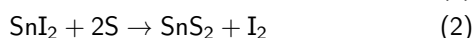
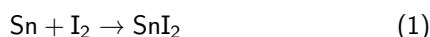


Figure 2. Schematic view of a two-zone furnace used in the CVT method.

elevated temperatures, iodine reacts with tin to form volatile tin iodides (e.g., SnI_2 or SnI_4), which then react with sulfur to form SnS_2 and regenerate iodine:



This closed-loop cycle is fundamental to the efficiency and sustainability of the CVT process. The solid reactants generally consist of high-purity elemental metals – such as Sn, Ti, Mo, Cu, or Fe – and sulfur powder, typically mixed in stoichiometric or slightly sulfur-rich ratios to ensure complete conversion. These components are loaded into a vacuum-sealed ampoule to prevent oxidation or contamination. High chemical purity is essential, as impurities may alter vapor-phase equilibria or act as unwanted nucleation sites, leading to defects in the resulting crystals.

The choice of transport agent is critical to the success of the process. Halogens such as iodine, bromine, and chlorine are commonly employed due to their ability to form volatile metal halides with well-defined thermodynamic behavior. In certain systems, volatile sulfur-containing compounds – e.g., carbon disulfide (CS_2) – can act simultaneously as a chalcogen source and a transport medium. Moreover, complex halides such as AlCl_3 or FeCl_3 are occasionally used to increase volatility or modify redox conditions in the system.

One of the primary advantages of CVT is its ability to yield single crystals of high crystallinity, phase purity, and compositional uniformity. The closed nature of the system minimizes contamination risk, while the use of a transport agent enables crystal growth at relatively moderate temperatures compared to melt-based methods such as Bridgman or Czochralski. This lower thermal budget reduces thermal stresses and suppresses structural defects. Additionally, CVT is a relatively simple and cost-effective approach that requires only basic equipment – a dual-zone furnace and vacuum-sealing tools (Tripathi et al., 2023). The technique is also scalable, allowing for both bulk crystal growth and nanoscale material engineering.

Nevertheless, CVT presents certain limitations. The most significant drawback is the lengthy duration of the process; crystal growth and deposition occur slowly, often requiring several hours or days. Furthermore, precise control over parameters such as temperature gradient, pressure, and transport agent concentration is necessary to avoid the formation of

secondary phases, incomplete transport, or structural inhomogeneities. Handling sealed ampoules containing volatile and reactive species also poses safety concerns due to potential overpressure during heating. Additionally, the applicability of CVT is inherently restricted to material systems in which volatile intermediates can be both generated and decomposed under experimentally accessible conditions.

Despite these challenges, CVT has enabled the successful synthesis of a broad range of metal sulfide materials, including binary compounds such as SnS_2 , TiS_2 , FeS_2 , and MoS_2 , as well as more complex ternary and quaternary systems (Tripathi et al., 2023; Wold and Dwight, 1993). Furthermore, the morphology of the resulting crystals can be modulated by adjusting synthesis parameters such as temperature, transport agent quantity, and growth time. As demonstrated in studies on titanium sulfides, morphologies including nanosheets, nanoribbons, and nanodiscs can be selectively obtained by varying the growth temperature (Talib et al., 2019). This level of control enables the tailoring of materials for targeted applications, particularly those in which surface area, anisotropy, or crystallographic orientation critically influence device performance.

3.4. Spray pyrolysis

Spray pyrolysis is a versatile and scalable technique employed for the fabrication of thin films and nanostructured materials, particularly metal sulfides. This method enables continuous, single – step deposition and is characterized by the atomization of a precursor solution into fine droplets, followed by thermal decomposition on a heated substrate or within a flame environment. The general principle involves preparing a precursor solution containing metal salts and sulfur donors dissolved in an appropriate solvent. This solution is atomized using pneumatic, ultrasonic, or electrostatic nebulizers, generating aerosol droplets that are transported by a carrier gas – typically air, nitrogen, or argon – into a heated reaction zone. Within this reaction zone, thermal energy induces solvent evaporation and precursor decomposition, leading to the nucleation and growth of nanoparticles or films on a substrate or within a collection chamber (Sayed et al., 2019; Shinde and Rout, 2021). For successful synthesis of metal sulfides, precise control of process conditions is essential to suppress oxidation and promote sulfidation. This is typically achieved through the use of sulfur-rich precursors such as thiourea, thioacetamide, or organosulfur compounds like tetrahydrothiophene (THT) (Pokhrel et al., 2023).

The gas-phase environment plays a critical role, especially in the flame-based variant known as flame spray pyrolysis (FSP), where the oxygen-to-fuel ratio must be carefully controlled to maintain reducing conditions conducive to metal–sulfur bond formation while minimizing oxide formation (Pokhrel et al., 2023). One effective strategy involves the use of enclosed flame reactors, which limit oxygen intrusion and ensure a stable, sulfur-rich atmosphere. This setup facilitates the

formation of binary and ternary sulfide nanoparticles such as Cu_2S , SnS , ZnS , MnS , In_2S_3 , and Bi_2S_3 . In many systems, sulfur-rich precursors form stable complexes with metal ions even before thermal treatment. Upon entering the flame, the droplets undergo rapid solvent evaporation and precursor decomposition, often accompanied by micro-explosions that enhance both atomization and diffusion. These phenomena favor the formation of uniform, nanoscale sulfide particles with tunable size and morphology.

A distinctive advantage of spray pyrolysis lies in its capacity for morphological control. Particle morphology – whether dense, hollow, core-shell, or porous – can be tailored by adjusting precursor concentration, solvent properties (e.g., viscosity, surface tension), carrier gas flow rate, substrate temperature, and the decomposition temperatures of individual components. Each aerosol droplet functions as a microreactor, and variations in drying rate, solute diffusion, and surface nucleation during evaporation govern the final structure. For instance, hollow particles often result from surface precipitation followed by shell solidification and internal gas evolution, while dense particles arise from uniform precipitation throughout the droplet volume.

In the synthesis of sulfide thin films – such as $\text{Cu}_2\text{MnSnS}_4$ – temperature plays a pivotal role in determining crystallinity and phase purity. Films fabricated below 360°C under ambient air conditions have been shown to adopt a tetragonal stannite structure with promising properties (Dridi et al., 2020). However, at higher temperatures, sulfur volatilization and oxidation become significant, often leading to the formation of metal oxides (e.g., CuO , SnO) instead of the desired sulfide phases. To counteract these effects, excess sulfur donors are used, and synthesis is constrained to optimized temperature ranges.

Spray pyrolysis offers numerous advantages that make it attractive for both academic research and industrial applications. It has gained widespread attention due to its operational simplicity, low equipment cost, and scalability, making it suitable for large-scale powder and coating production. The technique supports the synthesis of a broad range of high-purity binary, ternary, and quaternary metal sulfides, which are essential for semiconductor fabrication and advanced composite materials. Another benefit is its rapid processing capability, as fast thermal decomposition of precursors enables short reaction times and high-throughput production (Leng et al., 2019).

Despite these advantages, spray pyrolysis faces several challenges. These include the requirement for highly soluble precursors, careful coordination of evaporation and decomposition temperatures, and the need to manage the toxicity and volatility of sulfur-containing compounds. Additionally, ensuring uniform coating over large substrate areas and avoiding unwanted phase segregation or incomplete sulfidation remain difficult without sophisticated process control. Nevertheless, ongoing advancements in precursor formulation, reactor design, and process automation continue to mitigate these limitations (Ajiboye and Onwudiwe, 2021; Ebrahimi et al., 2019; Isac et al., 2007).

3.5. Physical vapor deposition

Physical vapor deposition (PVD) is a widely employed technique for the fabrication of metal sulfide thin films and nanostructures due to its versatility, precision, and scalability. In contrast to chemical vapor deposition or other reactive synthesis methods, PVD is a purely physical process that involves no chemical reactions – only phase transitions from solid to vapor and then to solid again. In most cases, pre-synthesized sulfides serve as the source material, with the primary aim of structuring and depositing the sulfide rather than synthesizing it in situ. Therefore, the PVD process is often preceded by a separate chemical synthesis step, typically involving the thermal decomposition of suitable metal-sulfur precursors (Umm-e-Farwa et al., 2018).

In a typical PVD process, source materials are vaporized under high vacuum conditions and transported in the vapor phase toward a substrate, where condensation occurs, forming a thin film. Vaporization is most commonly achieved via thermal evaporation or sputtering techniques (Shinde and Rout, 2021). Among the critical factors influencing the success of the deposition process are substrate surface preparation and the intrinsic adhesion characteristics between the sulfide layer and the substrate. Proper substrate preparation is essential to promote uniform film growth and reduce interfacial defects.

Key process parameters – including substrate temperature, chamber pressure, and carrier gas flow rate – strongly influence the resulting film's crystallographic phase, morphology, and defect density (Fazil et al., 2017). For example, ZnS nanobelts fabricated via thermal PVD have demonstrated tunable phase compositions between zincblende and wurtzite structures. These variations, which depend on the argon flow rate and thermal gradient within the chamber, result in significant changes in the material's optical and structural properties (Jin et al., 2018).

PVD offers several advantages, including high film purity, excellent adhesion to substrates, and the ability to construct complex multilayer architectures. Its vacuum-based, contamination-minimizing environment is particularly beneficial for applications requiring stoichiometric accuracy and defect minimization. However, PVD requires advanced equipment and precise control of deposition parameters to ensure uniformity, reproducibility, and structural integrity.

The method's compatibility with a wide range of substrate materials and its potential for upscaling make it especially suitable for use in optoelectronics, photovoltaic devices (Siol et al., 2013), and energy storage technologies. Despite its reliance on pre-synthesized target materials, the high degree of morphological and phase control afforded by PVD continues to drive its adoption in the fabrication of high-performance metal sulfide-based devices.

3.6. Radio-frequency sputtering

Radio-frequency (RF) sputtering is a reliable and controllable technique for the fabrication of high-quality metal sulfide thin films (Dittrich et al., 2009). This method has been successfully used to deposit various sulfide semiconductors such as SnS, SnS₂, ZnS, CuS, MoS₂, Bi₂S₃, as well as ternary CuSnS and quaternary Cu₂ZnSnS₄ sulfides (Raval et al., 2024).

RF sputtering is a variation of the PVD technique that involves bombarding a solid target composed of the desired sulfide compound or its elemental constituents with high-energy ions, mostly argon plasma (Ar⁺), generated by RF power. The impact of these energetic ions causes the ejection (sputtering) of atoms or molecular fragments from the target surface. These sputtered species travel through the vacuum chamber and then condense on a substrate, forming a thin film (Shinde and Rout, 2021).

The sputtering chamber is maintained under high vacuum to minimize contamination and control plasma characteristics. RF sputtering is often preferred for insulating or partially conducting sulfide targets, while direct current (DC) sputtering is suitable for metallic ones.

Two primary sputtering strategies are distinguished: standard and reactive sputtering (co-sputtering). The first approach employs a pre-synthesized sulfide target, typically obtained via wet-chemical methods such as hydrothermal synthesis (Ghribi et al., 2016) or sol-gel processing. In some cases, nanoparticle-based targets are compacted and sintered to form sputterable disks, offering improved stoichiometric control and enhanced grain structure (Hartman et al., 2011).

The second approach is preferred when the direct sputtering of sulfide targets is challenging or when precise control over chemical composition is required, as in the case of multinary sulfides such as Cu-Sn-S or Cu-Zn-Sn-S (Raval et al., 2024). In this technique, metallic targets – such as copper, zinc, and tin – are sputtered in a reactive atmosphere containing a sulfur-bearing gas, such as H₂S or CS₂, enabling in situ formation of the desired inorganic sulfide film on the substrate.

To obtain high-purity, crystalline thin films, it is essential to control key parameters influencing film growth, including deposition time, sputtering power, vacuum pressure, target-to-substrate distance, substrate temperature, and gas flow rate. These parameters significantly affect the structural, morphological, and electronic properties of the resulting films. In some cases, to meet the stringent requirements of optoelectronic devices, the properties of the sulfide thin films are further improved through post-deposition annealing.

Sputtering offers several advantages, including excellent adhesion, precise control over film thickness and uniformity, and the ability to deposit a wide range of inorganic sulfides, including those with high melting points. However, this technique also faces several challenges, such as target poisoning and the

high cost of equipment, which may limit its broader adoption. During deposition, sulfur can re-evaporate or react with residual gases, resulting in off-stoichiometric films. To mitigate this, sulfur-rich targets or post-deposition annealing in sulfur vapor are often employed. Additionally, sulfide targets may degrade or change composition under prolonged sputtering, requiring careful material selection and process optimization.

Despite these challenges, the sputtering technique remains a powerful and controllable method for the fabrication of functional sulfide-based thin films (Ajiboye and Onwudiwe, 2021; Iqbal et al., 2024; Shinde and Rout, 2021).

3.7. Hydrothermal method

One of the most widely used wet chemical methods for the fabrication of metal sulfide nanostructures is the hydrothermal method. This approach involves chemical reactions in aqueous solutions at elevated temperatures and pressures within sealed autoclaves, enabling the transformation of precursors into target nanostructured products under thermodynamically favorable conditions. The hydrothermal method is based on a precipitation mechanism resulting from the low solubility of sulfide products.

In this method, metal and sulfur precursors are dissolved in water or other polar solvents (solvothermal variant), and the resulting solution is subjected to temperatures typically ranging from 100 °C to 250 °C and elevated pressures (up to several tens of bars). These conditions enhance the solubility and reactivity of the precursors, promote nucleation and crystal growth, and allow control over phase formation (Liu et al., 2024; Shi et al., 2013). The sealed system prevents the loss of volatile species such as H₂S, which is critical for achieving stoichiometric and high-purity sulfide products.

The mechanism involves several sequential steps: dissolution of precursors, formation of intermediate species such as metal-thiourea complexes, nucleation, and subsequent crystal growth. Hydrothermal synthesis of metal sulfides typically employs soluble metal salts (e.g., nitrates, chlorides) as metal sources and sulfur-donating compounds such as thiourea, thioacetamide, or elemental sulfur. Upon heating, these sulfur sources decompose in solution to generate reactive sulfide species (HS⁻, S²⁻), which react with metal cations to form sulfide nuclei.

The hydrothermal method offers a robust platform for synthesizing metal sulfide nanoparticles (NPs) with precise control over particle size (Balakrishnan et al., 2021), crystal phase, and morphology (Zhu et al., 2008). Nanoparticle formation proceeds via two main stages: nucleation and crystal growth. Under high temperature and pressure, in-situ generated metal cations and sulfide anions become supersaturated, leading to the spontaneous formation of critical-sized nuclei. This nucleation process is influenced by local temperature gradients, ion

concentration, pH, and the decomposition kinetics of the sulfur precursor. Once nuclei are formed, crystal growth occurs via diffusion of ionic species toward the nuclei. The balance between nucleation and growth rates determines the final particle size: rapid nucleation with slow growth favors small, monodisperse nanoparticles, whereas slower nucleation with dominant growth leads to larger, potentially polycrystalline structures.

In practice, this balance is finely tuned by adjusting precursor concentrations, heating rate, and dwell time in the autoclave. Elevated temperatures generally enhance precursor solubility and mobility, promoting the formation of well-faceted, larger crystallites. In contrast, shorter reaction times limit growth and favor smaller particle sizes. For example, ZnS synthesized at lower temperatures (150–200 °C) typically yields nearly spherical particles with diameters of 5–10 nm, while synthesis above 250 °C can result in hexagonal rods or platelets.

Another important factor is the pH of the solution, which affects ionization states and surface charge, thereby influencing nucleation and colloidal stability. The role of capping agents is also noteworthy. Organic surfactants such as oleylamine, citrate, or polymers can be introduced to selectively adsorb onto specific crystal facets, modulating anisotropic growth. Although hydrothermal synthesis is often conducted without capping agents, their inclusion allows for enhanced shape control, enabling the formation of rods, flowers, or plate-like morphologies.

The hydrothermal method offers several distinct advantages, including low crystallization temperatures, morphological control, high purity, and versatility. In contrast to solid-state or vapor-phase techniques, it enables the formation of crystalline sulfide materials under relatively mild conditions. By adjusting synthesis parameters, a wide range of nanostructures, including spheres, rods, and sheets, can be obtained. Furthermore, the sealed reaction environment minimizes contamination and the loss of volatile components, improving product quality. This technique allows for the synthesis of a broad spectrum of binary and multinary sulfides, such as ZnS, MoS₂, SnS, Cu₂SnS₃, FeS₂, CuS, Bi₂S₃, CuInS₂, and Cu₂ZnSnS₄ (Balakrishnan et al., 2021).

Nevertheless, the hydrothermal method also presents certain challenges and limitations. It requires specialized equipment, particularly autoclaves capable of operating at elevated temperatures and pressures. These systems are often expensive to acquire and maintain. The need for corrosion-resistant materials and strict safety protocols further increases operational costs. Additionally, hydrothermal synthesis involves multiple stages – including precursor preparation, reaction setup, and post-synthesis processing – making the overall procedure relatively complex and time-consuming. Achieving optimal reaction conditions and precise control over reaction kinetics demands significant expertise in materials chemistry and experimental methodologies.

One of the major challenges is scaling up for bulk production. Conventional laboratory-scale autoclaves have well-

established, small-volume designs that allow for stringent control of reaction parameters. However, increasing the production volume introduces concerns about reproducibility due to temperature and concentration gradients within the reactor. Larger reactors also require more complex construction and enhanced safety features. The autoclave must withstand high pressure, temperature, and corrosive environments, resulting in design constraints such as increased wall thickness and the need for advanced pressure control systems. This leads to higher equipment costs due to the use of durable, yet expensive, construction materials.

To enable industrial implementation, it is essential to develop synthesis strategies that are both cost-effective and scalable while maintaining consistent product quality and reproducibility (Abid et al., 2022; Ajiboye and Onwudiwe, 2021; Rahman et al., 2024).

3.8. Chemical bath deposition

The chemical bath deposition (CBD) method is a versatile, low-cost technique widely employed for the synthesis of metal sulfide thin films (Akkari et al., 2011). In contrast to chemical vapor deposition is a low-temperature process, typically conducted below 100 °C. It involves the controlled precipitation of the desired material onto a substrate immersed in an aqueous solution containing metal salts and sulfur sources (Shinde and Rout, 2021). This technique requires prior surface preparation of the substrate as well as the preparation of a homogeneous bath solution, which typically consists of a solvent, pH adjusters, metal and sulfur precursors, and complexing agents. The process is generally carried out in a deposition chamber equipped with a magnetic stirrer and a heating plate.

The formation of sulfide films via CBD is governed by the gradual release of metal cations and sulfide anions in solution, followed by their nucleation and growth on the substrate surface. Common metal precursors include soluble metal salts such as chlorides, nitrates, and acetates. To prevent rapid precipitation, the sulfur sources are usually organic compounds such as thioacetamide and thiourea, although thiosulfate has also been reported as an effective sulfur donor. In acidic or mildly alkaline media, H₂S is released through the hydrolytic decomposition of the sulfur precursor, generating S²⁻ ions that react directly with metal cations to form the corresponding metal sulfide.

Complexing agents play a crucial role in regulating the reaction kinetics by controlling the release rate of metal ions. Following deposition, the substrate is removed, rinsed to eliminate any unreacted solution, and then dried – typically under ambient air or nitrogen flow.

Key parameters influencing film quality include pH, deposition time, temperature, precursor ratios, and the type of complexing agent used (e.g., EDTA, TEA) (Chalapathi et al., 2016). CBD allows the formation of sulfide films with

controlled microstructures, including nanobelts, nanosheets, and compact polycrystalline layers. Modulating the sulfur concentration and pH enables control over crystallite size and crystal phase (e.g., orthorhombic, cubic), while complexing agents stabilize metal ions and promote uniform nucleation, enhancing grain size and homogeneity.

This method is particularly suitable for the deposition of low-solubility metal sulfides such as ZnS, CdS, MnS, CuS, SnS, and SnS₂ (Cao et al., 2018). In multinary systems, such as Cu₂ZnSnS₄ (CZTS), CBD can be employed in a sequential manner by depositing binary sulfide layers (e.g., ZnS, SnS, CuS), followed by annealing to form the desired quaternary phase (Macias-Cabrera et al., 2021; Raval et al., 2024).

CBD yields films with tunable thickness, acceptable crystallinity, and good compositional control, offering a scalable and cost-effective approach for the fabrication of thin films used in solar energy applications (Ajiboye and Onwudiwe, 2021; Chaki et al., 2014).

3.9. Dip coating

Dip coating is a versatile, cost-effective, and scalable technique employed for the fabrication of metal sulfide thin films (Nayak et al., 1983). This method shares similarities with chemical bath deposition in that it is also solvent-based and requires prior preparation of both the substrate surface and the precursor solution. However, in contrast to CBD, the formation of the sulfide layer occurs during the subsequent annealing stage.

The technique is based on the principle of immersing and withdrawing a substrate from a precursor solution, enabling uniform thin-film deposition on a variety of substrates. The process typically comprises three sequential steps: immersion, withdrawal, and drying (Ajiboye and Onwudiwe, 2021; Shinde and Rout, 2021). In the first step, a cleaned substrate (commonly glass) is vertically immersed into a solution containing metal and sulfur precursors. Although these precursors are similar to those used in the CBD method, organic solvents such as methanol or isopropanol are sometimes added to enhance the solubility of organic sulfur sources.

After a dwell time, which allows sufficient adsorption of the solution onto the substrate, the substrate is withdrawn at a controlled speed, resulting in the formation of a uniform liquid film on its surface. During the withdrawal and drying phases, the solvent evaporates, leaving behind a solid precursor layer. In the post-deposition step, the substrate undergoes thermal treatment (annealing) at moderate temperatures, typically between 200 °C and 400 °C. This step facilitates chemical reactions between the precursors and promotes the formation of crystalline metal sulfide phases. For example, annealing tin and sulfur precursors in air results in the formation of SnS or SnS₂, depending on the stoichiometry and annealing temperature. Similarly, CdS and ZnS films prepared

via dip coating from sol-gel or polymeric precursors exhibit good homogeneity and optical clarity after heat treatment.

Key parameters influencing film quality include solution concentration, withdrawal speed, viscosity, surface tension, and annealing temperature. These factors collectively determine the resulting film's thickness, uniformity, and crystallinity. Typically, slower withdrawal rates and higher solution viscosities yield thicker films. The film thickness can also be controlled by varying the number of dip-dry cycles.

Morphological analysis via scanning electron microscopy (SEM) often reveals uniformly coated films exhibiting nanostructured or microstructured features, depending on the precursor chemistry and synthesis conditions. For instance, SnS₂ films often display hexagonal nanoplate morphologies, whereas CdS films may exhibit spherical or aggregated grain structures. X-ray diffraction (XRD) confirms the phase purity and crystallinity of the films, with common crystal structures including hexagonal for ZnS (Balachander et al., 2017) and CdS (Dhatchinamurthy et al., 2020), and orthorhombic or trigonal for SnS and SnS₂ (Ray et al., 1999).

Despite its simplicity, dip coating presents certain limitations. Film uniformity may be affected by surface tension effects and edge defects, particularly near the withdrawal points. Additionally, achieving precise thickness control over large areas may be challenging without automated systems. Nevertheless, the technique remains highly effective for research-scale fabrication of sulfide films due to its operational simplicity, low equipment requirements, and adaptability to various material systems.

3.10. Spin coating

Spin coating is another widely used technique for fabricating thin films of inorganic sulfides. While it shares similarities with previously discussed methods, it differs primarily in the way precursors are distributed across the substrate surface (Shinde and Rout, 2021). This method has attracted significant attention due to its capability to produce uniform coatings with controllable thickness, morphology, and crystallinity – parameters crucial in applications such as photovoltaics (Daem et al., 2025), photocatalysis (Vakalopoulou et al., 2022), and optoelectronics (Seon et al., 2009).

The spin coating process involves depositing a precursor solution onto a substrate, which is then rapidly rotated to spread the liquid evenly by centrifugal force. The final film thickness is primarily influenced by the precursor solution's viscosity, rotation speed, and spin duration. During spinning, volatile solvents evaporate quickly, leaving behind a thin and uniform precursor layer. This layer generally undergoes subsequent thermal treatment to initiate decomposition or crystallization, forming the desired inorganic sulfide phase (Soonmin, 2021). Multistep annealing procedures are commonly employed to enhance crystallinity and optimize microstructural features.

These thermal treatments not only promote solvent evaporation and precursor decomposition but also improve adhesion between the sulfide film and the substrate. In some cases, controlled temperature gradients and multi-stage annealing protocols (e.g., sequential steps at 100 °C, 180 °C, and 265 °C) are used to achieve specific crystalline orientations.

Post-deposition modifications, such as spin-coating sulfur-rich solutions or sulfurization treatments, can further improve film stoichiometry and reduce residual oxide phases. The spin coating technique is compatible with both dense and mesoporous substrates, rendering it adaptable for various device architectures. For example, in photovoltaic devices, Sb_2S_3 layers deposited on fluorine-doped tin oxide (FTO) glass substrates and compact TiO_2 electron transport layers (ETLs) have demonstrated efficient charge extraction. The incorporation of mesoporous layers can enhance light absorption but may also introduce challenges such as grain misorientation and increased recombination sites if not carefully optimized.

Moreover, spin coating facilitates the fabrication of multilayer heterojunctions, which are critical for improving photoresponse and charge separation. An example includes the n-ZnS/p-PbS bilayer (Aouf et al., 2023), where the combination of materials broadens the absorption spectrum and enhances carrier dynamics. Such bilayer films have been effectively applied in photocatalysis, achieving significant degradation efficiencies of dyes such as methylene blue, malachite green, and methyl orange under visible or solar light irradiation.

Despite its advantages, spin coating has some limitations. It is generally substrate-specific, favoring planar and rigid surfaces, and it faces challenges when applied to large-area substrates. Additionally, the technique generates relatively high material waste, as excess precursor solution is discarded during spinning. Nevertheless, its simplicity, reproducibility, and compatibility with diverse precursor chemistries establish spin coating as a leading method for fabricating functional sulfide-based thin films.

Overall, spin coating offers a robust platform for the controlled synthesis of metal sulfide films with tunable morphology, composition, and crystallographic orientation. By optimizing precursor formulation, spin parameters, and post-deposition treatments, researchers can tailor the physicochemical properties of sulfide films to meet the requirements of applications in sustainable energy, environmental remediation, and advanced optoelectronic devices (Abbas et al., 2020; Ajiboye and Onwudiwe, 2021; Liang et al., 2022).

3.11. Electrodeposition

Electrodeposition (ED) has emerged as a highly effective and versatile technique for synthesizing metal sulfide structures, particularly relevant for applications in energy storage, catalysis, and optoelectronics. This electrochemical method involves

the controlled reduction of metal cations and sulfur precursors onto a conductive substrate under the influence of an applied electric field. Its importance stems from the ability to directly deposit nanostructured films or composite architectures with excellent adhesion, uniformity, and tunable morphology.

In recent years, electrodeposition has gained significant attention for the fabrication of transition metal sulfides, including both binary and multinary compounds (Duan et al., 2025), owing to its scalability, cost-effectiveness, and environmentally friendly nature (Khattak et al., 2019). The underlying principle of electrodeposition is based on Faraday's laws of electrolysis, which state that the mass of the deposited material is directly proportional to the electric charge passed through the system (Burgos et al., 2016).

Typically, a three-electrode setup is employed (see Fig. 3), consisting of a working electrode (WE, serving as the substrate), a counter electrode (CE, usually platinum), and a reference electrode (RE, commonly Ag/AgCl) (Feyie et al., 2024). The electrolyte solution contains metal salts and a sulfur source such as thiourea or sodium thiosulfate. Upon applying a suitable potential or current, metal cations and sulfur species are simultaneously reduced at the working electrode surface, leading to nucleation and growth of a metal sulfide film (Chen et al., 2014; Mohapatra et al., 2024).

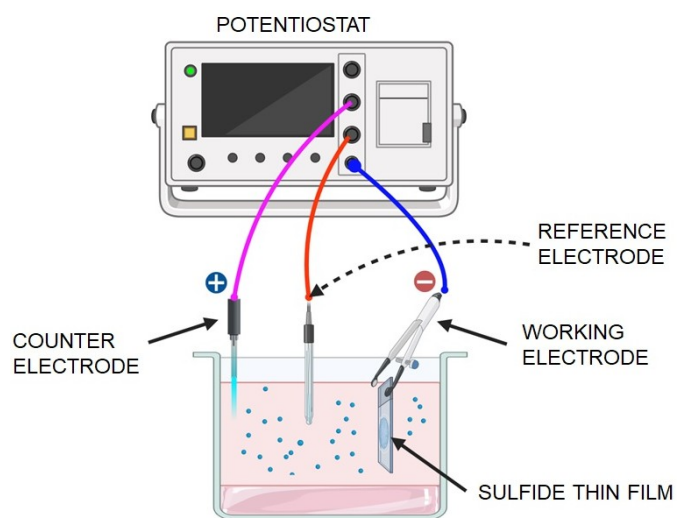


Figure 3. Schematic diagram of the electrodeposition setup for metal sulfide synthesis. Reprinted with permission from (Mohapatra et al. 2024). Copyright © 2023 The Chemical Society of Japan & Wiley-VCH GmbH.

The electrochemical parameters – including applied potential, current density, deposition time, pH, temperature, and electrolyte composition – critically influence the morphology, crystallinity, and stoichiometry of the deposited sulfide structures. For example, potentiostatic deposition enables precise control over nucleation kinetics, resulting in uniform, well-adhered films. Conversely, galvanostatic deposition maintains

a constant material accumulation rate but may produce films with less controlled morphology. Pulse electrodeposition is also utilized to tailor grain size and porosity by alternating periods of high and low potential.

The choice of precursors plays a pivotal role in determining the sulfide phase formation. Thiourea is commonly employed as a sulfur source because it releases sulfide ions electrochemically under mild conditions. Typically, thiourea decomposes at the cathode surface, generating sulfide ions that react with metal cations to form insoluble metal sulfide compounds (Mohapatra et al., 2024). Complexing agents such as citrate or tartrate are frequently added to the electrolyte to regulate the concentration of free metal ions, thereby preventing premature precipitation and enhancing deposition uniformity (Burgos et al., 2016).

Electrodeposition has demonstrated particular efficacy in synthesizing nanostructured binary sulfides like CuS, NiS, and CoS, as well as multinary compounds such as $\text{Cu}_2\text{ZnSnS}_4$ and NiCo_2S_4 (Duan et al., 2025; Khattak et al., 2019). These materials exhibit superior electrochemical performance due to increased surface area, abundant redox-active sites, and high electrical conductivity. Furthermore, direct deposition onto conductive substrates – such as nickel foam or carbon cloth – eliminates the need for binders and conductive additives, which can otherwise introduce interfacial resistance and degrade long-term device stability.

Despite these advantages, challenges persist in achieving reproducible and uniform films on a large scale. Precise control over electrochemical parameters is essential, as deviations can cause film non-uniformity, poor adhesion, or the formation of unwanted phases. Additionally, the simultaneous reduction of multiple metal ions necessitates careful optimization of deposition potentials to obtain the correct stoichiometric ratios in multinary systems. To address these complexities, advanced strategies including in situ monitoring and computational modeling are increasingly employed to refine and optimize electrodeposition processes (Chen et al., 2014; Feyie et al., 2024).

3.12. High-energy ball milling

One of the simplest and most widely used bottom-up approaches for fabricating inorganic sulfide structures is the mechanochemical method, commonly known as high-energy ball milling. This technique involves mechanosynthesis through high-speed grinding of reactants inside a cylindrical mill under an inert atmosphere, employing hardened steel balls as the milling media (see Fig. 4) (Baláz et al. 1999; Koteeswara Reddy et al. 2015). The reaction mechanism is based on tribochemical interactions between stoichiometric amounts of the required substrates. Unlike conventional furnace synthesis, the energy necessary to initiate the solid-state reaction is supplied mechanically through friction and impact during milling.

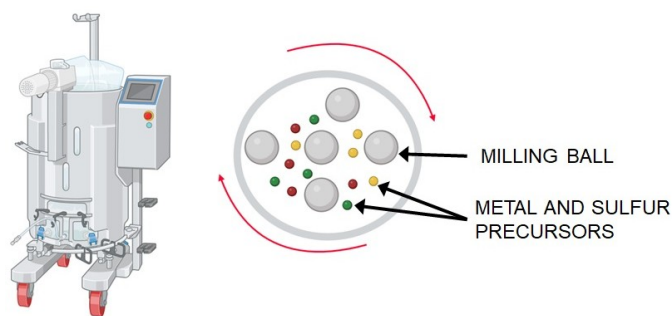


Figure 4. Schematic illustration of the ball milling synthesis process.

Thanks to the high-speed rotation of the milling container, atomic-level homogeneity is achieved, which enhances the interfacial area and shifts the reaction mechanism from diffusion-controlled to kinetically controlled (Nautiyal et al., 2023). High-energy ball milling enables the synthesis of sulfides with a broad range of particle sizes, from nanoparticles to micron-sized grains. The particle size distribution can be regulated by the size of the milling balls, with larger steel balls generally promoting the formation of smaller particles (Balakrishnan et al., 2021). For nanoparticle synthesis, surfactants are often employed to facilitate structural control (Ullah et al., 2014). Mechanochemical synthesis via high-energy ball milling offers a significant advantage by enabling the formation of various disordered polymorphs of inorganic sulfides. This one-step, solvent-free process allows the alloying of materials with different melting points, including transition metals and chalcogenides (Dutková et al., 2023). Such capability arises from the highly entropic conditions generated during the milling process (Ajiboye and Onwudiwe 2021; Jung et al., 2011).

4. OVERVIEW OF APPLICATIONS OF INORGANIC SULFIDES

Inorganic sulfides constitute an important class of materials that have attracted considerable attention due to their diverse physicochemical properties and broad applicability across various technological fields. These compounds are central to solid-state chemistry and materials science owing to their structural diversity (Makovicky, 2006; Weber et al., 1998), tunable bandgaps (Wold and Dwight, 1993), and favorable magnetic, electronic, and optical characteristics (Chhowalla et al., 2013; Saeed et al., 2025; Talib et al., 2019).

One of the key parameters of photodetectors includes spectral response, photoresponsivity, external quantum efficiency (EQE), and response time. The spectral response defines the usable wavelength range of the photodetector, whereas photoresponsivity represents the ratio of the photocurrent generated to the incident optical power on the detector. The EQE is defined as the ratio of the number of charge carriers generated to the number of incident photons, reflecting how efficiently light is converted into photocurrent. Finally, the

response time indicates the duration required for the detector to respond to changes in illumination, playing a crucial role in evaluating the applicability of sulfide nanostructures in photodetectors (Raval et al., 2024; Ramakrishnan et al., 2023; Saeed et al., 2025). Examples of absorption spectra for inorganic sulfide-based materials are provided in Table 1.

In recent decades, interest in sulfides has surged, driven by global efforts toward energy-efficient, sustainable, and miniaturized technologies. Their semiconducting nature (Kotteeswara Reddy et al., 2015) and catalytic abilities make them integral to numerous applications including electronics (Abbas et al., 2020), optoelectronics (Wang et al., 2012), medicine (Li et al., 2017), photovoltaics (Raval et al., 2024; Senthamilselvi et al., 2012), catalysis (Topsøe, 2007), energy storage (Leng et al., 2019), and environmental remediation (Rohit et al., 2024; Wu et al., 2022).

Metal sulfides are especially noted for their exceptional catalytic activity in many hydroprocessing reactions such as hydrogen evolution reactions (HER), hydrodesulfurization, Fischer–Tropsch synthesis, hydrogenation, and hydrocracking (Chianelli et al., 1994). Notably, MoS₂, NiS, WS₂, and Co-Mo-S are effective catalysts due to their high surface areas, active edge sites, and favorable electronic structures that promote charge transfer reactions (Topsøe, 2007). MoS₂, in particular, is considered as a promising non-precious metal catalyst for HER (Jaramillo et al., 2007; Radhakrishnan and Biswas, 2023), providing a cost-effective alternative to platinum-based catalysts in water-splitting applications.

Furthermore, sulfide catalysts play a vital role in petroleum refining by removing impurities such as sulfur and nitrogen from fuels (Chianelli et al., 2006; Chianelli et al., 2009; Weber et al., 1998). Due to their layered structures, sulfides are also used in demanding tribological applications where conventional fluid lubricants are ineffective, such as in high-load vacuum systems and friction materials (Balaji and Surya Rajan, 2023; Dante, 2016; Rapoport et al., 2005).

A general summary of inorganic sulfide fabrication methods and their resulting applications is presented in Table 2.

5. FUTURE PROSPECTS

The future of inorganic sulfides is strongly aligned with their integration into next-generation technologies such as flexible electronics, quantum computing, and solid-state energy storage systems. Research on heterostructures, doped and alloyed sulfides is anticipated to unlock new functionalities and address current performance bottlenecks (Rahman et al., 2024; Rawat and Kala, 2025).

A major challenge remains the development of scalable, cost-effective, and environmentally benign synthesis methods. The application of green chemistry principles – challenge such as the use of bio-derived precursors, solvent-free reactions, and low-waste processes – supports broader sustainability goals while minimizing the environmental footprint of toxic sulfur sources and chemical by-products (Botha and Matinise, 2024). These requirements are addressed by so-called green synthesis, which offers an eco-friendly alternative to conventional methods for producing metal sulfide nanomaterials. Rather than relying on high energy inputs and toxic reagents, green synthesis utilizes plant extracts, microorganisms, or mild aqueous systems, in which natural biomolecules function as reducing and stabilizing agents. This approach is cost-effective, bio-compatible, and avoids the use of hazardous chemicals such as hydrogen sulfide gas. Plant-derived metabolites, including flavonoids, proteins, and organic acids, have enabled the synthesis of ZnS, CuS, and CdS nanoparticles with tunable sizes and morphologies, while microorganisms such as fungi and sulfate-reducing bacteria (SRB) facilitate sulfide formation through enzymatic reduction of sulfur sources. These biogenic nanoparticles retain optical and electronic properties comparable to those obtained via conventional synthesis (Botha and Matinise, 2024; da Costa et al., 2016; Langa et al., 2025).

Table 1. Overview of spectral application and parameters of inorganic sulfides photodetectors, adapted from (Ramakrishnan et al., 2023).

Sulfide formula	Bandgap (eV)	Spectral response range	Reference
ZnS	3.56	UV	Popov et al., 2018
TiS ₃	1.1		Talib et al., 2019
Bi ₂ S ₃	1.3		Ranjitha et al., 2014
SnS ₂	2.88	UV/Visible	Voznyi et al., 2016
Sn ₂ S ₃	2.1	Visible	Shinde and Rout, 2021
In ₂ S ₃	1.88		Chaudhary et al., 2021
CdS	2.42		Senthamilselvi et al., 2012
Bi ₂ S ₃	1.9	Visible/NIR	Xiao et al., 2012
Cu ₂ SnS ₃	1.16	Visible	Jia et al., 2015
Sb ₂ S ₃	1.8	Visible/ NIR	Kondrotas et al., 2018
PbS	0.4	IR	Şahin et al., 2019
SnS	1.32	IR	El-Nahass et al., 2002

Table 2. Overview of applications of inorganic sulfide materials and related fabrication methods.

Sulfide formula	Fabrication method	Application	Type of structure	Reference
MoS ₂ – ReS ₂	CVD	photodetectors	2D – heterostructure	Liu et al., 2022
MoS ₂ – WS ₂				Kanade et al., 2021
MoS ₂		transistors, HER, photodetectors, energy storage	2D – monolayer	Chhowalla et al., 2013
ZnS	PVD	gas sensors	1D – core-shell nanowire	Mun et al., 2013
Cu ₂ S		solar cells	thin film	Siol et al., 2013
MoS ₂	ALD	Transistors	2D – monolayer	Radisavljevic et al., 2011
SnS ₂		high performance supercapacitor electrode	2D – monolayer	Ansari et al., 2019
SnS ₂		photodetectors, FET transistor, optoelectronics, single crystal growth	2D – monolayer	Tripathi et al., 2023
TiS ₂	CVT	photodetectors Li-ion batteries, solid lubricants	nanosheets, nanoribbons, nanodiscs	Talib et al., 2019
CuS	CBD	gas sensor, solar cell	nanocrystalline thin films	Chaki et al., 2014
SnS		solar cell	thin film	Chalapathi et al., 2016
ZnS		photocatalyst	nanoparticles	Popov et al., 2018
CuS	dip coating	gas sensor, solar cell	nanocrystalline thin films	Chaki et al., 2014
CdS		solar cell, LED		Dhatchinamurthy et al., 2020
SnS, SnS ₂		Photovoltaic	thin film	Ray et al., 1999
Sb ₂ S ₃				Daem et al., 2025
ZnS / PbS	spin coating	photocatalytic degradation, antimicrobial activity		Aouf et al., 2023
SnS		photoelectronic		Liang et al., 2022
Cu ₂ MnSnS ₄		Photovoltaic		Dridi et al., 2020
Cu ₂ SnS ₃	spray pyrolysis			Sayed et al., 2019
Li-S		energy storage, photovoltaic	nanoplates, nanorods, nanowires, thin films	Leng et al., 2019
ZnS		photodetectors	thin film	Zeng et al., 2013
MoS ₂	RF sputtering	FET transistor	2D – monolayer	Hussain et al., 2016
ZnS	hydro-thermal / RF sputtering	Photovoltaic	nanoparticles / thin film	Ghribi et al., 2016

Table 2 continued at the next page

Table 2 continued from the previous page

Sulfide formula	Fabrication method	Application	Type of structure	Reference
SnS	RF sputtering	solar cell	thin film	Hartman et al., 2011
CoS	electrodeposition	supercapacitors	nanosheets	Shi et al., 2015
FeS ₂		electrode material for thermal batteries	thin film	Wang et al., 2013
Cu ₂ ZnSnS ₄		solar cell		Khattak et al., 2019
MnIn ₂ S ₄	hydro-thermal	Li-ion batteries	nanoparticles	Muruganantham et al., 2023
ZnS, CdS, PbS, CuS, FeS, Bi ₂ S ₃		Photovoltaic		Dunne et al., 2014
Bi ₂ S ₃				Salavati-Niasari et al., 2013
Cu ₂ FeSnS ₄		electrocatalysts		Hausmann et al., 2020
CuFeS ₂ , Cu ₂ FeSnS ₄	ball milling	antibacterial materials		Baláz et al., 2022
Bi ₂ S ₃		Li-ion batteries		Jung et al., 2011

Advancements in material performance will increasingly depend not only on deeper understanding of their intrinsic properties but also on innovations in how these materials are synthesized. To this end, conventional fabrication techniques are being complemented with advanced process control and predictive modeling, enabling greater precision in morphology, composition, and phase engineering.

A particularly promising avenue is the integration of computational modeling and machine learning with experimental synthesis. Artificial intelligence (AI) is rapidly transforming the landscape of materials design, allowing for the predictive optimization of key synthesis parameters – such as temperature, pressure, precursor ratios, and deposition time ([Butler et al., 2018](#); [He et al., 2023](#); [Karpovich et al., 2021](#)). These data-driven approaches reduce trial-and-error experimentation and accelerate discovery cycles ([Cao et al., 2024](#); [Ye et al., 2025](#)).

For example, supervised learning algorithms trained on experimental datasets can accurately forecast phase formation and crystallinity based on given process conditions. This facilitates targeted synthesis strategies and accelerates the development of materials with precise structure–property relationships. As the fabrication of 2D and 3D sulfide architectures demands increasingly high accuracy, the convergence of AI with advanced synthesis techniques offers a transformative approach for tailoring properties at the atomic scale.

In summary, the future of inorganic sulfide materials will be shaped by a synergy of interdisciplinary innovation – uniting synthetic chemistry, materials science, and data-driven engineering. This integrated approach will be critical to unlocking the full technological potential of sulfide-based materials in a sustainable and efficient manner.

6. CONCLUSIONS

Inorganic sulfide structures, particularly those incorporating transition metals, exhibit remarkable versatility due to their tunable electronic, optical, and catalytic properties. This review highlights the pivotal role of fabrication techniques in determining the structural, morphological, and functional characteristics of these materials. Among the various synthesis routes discussed – including CVD, ALD, hydrothermal methods, spray pyrolysis, and electrodeposition – each offers distinct advantages in terms of scalability, compositional control, and compatibility with modern device architectures.

Despite notable progress in the development of high-quality sulfide nanostructures, significant challenges remain, particularly regarding reproducibility, large-scale implementation, and environmental sustainability. Scaling up the synthesis of inorganic sulfides faces several practical challenges. One of the key concerns affecting implementation is the cost of precursors and associated chemical safety considerations. In the case of advanced deposition techniques such as CVD, PVD, and ALD, the precursors must be of ultra-high-purity grade, which can be costly, particularly at an industrial scale, potentially limiting economic feasibility compared with oxide-based materials. Regarding safety and environmental aspects, processes that utilize sulfur precursors, such as H₂S, present significant hazards. Hydrogen sulfide is a toxic and highly poisonous gas, requiring specialized handling, ventilation, and monitoring systems. Furthermore, industrial adoption is constrained by strict environmental regulations concerning sulfur emissions, toxic effluent treatment, and worker safety protocols, all of which increase operational costs.

In the context of process scalability, a commonly used parameter is the Technology Readiness Level (TRL), which describes the maturity of a technology. Regarding the fabrication methods of inorganic sulfides, solid-state synthesis, such as high-energy ball milling, is simple and already implemented at an industrial scale; therefore, it is considered technologically mature, typically at TRL 8–9. On the other hand, novel biogenic or green synthesis routes are estimated at TRL 3–5, as they are currently at the proof-of-concept stage. In the case of solution-based methods involving precipitation, they are moderately scalable, although challenges such as waste management and batch-to-batch reproducibility remain. Depending on process optimization, these methods are estimated at TRL 5–7. Additionally, deposition techniques such as CVD and PVD, which are widely used for thin-film sulfides in electronics, are rated at TRL 6–8, depending on the material and process.

The integration of experimental synthesis with computational modeling and machine learning represents a powerful strategy to overcome these limitations, thereby accelerating the discovery of new materials and refining synthesis pathways toward greater precision and efficiency.

Future research should prioritize environmentally benign synthesis strategies, intelligent process automation, and interdisciplinary collaboration to unlock the full potential of sulfide-based materials as key enablers of next-generation technologies. These advancements are expected to directly impact sectors such as renewable energy, catalysis, optoelectronics, and environmental remediation.

7. ACKNOWLEDGEMENTS

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