Review Article

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Comprehensive reviews on the potential applications of inorganic metal sulfide nanostructures in biological, environmental, healthcare, and energy generation and storage

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Abstract: The versatile nature of metal sulfide nanostructures has led to their meteoric rise in popularity. The compositions, morphologies, and sizes of these nanostructures may be tuned, giving them distinct features. Here we look at the many uses of metal sulfide nanostructures, with an emphasis on their possible benefits in

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the fields of biology, ecology, and energy storage. Because of their remarkable optical characteristics and high degree of biocompatibility, metal sulfide nanostructures have great potential in the biological fields of bioimaging, medication administration, and photothermal treatment. Additionally, because of their large surface area and adsorption capability, these nanostructures outstanding performance in environmental remediation, which includes pollutant removal and wastewater treatment. Because of their great conductivity and electrochemical activity, metal sulfide nanostructures are also in great demand for energy storage applications such supercapacitors, hydrogen storage, and lithium-ion batteries. This review provides a comprehensive analysis of recent progress in synthesizing various metal sulfides with transition metal elements. Effective physiochemical and biological approaches are employed in their production to control the structures, dimensions, and compositions of these sulfides.

Keywords: supercapacitor; solar cell; photocatalysis; metal sulfides; bioimaging; cancer photothermal therapy

1 Introduction

Nanotechnology has garnered significant interest in the 21st century because of its wide-ranging applications in several fields, for example, biomaterials, energy storage, water purification, and medicine. Nanostructures (NSs) with dimensions ranging from 1 to 100 nm are crucial in advancing nanotechnology. Their remarkable control over a wide range of physical and chemical properties including melting point, electrical and thermal conductivity, catalytic activity, light absorption, and scattering explains why. Consequently, NSs exhibit superior performance compared to bulk materials. Various physiochemical and biological techniques have produced a diverse

range of nanostructures (including zero-dimensional, onedimensional, two-dimensional, and three-dimensional structures). Among the many uses for these nanostructures are electrical appliances, sensors, catalysts for light, antibacterial substances, and catalysts. 1-3 Many classes of nanomaterials exist, including carbon-based materials, ceramics, polymers, metal sulfides, metal oxides, and metals. Their size, shape, and a plethora of properties including electrical, optical, magnetic, chemical, and mechanical traits affected by their constrained dimensions form the basis of this categorization.⁴⁻⁷ MOs and MSs, as nanomaterials, have exceptional semiconductor properties that enable them to efficiently capture solar radiation over a wide range of wavelengths, the ultraviolet (below 300 nm), visible (between 300 and 700 nm), and infrared (beyond 700 nm) wavelengths. For years, nanomaterials incorporating MOs and MSs have been employed in photocatalysis, water splitting, and photovoltaics.

An important fact is that several MOs possess a significant band gap energy. This is because the band of energy levels occupied by valence electrons is exclusively made up of deep 2p oxygen orbitals, resulting from their restricted structure. Additionally, hole carriers in MOs have a comparatively high effective mass.8-14 The chemical composition of MSs differs from MOs in a few keyways. One reason is the disparity in atomic numbers and dimensions between oxygen (O) and sulfur (S) atoms, as well as the dissimilarity in negatively bivalent anions that attach to them. For example, the ionic radius of O²⁻ ranges from 1.35 to 1.42 Å, and the ionic radius of S²⁻ is 1.84 Å. 15-17 Accordingly, S exhibits greater average polarizability ($\alpha S = 2.90 \times 10^{-24} \text{ cm}^3$) compared to O $(\alpha O = 0.802 \times 10^{-24} \text{ cm}^3)$. The electronegativity of sulfur (S) is significantly less than that of oxygen (O), indicating that the M–S interaction is more covalent than the M–O link.¹⁹ Compared to MOs. MSs have several desirable properties. such as extended lifespan, low melting point, nanocrystalline shape, low redox potential, exposed active sites, strong photosensitivity, and appropriate electronic band gaps and locations.²⁰ MSs, M₂S, M₃S₄, and MS₂, are stoichiometric compositions of compounds formed by sulfur anion and cationic metal or semimetal, abbreviated as MX Sy.²¹ Ammonium sulfide, thiols (such as decanethiol or DDT), and organosulfur compounds (such as thiourea and thioacetamide) are sources of the comparatively cheap and readily handled element sulfur.

MSs have attracted much attention as potential catalysts or photocatalysts for various applications in the last few decades. A few instances involve sensors, power sources, splitting of water by photo electrochemistry (PEC), electrocatalytic hydrogen generation, environmental cleanup, and many more.²² Metal sulfides (MSs) have garnered growing interest

in diverse fields including medical, electrochemistry, absorption, capacitors that store energy and rechargeable. 23,24 3D transition metal dichalcogenides, such as FeS2, are electronic materials with structures that span both the localization and itinerant regimes of 3D electron properties. There is great promise for using FeS₂ nanosphere material in inexpensive solar systems.

Various methods, both vertical and horizontal, are currently employed to produce high-quality mono-, bi-, and multi-MS nanomaterials with precise sizes and structures. Top-down synthesis techniques include ball-milling, sputtering, lithography, and etching processes. Bottom-up approaches encompass chemical vapor deposition, laser pyrolysis, atomic condensation, and spray pyrolysis. Given the significant influence of nanoscale structures (NSs) on functional properties, there is a growing focus on research aimed at controlling morphologies, such as nanoparticles (NPs), nanorods (NRs), nanotubes, nanoplates, nanofibers (NF), nanosheets, nanowires, and nanoflakes, within the realm of nanotechnology.

This study explores recent advancements in synthesis techniques for producing MSs. These methods facilitate large-scale production of MSs with high efficiency and moderate cost. MSs can exhibit structures ranging from zero to three dimensions. Each MS is summarized, emphasizing its key features and potential applications across various fields including sensing, photocatalysis, antimicrobial properties, manufacturing, medical science, and energy storage and conversion, encompassing technologies like solar panels, solid-state batteries, and supercapacitors.

This review article provides a comprehensive analysis of recent progress in synthesizing various metal sulfides, including manganese sulfide (MnS), iron sulfide (FeS), cobalt sulfide (CoS), nickel sulfide (NiS), copper sulfide (CuS), zinc sulfide (ZnS), silver sulfide (AgS), cadmium sulfide (CdS), tungsten sulfide (WS), tin sulfide (SnS), lead sulfide (PbS), and molybdenum disulfide (MoS₂). It highlights the significance of metal sulfide nanoparticles in addressing contemporary challenges such as environmental contamination and sustainable energy storage needs, driven by population growth, industrialization, and urbanization.

The review emphasizes the diverse applications of metal sulfide nanoparticles in fields like health, biology, environmental remediation, and energy generation and storage. It underscores their optical properties, high specific capacitance, photocatalytic abilities, and light-absorbing capacities, which make them promising candidates for various technological advancements.

Furthermore, the review discusses recent advancements in utilizing metal sulfide nanoparticles as electrode materials for solar cells, supercapacitors, and ion batteries, including those based on lithium, sodium, potassium, and magnesium. It also explores their capabilities in gas and chemical sensing, electrocatalysis for oxygen and hydrogen evolution, and remediation of polluted areas when employed as catalysts or photocatalysts.

A unique aspect of this review is its focus on identifying cost-effective methods for mass-producing highquality metal sulfides, heterogeneous structures, and composites. It discusses effective physiochemical and biological approaches employed in the production process to control the structures, dimensions, and compositions of these sulfides, aiming to unlock their full potential for various applications.

Overall, this review provides valuable insights into the current state of research on metal sulfide nanoparticles and their diverse applications, offering a comprehensive overview of their synthesis methods, properties, and potential implications across different fields.

2 Metal-sulfide classification

MSs can be classified based on the number of metal elements they contain, leading to alternate names such as ternary (e.g., ZnIn₂S₄, CuInS₂) and binary (e.g., AgS, CuS), or polymer (e.g., Cu₂ZnSnS₄). These materials may feature sulfide 3D electrons, which can either be confined or migratory, or even both. The stability of the cation of the nearest neighbor is upheld by sulfide 3s and 3p orbitals, in conjunction with various forms of anion arrays such as trigonal, octahedral, and tetrahedral. These arrangements facilitate the formation of covalent bonds between metals (M-M) and sulfur (S-S). The interaction between layered sheet formations is reinforced by enhanced polarization and covalency, mediated through van der Waals interactions. MSs are typically composed of atomic configurations, ionic sizes, and charges, which form various close-packing combinations.

Several sulfur-containing nanoscale structures, such as metal sulfides, lithium sulfide materials, sulfur-containing organosilicon compounds, sulfur-containing quantum dots, have been documented.²⁵⁻²⁸ Figure 1 demonstrates the growing global research interest in many nanomaterials, elements such as manganese, iron, copper, zinc, molybdenum, silver, lead, zinc, and WS.

3 Applications in synthesis, biomedicine, the environment, and energy

3.1 Manganese sulfide (MnS)

The electrochemical and magneto-optical characteristics of manganese sulfide (MnS) are unique, and it has been successfully synthesized in a variety of morphologies, including NPs, spherical, NR, nanotube, nanosheet, microfiber, and nanoflakes. 29-32 There are three different polymorphic forms of manganese sulfate: α-MnS, the one with the rock salt framework, the one with the zinc blende framework, and the one with the spherite and the quartz arrangement, γ-MnS. Among these compounds, α-MnS is the most stable across a wide range of ambient temperatures and pressures, instead β-MnS and y-MnS need specific conditions in the lab to be manufactured.^{33–38} Molten salts can be made in several different ways. Still, the most common ones are chemical pathways, as well as the thermolysis process, chemical-based bath accumulation, solgel synthesis, hydrothermal processes, solvothermal processes, and wet chemical methods. 39,40 A combination of the α-MnS phase's polymorphism, thermodynamic stability, and plentiful and inexpensive manganese makes it an

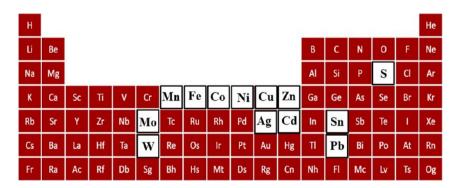


Figure 1: MS synthesis chemical.

attractive candidate for energy storage applications. A1-43 However, due to its poor cycling efficiency, it is not suitable to be employed as an electrode material in supercapacitors and low inherent electrical conductivity. Investigators have mostly focused on studying the electrochemical characteristics of the α -MnS transition in lithium-ion batteries and supercapacitors, rather than γ -MnS and associated combined stages. This choice is because γ -MnS has better electrical conductivity than other materials. This is because its layered Wurtzite structure makes it easier for electrolytes to penetrate and ions to intercalate and deintercalated.

Table 1 and Figure 2 highlight the extensive efforts of various research groups in controlling synthesis methods to achieve desired morphologies, crystalline phases, and applications of MnS nanosheets (NSs). Table 1 illustrates the diverse uses of MnS in recent studies. Investigations have focused on applications such as supercapacitors, which exhibit an energy storage capability of 91 Wh kg $^{-1}$ at 7.78 kW kg $^{-1}$, lithium-ion batteries with an energy capacity of 495 mAh g $^{-1}$ at 2000 mA g $^{-1}$, drug removal with an efficiency of 80 %, and the degradation of malachite green oxalate dye, achieving a breakdown rate of 56 %.

Table 1: A recent research investigation delved into the synthesis of manganese sulfide (MnS), exploring its formation, crystal structure, particle dimensions, and potential applications.⁵⁴⁻⁶⁷

Materials	Precursors	Synthesis techniques	Crystal structure	Morphology	Applications
MnS films	(CH ₃ COO) ₂ , (CH ₃ CSNH ₂), (C ₆ H ₅ Na ₃ O ₇), (NH ₃ /NH ₄ Cl)	Chemical deposition	Hexagonal	36	
MnS ₂	C ₄ H ₆ MnO ₄ CH ₃ CSNH ₂	Solvothermal			Electrochemical detection of cortisol in bio-fluids e.g., human serum, urine, and milk
MnS NSs	C ₄ H ₆ MnO ₄	Thermolysis	Hexagonal		
MnS NPs		Plasma evaporation			Li-ion storage with capacities 705, 684, 643, 578, and 495 mAh g^{-1} at current densities 100, 200, 500, 1000, 2000 mA g^{-1}
MnS NPs	MnCl ₂ ·4H ₂ O Na ₂ S (CH ₂ OH) ₂	Solvothermal	Hexagonal		
Nanosheets	Tu MnCl ₂ ·4H ₂ O	Hydrothermal	Hexagonal		Photocatalytic degradation of (MV, MG, MB and RhB) dyes. In batteries electrochemical discharge at voltage 0.2–3.2 V
MnS NPs	$MnCl_2 \cdot 4H_2O$ $Na_2S \cdot nH_2O$	Solvothermal			Photovoltaic thin film solar cells
Microspheres 2018s	Wurtzite				Magnetic resonance imaging with a coercivity of 3320 Oe and magnetization 17 emu g ⁻¹
Nanoflakes	[Mn(EN) ₃] ² CS ₂	Hydrothermal			
	MnCl ₂ ·4H ₂ O Na ₂ S·9H ₂ O	Hydrothermal			Supercapacitor demonstrated.

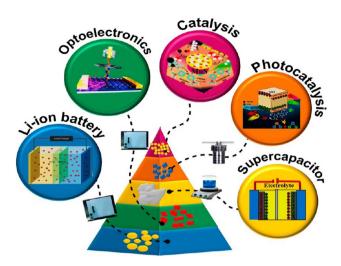


Figure 2: Diagram showing MnS production methods, morphologies, and applications. Permission to reproduce references.^{68–70} 2018, 2019, and 2020 copyrights.

3.2 Iron sulfide

Various phases of FeS exist with Fe:S ratios ranging from 0.5 to 1.05, encompassing minerals such as marcasite, troilite, mackinawite, pyrrhotite, smythite, and greigite. The Fe:S proportions for these phases are as follows: pyrite, marcasite, troilite, smythite, greigite, hexagonal-Fe₃S₄, smythite, and greigite-Fe₃S₄. The electrical and magnetic properties of iron sulfide minerals are influenced by both their crystal morphology and the stoichiometric balance of iron to sulfur.⁷¹ Concerning magnetic characteristics, naturally occurring

FeS crystals include electromagnetically active pyrite and marcasite, ferromagnetic greigite and pyrrhotite, paramagnetic mackinawite, and antiferromagnetic troilite.⁷²

Due to its diverse array of beneficial electrical, magnetic, and optical characteristics, iron chalcogenide (FeS) has attracted considerable attention from researchers across multiple fields. Exciting advancements have been made in various applications, including medicine, environmental remediation, energy storage (such as in solar cells and lithium-ion batteries), and catalysis. Particularly noteworthy is its role in addressing soil and groundwater pollution caused by both organic compounds like trichloroethene and tetrachloroethene, as well as inorganic contaminants like uranium, chromium, selenite (Se-IV), and mercury.⁷³

Under reduced and anoxic conditions, FeS maintains its thermodynamic stability. It is typically synthesized through coprecipitation in oxygen-depleted water. Pyrite FeS2, prevalent across vast regions of the Earth's surface, is valued as a low-cost mercury adsorbent due to its abundance and high surface reactivity. However, natural FeS2, characterized by its dense structure, exhibits limited mercury absorption capacity, achieving rates of less than 42 % at temperatures ranging from 40 to 100 °C. FeS2 synthesized via solvothermal methods demonstrates optimal performance only within the temperature range of 60–100 °C. Subjecting pyrite FeS2 nanospheres to a brief heat treatment at 500 °C can transform them into hexagonal FeS nanosheets.

Researchers are currently focusing on using FeS nanosheets by physiochemical synthesis methods, which lead to various shapes and crystal morphology, as described in Table 2

 Table 2: Recent FeS fabrication research involves structure, crystal structure, particle dimensions, and uses.

Materials	Precursors	Synthetic techniques	Crystal structures	Morphology	Applications
FeS ₂ NRs 2022		Molten salt		1	Removal of Hg efficiency (96.2 %)
FeS NPs	FeSO ₄ ·7H ₂ O and Na ₂ S FeSO ₄ ·7H ₂ O and Na ₂ S				
FeS ₂ NRs					
FeS ₂ NPs 2021	FeCl ₃ .6H ₂ O SC(NH ₂) ₂	Polyol/coprecipitation			
FeS NPs	FeCl ₃ ·6H ₂ O Na ₂ S· <i>x</i> H ₂ O				

Table 2: (continued)

Materials	Precursors	Synthetic techniques	Crystal structures	Morphology	Applications
FeS NPs	(NO ₃) ₃ ·9H ₂ O C ₄ H ₄ Na ₂ O ₆ · 2H ₂ O		Tetragonal		
		Chemical reduction			
FeS ₂ NPs 2020	FeCI ₃ ·6H ₂ O, C ₃ H ₃ NaO ₂ Na ₃ C ₆ H ₅ O ₇				Biosensing application for detection of H_2O_2 and glutathione
FeS ₂ Nanowire	(NO ₃) ₃ ·9H ₂ O CH ₄ N ₂ S				Remediation
FeS ₂ nanosheets (NS) 2020	FeCI ₃ and sulfur	.1		M. K.	Pseudocapacitive sodium storage with capacity 391 mAh g ⁻¹ at current density 10 Ag ⁻¹
FeS ₂ Nanosphere 2018	FeSO ₄ ·7H ₂ O CH ₄ N ₂ S	Solvothermal	Hexagonal		Solar absorber
FeS ₂ thin film	FeSO ₄ ·7H ₂ O		Electrochemical deposition		Photovoltaic application with superior catalytic and photocurrent properties

and Figure 3. FeS_2 nanoparticles have been fabricated for diverse purposes using several synthesis processes, fluid-phase removal, solvothermal processes, and molten salt extraction, as shown in recent works. It is incredible how well these

applications work. For example, they remove mercury 96.2 % of the time, store 391 mAs of electricity in a gram at a current density of 10 A per g, and store 900 mAs of electricity in a gram at a current density of 0.1 A per g, as shown in Table 2.

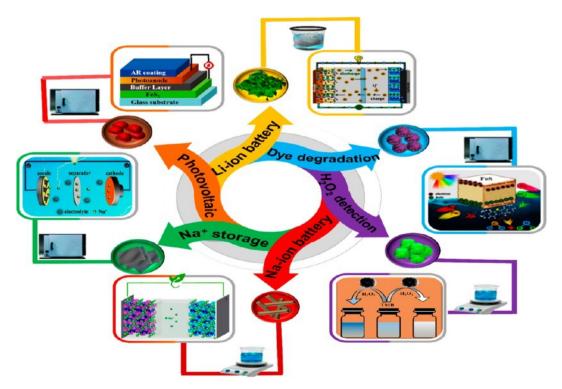


Figure 3: Illustrates graphical representations of FeS synthesis routes and their resulting morphologies tailored for various applications. Permission has been obtained to reproduce content from references, ^{76,79,85–87} copyrighted in 2020, 2020, 2020, 2018, and 2018, respectively.

3.3 Cobalt sulfide

CoS belongs to a group of II–IV semiconductor materials, which can exist in various stoichiometric compositions and phases, including CoS₂, CoS, Co₂S₃, Co₉S₈, Co₃S₄, Co₄S₃, and Co_{1-x}S. Synthesis methods have yielded diverse morphologies of CoS, such as nanotubes, nanowires, and hollow spheres. Factors like temperature, reaction duration, and reactant concentrations significantly influence the shape and size distribution of these particles in the samples.^{88–102} Structural materials prone to corrosion may exhibit two crystalline forms, cubic and hexagonal. Introducing sulfide, produced by bacteria through sulfate reduction or from inorganic sources, is a promising approach to manage heavy metals like cobalt (Co) in lowoxygen environments. Metal sulfides (MSs) formed by the rapid reaction of sulfide with metal cations are insoluble precipitates, enhancing the sequestration of aqueous metal cations, especially in nanoparticle (NP) synthesis, due to the significantly lower solubility of MSs in anaerobic to subtoxic conditions. 103,104 The sulfidic waters of early Earth may have naturally facilitated this process, potentially impacting life development by limiting cobalt supply. 105,106 Cobalt sulfides (CoS) attract considerable interest for their unique chemical, electrical, physical, and optical properties, finding applications in electrochemical supercapacitors, solar energy devices, ultrahigh-density magnetic recording, hydrodesulfurization and dehydrodearomatization catalysts, and lithium-ion batteries. Among various stoichiometries, Co₉S₈ is a frequently studied transition metal chalcogenide with potential in battery and supercapacitor technologies. However, its mechanical stability

and poor electrical conductivity currently limit its use as an energy storage device. 93,107

Table 3 and Figure 4 provide comprehensive insights into the various structures, stages of crystallization, and applications of CoS nanomaterials, showcasing diverse manufacturing techniques. In a recent study, CoS nanosheets (NSs) were extensively utilized in supercapacitors, demonstrating remarkable performance with a specific capacitance of 1072 Fg⁻¹ at a scan rate of 100 mV/s. These nanosheets also exhibit promising applications in Na-ion storage, achieving a capacity of 705 mAh g⁻¹ at a current density of 0.2 Ag⁻¹. Additionally, Table 3 highlights the successful synthesis of CoS, Co₉S₈, and CoS_{1.97} nanosheets through combustion methods, which proved highly effective in degrading methylene blue (MB) dve with an efficiency of 89.5 %.

3.4 Nickel sulfide

Nickel sulfide (NiS) may be found in many forms, including α-NiS and β-NiS, NiS₂, Ni₃S₄, Ni₃S₂, Ni₇S₆, and Ni₉S₈. The development of various phases of NiS is greatly influenced by factors such as reaction temperature, duration, quantity of reagents, and pH level. 119 One of the primary phases is rhombohedral β-NiS at low temperatures, while the other is hexagonal α-NiS at high temperatures. According to reference¹²⁰, the α-NiS undergoes a phase change at a temperature of 282 °C. There are several applications for the various NiS phases; for example, Ni₃S₂ conductors have the potential

Table 3: Recent research explored CoS production, structure, crystalline structure, dimensions of particles, and uses. 108-116

Materials	Precursors	Synthetic techniques	Crystal structures	Morphology	Applications
Cobalt	Co(NO ₃) ₂ ·6H ₂ O CH ₄ N ₂ S and glycine	Combustion method			MB dye degradation
CoS nanocrystal 2019	Cobalt chloride sulfanilamide	Hydrothermal			Supercapacitors with capacity 1072 Fg ⁻¹ and retention of 1000 cycles at 100 mV/S
CoS hollow struc- ture 2019	ZIF-67 nano cubes, ethanol, deionized water, Na ₂ S	Reflux reaction			Li/S batteries
Co ₃ S ₄ nanosheets 2018	Lamellar CO₃S₄/TETA	Plasma inducing dry exfoliation.	93333 9333 2033	4	Hydrogen evolution performance at overpotential 18 mV and 63 mV for 10 mA cm ² .
CoS ₂ NPs 2017	CO ₆ Al ₂ CO ₃ ·4H ₂ O	Hydrothermal			Electrochemical supercapacitors as specific capacitance 507 Fg ⁻¹ at scan rate 5 mVs ⁻¹

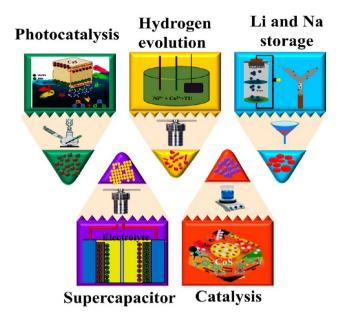


Figure 4: Illustrate the synthesis pathways of CoS, the structures of matter and their uses. Reproduced with authorization from. ^{68,117,118} 2020–2019–2017 copyrights.

to enhance the performance of sodium-ion rechargeable batteries, sensors, storage devices, and thermoelectric appliances, while fluorescence devices and hydrogen evolution reactions can make use of NiS₂. ¹²¹ There are two main phases of NiS₂: the triclinic stages are used in the processes of producing hydrogen through photocatalytic processes and supercapacitors, while the cubic phase is more effective in

HER. Additionally, in a basic solution, NiS_2 may effectively function as a catalyst for HER in water splitting. More precisely, structures with a pentlandite-type composition (Ni_9S_8) have shown superior performance in the hydrogen evolution process, because of their inherently high conductivity. 123

Several fabrication techniques, including microwave, solvothermal, hot injection, and hydrothermal methods, have been investigated to achieve precise synthesis of different phases of NiS. 119 These methods result in NiS with unique properties attributed to characteristics such as high durability, low resistivity (approximately $1.2\times10^{-4}\,\Omega$ cm), excellent dye adsorption capabilities, affordability, abundant availability, electrostatic forces, hydrogen bonding, surface/pore diffusion, coordination effects, and hydrophobic interactions. Various industries, particularly those involved in electrocatalytic water splitting, manufacturing dye-sensitized solar cells, water treatment, and production of electrical energy storage devices like batteries and Li/Na/K ion batteries, have shown significant interest in NiS. $^{84,124-127}$

Table 4 and Figure 5 document the utilization of NiS nanoparticles across various applications, emphasizing the production methodologies enabling precise control over their phases and morphologies. Recent research, as depicted in Table 4, illustrates how NiS nanomaterials can enhance the electrochemical performance of Na/K ion batteries. At current densities of $0.2\,\mathrm{Ag}^{-1}$ and $100\,\mathrm{Ag}^{-1}$, they exhibit capacities of 610 and 154 mAh g^{-1} , respectively. Additionally,

Table 4: Recent studies have focused on the production of NiS isotopes, as well as exploring their structure, crystallization system, particle dimensions, and applications. 119,121,123–125,127–135

Materials	Precursors	Synthetic techniques	Crystal structures	Morphology	Applications
NIS NPs	(Ni (SO) ₄) ₂ H ₂ O		Hexagonal		Catalytic and photovoltaic activities
Mesopores Nis NPs	Acetate tetrahydrate and thioacetamide	Solvothermal		8380	Photothermal chemotherapy of cancer
NiS nanomaterial	Nickel acetate tetrahydrate, gluta- thione and thioacetamide				Removal of methylene blue and crystal violet with adsorption capacity
NiS microtubes	NiCl ₂ ·6H ₂ O thiourea and polyvinylpyrrolidone	0 0		1	Water disinfection and cold cathode emission
NiS NPs	Ni (NO ₃) ₂ ·6H ₂ O CH ₄ N ₂ S	Solvothermal	Rhombohedral	(6)	

Table 4: (continued)

Materials	Precursors	Synthetic techniques	Crystal structures	Morphology	Applications
Mesopores thin film NiS ₂ 2020	Dimensional	Soft templating			Hydrogen evolution
NiS nanoflower	NiCl ₂ ·6H ₂ O Acetic acid and acetamide	Solvothermal			Pseudocapacitive properties with capacitance 89.1 % at current density of 7.3 Ag ⁻¹
NIS NS					Oxygen evolution and supercapacitor with capacitances 1097 and 869 Fg ⁻¹ at current densities of 2 and 20 mA cm ²
NiS nanowire	Ni (NO ₃) ₂ ·6H ₂ O, sodium diethyldithiocarbamate hydrate and diethyldithiocarbamate	Vapor deposition			Electrochemical water oxidation with current density 500 mA cm ⁻² of potential 340 mV

these materials have demonstrated efficacy in substance extraction, with a mass extraction efficiency of 1946.61 mg per g, and in the production of supercapacitors, achieving a capacitance of 1745.50 F per g.

3.5 Copper sulfide

The stoichiometric compositions of CuxS, a P-type semiconducting material, may range from Cu₂S to CuS₂. ^{137,138} Other possible stoichiometric compositions are Cu_{1.94}S,

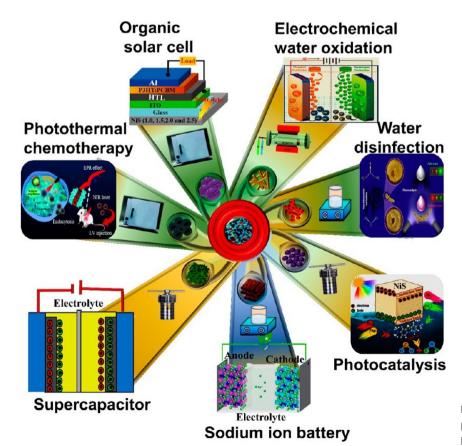


Figure 5: Diagram showing NiS manufacturing pathways, structures, and uses. Used with permission from. 68,85,130,133,135,136

Cu_{1.8}S, Cu_{1.75}S, CuS, and CuS₂. Depending on the copper concentration, the Eg of CuxS might vary between 1.2 and 2.2 eV. ¹³⁹ Because of its large band gap of 2.2 eV, CuS can soak up as much solar radiation as possible, regardless of its stoichiometric composition. 140,141 Because of its larger band gap and ability to absorb visible light, CuS is a fortunate material. 138,139,142 According to references, 143-147 CuS may take on a variety of forms, such as nanoparticles (NPs), nanorods (NRs), nano structures resembling flowers and spheres, nanowires, plates, belts, and nanoribbons. 448 Methods for synthesizing CuS are currently extensively documented, including chemical vapor deposition, template-assisted growth, hydrothermal treatment, sol-gel synthesis, solvothermal processes, microwave use, and polyol methods. 149,150 Among the many uses for CuS as a photocatalyst are in photovoltaics, optical filters, photoelectric devices, chemical sensors, thermoelectric cooling materials, photoelectric devices, photoelectric devices, liquid batteries, 151-153 and photoelectric devices. 154 A possible stumbling block for solar light-prompted photocatalysis, CuS is nontoxic, has excellent photosensitivity, great physical and chemical stability, and is inexpensive. 155,156 As a disinfectant for medical therapies, CuS is the main since it is harmless to human cells and has great antibacterial properties. 157 The large specific capacity (560 mAh g⁻¹) of CuS makes it an excellent cathode material for rechargeable Mg batteries, which leads to remarkable electrical properties. 158,159 Typically, the reversible capacity of CuS is lower than its real value at ordinary temperature because Mg²⁺ is trapped in the host material. 160 As a result of a scalable technique based on two factors, CuS is also used in sodium ion batteries. The present collector regards Cu as an intimate substance first and foremost, which is a key component of batteries. Additionally, sulfur reacts strongly with several transition metals, copper specifically. At 80 °C. CuS was consistently produced on a Cu current collector. 161 Electrodes made of CuS are utilized in lithium-ion batteries due to the material's outstanding ability to conduct electricity. 162,163 Thorough discussion was captivated by the CuS plasmonic property.¹⁶⁴ The vacancies are often caused by inadequate filling of sulfur's 3p orbitals, which happens when copper is scarce and belongs to the non-stoichiometric class. Because of the free holes created by the vacancies, pure, self-doped CuS may conduct electricity. There are more carriers of electricity as the compound's copper content drops, reaching higher concentrations of carriers at around 1020–1021 cm⁻³. The particular structure determines whether the covellite CuS has an abnormally high number of holes, up to 1022 cm⁻³. Covellite CuS has inherent high-extremity hole delocalization and a distinct anisotropic metallic conductivity. 165 Of all the semiconductor

photothermal brokers. CuS has been the most extensively researched. 166,167 Nanomagnets derived from copper show a strong photothermal seguel for the targeted removal of tumors when exposed to near-infrared laser light. 168-170 The majority of these CuS-based NSs often include polymers (polyvinylpyrrolidone, or PVP), oleyl amine, sodium citrate, or PEGDMA-based gel¹⁷¹ attached to their surfaces as ligands. Although these CuS nano agents coated with organic molecules or polymers disperse readily in water, their presence in biological fluids does not endure. As a result, improving the biocompatibility and stability of CuS-based NSs using an ecofriendly, straightforward manufacturing method with superior ligands is crucial.¹⁷²

Several research organizations have dedicated substantial resources to obtaining specific shapes, crystal structures, and uses for CuS NSs produced using various synthesis methods, as seen in Table 5 and Figure 6. Table 5 displays literature that shows whether CuS NSs are used in Mg/Na/Li-ion batteries, with 100 Ag⁻¹, 350 mAh g⁻¹, and 300 mAh g⁻¹ functions, correspondingly. The decomposition of various colorants, such as the green color of malachite, the orange color of methyl, safranin O, and rhodamine B, has been accomplished using CuS nanomaterials. The corresponding clearance rates were 95.5 %, 99–100 %, 80.53 %, and 83.22–99 %. In addition, a remarkable 47 % productivity was achieved in the radiation treatment of tumors using CuS quantum dots (QDs) that were green synthesized.

3.6 Zinc sulfide

ZnS is a compound made up of transition metals and semiconductors from the II–VI group. Its band gap approximates 3.7 eV, a short Bohr radius, and a significant excitation binding energy of 40 meV. 192-195 Multiple forms of ZnS, such as nanoparticles (NPs), nanowires, nanorods (NRs), nanoclusters, nanosheets, nanoflowers, hollow spheres, and nanotubes, have been created. 196-202 The shape of NPs is influenced by many parameters, including the choice of a zinc and sulfur precursor, reaction duration, and temperature, due to its notable characteristics such as non-toxicity and temperature regulation. There are two different crystalline forms of ZnS: wurtzite and zinc blender, the latter of which has an energy bandgap of 3.77 eV. Zinc blende's rectangular shape appears more persistent than wurtzite's hexagonal structure, since the latter is created at temperatures above 1000 °C. Various efforts have already been made 203-212 to track the shape and dimensions of the crystals in ZnS nanostructures. Various methodologies were used to create these

 Table 5: Current research on CuS synthesis, structure, crystalline system, particle dimensions, and its uses.

Materials	Precursors	Synthetic techniques	Crystal structures	Morphology	Applications
CuS NPs 2021	C ₁₈ H ₃₅ NH ₂ /1-octadecene C ₁₈ H ₃₆ , copper nitrate		Hexagonal	2 (.)	
CuS QDs 2019	Cupper chloride dehydrates, sodium sulfide hydrates, chitosan, folic acid		Hexagonal		Photothermal therapy of tumor efficiency 47 %
CuS Ns 2021	Cupric		Hexagonal		
CuS NRs 2019	Cobalt chloride and thiourea		Hexagonal		In optoelectronic devices with energy band gap in visible region
CuS nanosheets 2020	Thioacetamide		Hexagonal	SPA	
CuS Nps 2019			Hexagonal		
CuS Nps 2019	Sulfur powder, current collector		Hexagonal	Sodium-ion batteries with ultrahigh rate capability 100 Ag ⁻¹	
CuS hollow micro flower 2018	Ionic liquids 1-butyl- 3-methylimidazolium chloride, copper chloride dehydrates and thioacetamide.		Hexagonal	Asymmetric supercapacitor exhibited energy density 15.97 Wh kg^{-1} power density 185.4 W kg^{-1}	
CuS NPL 2019	Cu (NO ₃) ₂ ·3H ₂ O, thiourea and NiCl ₂ · 6H ₂ O		Hexagonal		
CuS nano- spheres 2019			Hexagonal	W.C	
CuS NPs 2017	Copper acetate and sodium sulfide		Hexagonal		

structures, such as hydrothermal, template route, ultrasonic, template-free, solid–liquid reaction, solvothermal, coprecipitation, and electrospray pyrolysis. ^{213–220} Compared to bulk, ZnS NPs have several desirable characteristics, such as (a) Intense light absorption, (b) an increased ratio of surface area to volume, (c) optical tunnelling's little impact, and (d) a lower melting point due to outstanding properties like nontoxicity and thermal stability. Among the many fields where ZnS finds

use are photocatalytic wastewater treatment, sensors for gases, photoelectric components, SSCs, photovoltaic window coverings, FET, light-emitting diodes, solar cells, and electroluminescent devices. 199,221–226

Table 6 and Figure 7 describe certain synthesis approaches for monitoring the shape and dimension of the crystals in ZnS NSs, along with their relevant applications. According to recent investigations (Table 6), ZnS NPs

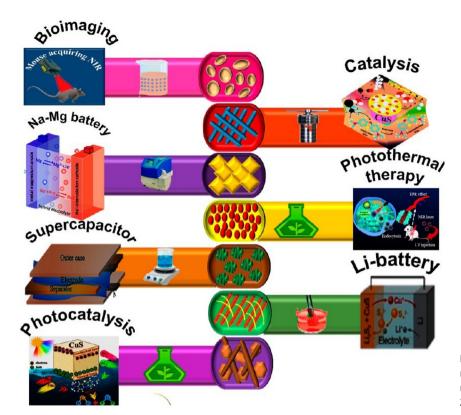


Figure 6: Diagram showing CuS synthesis methods, structures, and uses. Permission to reproduce provided. ^{133,188–191} 2020, 2018, 2008, 2019, and 2022 reproduction rights.

produced using the Sono chemical approach had an efficiency of 86.36 % for blue 14 degradation, whereas those synthesized using the hydrothermal method had an efficiency of 100 %. More than that, ZnS NPs have degraded MB, the elimination rates of mety orange at 75 %, blue 21 at 100 %, and cyano blue at 75 %.

3.7 Molybdenum disulfide

Many ground-breaking innovations have been made possible by the exceptional electrical and physical characteristics of 2D materials.²⁴⁵ 2D materials' exceptional properties might revolutionize several industries, examples of which are batteries for storing energy and electronic technology.²⁴⁶⁻²⁴⁸ Stretching these 2-D substances across their entire region gives compounds precisely thick layers, that in turn renders them sensitive to forces of gravity, gives molecules a lot of room to interact with one another, and affects quantum confinement. The impact was caused by unexpected features that set these materials apart from their 3D equivalents. 249-251 More and more applications for MoS₂ have emerged in fields such as electrochemistry, solid lubricants, capacitors, catalysis, hydrogen storage, and electrochemical devices. The primary rationale for such applications is the sheet-like framework, which takes use of the enormous surface area of

intermediate double-layer storage, the high intrinsic and rapid ion conductivity, and the weak van der Waals interactions in the sandwich layers, which enable nanoparticles to split from the outermost layer of the layers. With a 0.62 nm interlayer spacing and mainly covalent MoS2 bonds, the material is highly conductive. When molybdenum is in an oxidation state between +2 and +6, it shows a faradic capacitance, which means it can store more energy. When stacked with MoS₂ sections, the loss of capability, specific capacitance, and conductivity for electricity was less severe than with carbon materials. To overcome these limitations, researchers have created several nanocomposites that combine MoS₂ with conductive polymer to get better electrochemical characteristics. 252,253 The electrode materials' capacitance and cycle life were enhanced because of the complementary actions of the MoS₂ nanosheet's contact with the CFC at the interface. Because the produced materials have a fast charge transfer rate and a low polarization resistance value, the electrode capacitance is quite high. Energy storage systems may use MoS₂ nanospheres as electrode materials. 1-3 Rechargeable Liion batteries may employ MoS2 as an electrode material because of its layered structure and its substantial theoretical capacity of 670 mAh g⁻¹ that comes through the 4 electrons transfer process upon discharging. This exceeds the most common graphite material by 1.8 times, with 372 mAh g⁻¹. According to the estimated redox potential, MoS2 has an

 Table 6:
 Latest research on ZnS production, structure, crystallization framework, dimension of particles, and uses.

Materials	Materials Precursor	Synthesis techniques	Crystal structure	Morphology	Morphology Applications	MnS MSs morphology	Precursor	Synthesis technique	Crystal structure	Morphology	Morphology Applications
		Chemical bath			Photocatalysis with 63–75 % efficiency	ZnS NPs		Chemical reaction	Wurtzite		Potential applications in nonlinear optics
ZnS NPs	Zinc acetate					ZnS NPs			X		Efficiency photocatalysis against methyl orange shows 75 %
ZnS NPs	Zinc acetate, Na ₂ S	Microwave assisted				ZnS NPs	Polyethylene gly- col, ZnSO ₄ ·7H ₂ O	Chemical reaction	X	0	
ZnS NPs	Zn (CH ₃ COO) ₂ 2H ₂ O SC (NH ₂) ₂		×	3		ZnS NPs	Zn (CH ₃ COO) ₂ 2H ₂ O	Wet chemical	X		Optical devices
ZnS NPs	Zn (CH ₃ COO) ₂ 2H ₂ O ethanol				Optoelectronics due to its large band gap	ZnS NPs	Zn(NO ₃) ₂ ·6H ₂ O C ₂ H ₅ NS		X		Photo catalytic activity against reactive effi- ciency 100 %
ZnS NPs		Sol-gel precipitation		Marie Street	Anti-bacterial	ZnS NPs	Zinc acetate dihy- drate and sodium sulfide	Sonochemical	X		Photocatalytic degrada- tion against direct blue 14 shows 86.36 %



Figure 7: Diagram showing ZnS production methods, structures, and uses. Permission from. ^{70,191,243,244} 2019–2022, 2020, and 2013.

electrical conductivity of $10^{-4}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ versus Li+/Li. When using nanosized MoS $_2$ to avoid problems, it is important to note that the reaction volume increases by 107 % for the MoS $_2$ electrode and by 21.7 % for the cell reaction. ²⁵⁴

Both Table 7 and Figure 8 detail the most up to date MoS_2 morphologies and phases that have been synthesized utilizing various techniques, along with their respective applications. Table 2 shows the current state of the art in preparing MoS_2 nanosheets. Different synthesis routes, techniques that include exfoliation, liquid phase exfoliation, and microwaves have found usage in a range of contexts. Among them, one may find a 98 % reduction in dye rate in supercapacitors operating at 0.5 Ag^{-1} per unit of current, and a different one in Li-ion batteries with a capacity of 439 mAh g^{-1} .

3.8 Silver sulfide

Many other chemical processes, such as microwave, waterphase, hydrothermal treatment, thermal breakdown, conjugation, and opposite microemulsion manufacturing, have

Table 7: Current research on MoS₂ production, structure, crystallization system, dimensions of particles, and their uses.^{253–263}

Materials	Precursors	Synthesis techniques	Crystal structure	Morphology	Applications
	Sodium oxalic acid	Microwave-assisted.	Rhombohedral		Super-capacitors with high specific capacitance of 348 F/g at 0.5 A/g
MoS ₂ -SDS	Molybdate disulfide powder, sodium dodecyl sulfate		Rhombohedral		Photo-catalytic dye degradation (efficiency 91.84 %) and dye-sensitized solar cell
MoS ₂ nanosheets	Molybdenum disulfide, boron nitride, hydrazine hydrate and sodium	Liquid phase- exfoliation	Hexagonal		Dye degradation (efficiency 98 %) and antibacterial behavior.
1T-MoS ₂ 2H-MoS ₂ NF-2021		Solvothermal Combustion			Anti-bacterial activity
MoS ₂ 2020	Polystyrene microspheres, sodium molybdate, thiourea, polyvinyl pyrrolidone			C	NO ₂ gas sensors
MoS ₂ nanosheets	NaBr, KBr Bulk MoS ₂			A.	Super-capacitors with capacitance 76 ${\rm Fg^{-1}}$ at 5 mVs $^{-1}$ with an aerial capacitance of 58.5 mF/cm $^{-2}$



Figure 8: Diagram showing MoS₂ synthesis pathways, structures, and uses. Permission to reproduce. 254,256,264-269 The copyrights are valid for the years 2019, 2021, 2020, 2016, 2018, and 2020.

been used to produce Ag₂S nanomaterials.^{270,271} In the presence of organic ligands, Ag₂S quantum dots (QDs) typically undergo physical and chemical transformations into their hydrophobic inorganic phase; the stage of transformation has practical uses in the biomedical field throughout the NIR and IR wavelength ranges. 272,273 Additionally, colloidal Ag₂S NPs were created using synthesis of green method with the use of water-based extracts from various plant parts (for instance, rhizomes, vegetables, seeds, and stems) and macronutrientcontaining albumins or royal ielly as stabilizing agents.²⁷⁴ The chemical element Ag₂S may undergo three different polymorphic changes: acanthine, a body-centered cubic (bcc) superionic phase of β-Ag₂S called argentite, and sulfide, a facecentered cubic (fcc) phase of y-Ag₂S. These modifications occur at temperatures below 450 K, between 452 and 859 K, and approximately at 860 K, respectively. The Ag₂S compound exhibits a monoclinic crystal structure with a particle size less than 60 nm, as reported in reference.²⁷⁵ Bioimaging, cancer photothermal therapy, food packaging, solar cells, and photocatalysis are just a few of the many areas that benefit from this material's unique combination of near-infrared (NIR) emission, antimicrobial qualities, high quantum yield, efficient photothermal conversion, chemical stability, outstanding photostability, narrow bandgap energy (0.9-1.1 eV), high optical absorption coefficient, and lack of toxicity. 270,271

Recently, researchers have explored many important uses of distinct Ag₂S nanomaterials with varying structures, which

were synthesized using diverse methods. These findings are detailed in Table 8 and Figure 9. The study demonstrates that Ag₂S nanospheres (NSs) have been synthesized using different methods such as coprecipitation, precipitation, and green synthesis. These NSs have shown potential in various applications, containing properties that inhibit the growth of bacteria and fungi, with MIC values between 5 and 75 µg mL⁻¹ for bacteria and 80–310 µg mL⁻¹ for fungi. Additionally, they have exhibited a high efficiency of 58.6 % in cancer photothermal therapy. Furthermore, they have demonstrated bioimaging capabilities and efficiency in inhibiting the growth of both Gram-negative Escherichia coli and Gram-positive Bacillus thuringiensis (70 % and 90 %, respectively). Also, methyl green dye was removed, and a photodetector was used using Ag₂S nanoparticles made using a mix of sonochemical and microwave processes. When subjected to light with a wavelength of 550 nm and an intensity of 0.89 mW cm⁻², the photodetector had a response of 2723.2–4146.0 A W⁻¹. The nanoparticles also achieved a degradation efficiency of 99 % in the removal of methyl green dye.

3.9 Cadmium sulfide

Material having three dimensions less than a nanometer and a diameter of a few nanometers, like that of a molecule, is called a nanoparticle. 286 The optical characteristics, size, and

 Table 8:
 Recent research on Ag₂S synthesis, structure, crystallization framework, dimensions of particles, and uses.

Materials	Precursors	Synthesis techniques	Crystal structure	Morphology	Applications
Ag ₂ S QDs 2022	Silver nitrate, sodium	Thermal	Monoclinic		
Ag₂S QDs 2022	AgNO ₃ , Na ₂ S-9H ₂ O			.0.	Antibacterial and antifungal activities
Ag ₂ S QDs 2022					
Ag ₂ S NPs 2022	Ag/AgCl Na ₂ SO ₄				Electrochemical monitoring nitrite in food potential with sensitivity of 0.05 uA umol $\rm L^{-1}\ cm^{-2}$
Ag ₂ S QDs 2021					Bio-imaging of Hela cells with promising compatibility
Ag ₂ S QDs 2021	Diphenyl tetra zoilum bromide, glutathione	Aqueous precipitation	Mono clinic		Photo-thermal therapy with photo thermal conversion efficiency 58.6 %
Ag ₂ S NPs 2021	AgNO ₃ and polyvinylpyrrolidone			E	
Ag ₂ S QDs 2018	Trioctyl phosphine		Monoclinic		Photovoltaic performance with power conversion efficiency 0.1 % at current density 0.62 mA/cm ²
Ag ₂ S NPs 2020	AgNO ₃ , Na ₂ S Pleurotus Ostreatus mycelium			9.4	Bioimaging/Antibacterial activity against –ve <i>E. coli</i> (90 %) and + ve <i>thuringiensis</i> (70 %)
Ag ₂ S NPs 2020	AgNO ₃ and bay leaf extract				Inflammatory activity against drug acetyl salicylic acid
Ag ₂ S NPs 2020	AgNO ₃ ·6H ₂ O Na ₂ S·6H ₂ O		Monoclinic		
Ag ₂ S NPs 2020	AgNO ₃ Na ₂ S	Microwave	Monoclinic		Degradation of methyl green dye UV and visible light with efficiency (99 %) and (62–85 %)
Ag ₂ S QDs 2019	AgNO₃ Na₂S				
Ag ₂ S NPs 2019	AgNO ₃ , Na ₂ S·9H ₂ O and rose- mary plant leaves				Antibacterial activity

structure of NSs sulfide and selenides, namely CdS, CdSe, ZnS, and ZnSe, have been the subject of a great deal of research.²⁸⁷ Typically, since they are easy to make in the

right size range, there is more focus on II–VI semiconductor NPs. The wide range of fields that have found uses for CdS – from photovoltaics and photodetectors to photocatalysts and



Figure 9: Diagrams showing Ag₂S production pathways, structures, and uses. By permission of. 191,271,277,279,280,284,285 Copyrights: 2022, 2021, 2020, 2020, 2018, and 2018.

nonlinear optical materials - as well as its antibacterial potential - transformed it into a very interesting straight bandgap semiconductor. 288-294 The crystal structure of CdS might be cubic, hexagonal, cubic, or deformed rock. With a value of 2.4 eV, CdS bulk semiconductors have a bandgap. ²⁹⁵ In solar cells, it acts as a layer that lets light in.²⁹⁶ Its n-type semi conductivity makes it a perfect match for heterojunction solar cells that use p-type materials.^{297,298} The photo-catalytic degradation of dyes may be facilitated by CdS NPs because of their wide surface area, strong oxygen

adsorption capabilities, rapidly recombining electron-hole pairs, and enhanced surface absorption of target molecules. Enhancement of CdS NPs photocatalytic activity via decreased hole-electron rearrangement and extremely effective light absorption is possible, depending on their crystal structure and band gap.²⁸⁷ Along with a more negative conduction band and apparent absorbance, CdS also has a lower reduction potential than H+/H₂.^{299,300} Table 9 and Figure 10 indicate that different phases and morphologies of CdS NSs, which were synthesized using different routes,

 Table 9: Recent CdS NS synthesis, structure, crystalline system, dimension of particle, and uses. Studies. 287,295,298,300-310

Materials	Precursors	Synthesis techniques	Crystal structure	Morphology	Applications
	Cadmium nitrate, nitric acid and acetamide	Co-precipitation			In photodetectors
	Cadmium acetate dehydrates, so- dium sulfide and 2 mercaptothion.	Chemical bath			Solar cell efficiency (1.15 %)
CdS NRs and cubes	Cadmium acetate, methanol, nickel chloride				Photocatalytic degradation efficiency 94 % for MO dye in 75 min
Spherical 2020		Solution	Hexagonal		Super-capacitors exhibited energy density of $8.4~\mathrm{Wh~kg^{-1}}$ power density of $7.56~\mathrm{kW~kg^{-1}}$ at current density of $20~\mathrm{Ag^{-1}}$

Table 9: (continued)

Materials	Precursors	Synthesis techniques	Crystal structure	Morphology	Applications
CdS 2020		Chemical solution	Hexagonal		Solar cells and hydrogen production via photo- electrical water splitting
		Pulsed laser ablation	Hexagonal	8	Anti-microbial activity
Needle shaped	Cadmium chloride monohydrate, thiourea, ammonium and triethanolamine		Hexagonal		
Spherical 2019	Cadmium chloride, thioglycolic acid		Hexagonal		Dye degradation
Spherical 2019	Cadmium chloride, Na ₂ S, 2-merceptoethano				Dye degradation
	Cadmium acetate and thiourea		Hexagonal	4	
	Cadmium acetate, sodium sulfide nanohydrate				In solar cell power conversion efficiency at 0.5 M upon Mn incorporation efficiency was 0.42
			Hexagonal		RhB dye degradation rate 78 %
Spherical 2018	Cadmium sulphide	Chemical	Hexagonal		In photovoltaic cells
Spherical 2017	Cadmium sulphide		Hexagonal		

were widely used in various applications. New studies have shown that CdS nanoparticles excel in a variety of uses, using the use of photocatalytic dye degradation, solar cells, and supercapacitors among others. Crystals of CdS NSs with hexagonal structures have been produced using sol gel. The

hydrothermal method was shown to be appropriate for degrading methyl orange by 94 % and RhB dye by 78 %. They demonstrated an efficiency of 1.15% in solar cells and a supercapacitor with an energy density of 8.4 Wh kg⁻¹ and a current density of 20 Ag⁻¹.

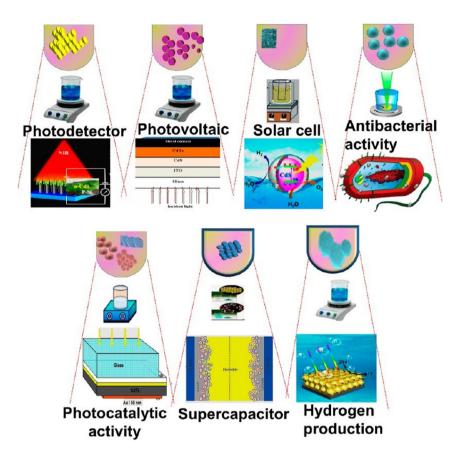


Figure 10: Diagram showing CdS production pathways, structures, and uses. Permission for a reproduction.^{311–316} Copyrights for 2021, 2013, 2018, 2016, 2020, and 2014.

3.10 Tungsten sulfide

Impressive electrical conductivity, exceptional catalytic activity, and great thermochemical stability are some of WS2's fascinating properties.317-319 Research on various WS2 morphologies has been thorough. 320–322 Chemical vapor deposition, sonication, and hydrothermal processes may all produce WS₂ in single or multiple layers. Catalytic activity toward H₂ generation is very high in both single and multilayer WS₂.^{323–326} Research has been conducted on WS₂ NPs, nanoflakes, and nanoflowers.³²⁷⁻³³¹ Several techniques for synthesis have been reported for NSs with desirable features, including biological compatibility, large surface area, effective photocatalyst, excellent electrochemical activity, benign technological properties, and high mobility.332-343 These methods include hydrothermal, sonochemical, solvothermal, ultrasonic spray pyrolysis, colloidal, chemical vapor deposition, and electrochemical approaches.

Figure 11 and Table 10 demonstrate the many synthesis pathways that have been devised in recent years to create CdS NSs with the necessary phases and morphologies for a range of applications. Photocatalytic activity was well-suited to WS2 nanosheets produced by a hydrothermal synthesis technique, which degraded the MB dye with 90 % efficiency. Also, supercapacitors made of hydrothermally prepared

WS₂ NPs with hexagonal and tetragonal structures may be used capacitance is 102.909 mAh g⁻¹ at 226.67 mF cm⁻², and the current density is 1 Ag⁻¹. The synthesis of WS₂ QDs and NRs, on one hand, and electrochemical detection of psychotropic compounds on the other, are two areas where these materials excel, was accomplished using ultrasonic, electrochemical, and sonochemical technique methods.

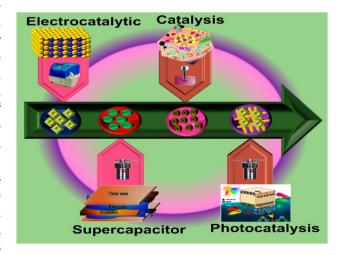


Figure 11: Diagram showing WS₂ manufacturing pathways, structures, and uses. Used with authorization by. 344,345 2016 and 2019 copyrights.

Table 10: Recent developments on WS₂ production, structure, crystallization system, dimensions of particles, and uses. 332-338,346-352

Materials	Precursors	Synthesis techniques	Crystal structure	Particles	Morphology	Applications
WS ₂ MSs			X	300 nm length		Photocatalytic degradation effi- ciency 90 % against MB dye
		Hydrothermal			0	Supercapacitor with capacity 102.909 mAh g ⁻¹ at current density 1 Ag
		Solvothermal		500-600 nm		Electrocatalytic activity exhibited low potential 172 mV at 10 mA cm ⁻²
		Ultrasound assisted (liquid phase exfoliation)	X		1	
		Horizontal reaction		20–150 nm diameter		Photocatalytic activity
				100 nm		
		r <mark>ad</mark> i		200 nm		
WS ₂ hollow sphere 2020	Tungsten chloride, thioacetamide	Hydrothermal	X	300 nm ⁻² um		Electrochemical activity
WS ₂ NRs 2019			Hexagonal	80–100 nm	3	Electrochemical detection of psychoactive drug
		Ultrasonic spray pyrolysis	Hexagonal	200–300 nm		
WS NSs 2018						Supercapacitor with specific capacitance 107.93 Fg ⁻¹
WS ₂ QDS 2017 WS ₂ powder, e	thanol II			5 nm		Catalytic activity
WS ₂ QDS 2017				118 nm		
WS ₂ , prop WS ₂ QDS 2017	oylene carbonate LiCLO $_4$		Hexagonal	3 nm		Photo electrochemical

3.11 Tin sulfide

Due to their strong light-harvesting capabilities and low band gap energy, there was extensive usage of Sn-based metal chalcogenides in optoelectronic devices.³⁵³ Tin sulfide (SnS) has strong anisotropic optoelectronic and mechanical properties, in addition to two band gaps, either direct or

indirect. According to publications, 354-356 the band gap energy of SnS may be found between 1.07 and 1.25 eV when measured indirectly, and between 1.30 and 1.39 eV when measured directly. In the UV, visible, and near-infrared parts of the spectrum, its absorption constants are quite high, exceeding 104 cm⁻¹.357,358 In addition, the materials used to make it are plentiful, inexpensive, and safe. 359,360 The

synthesis of WS2 from amphoteric SnS is a very significant development since WS₂ may, depending on the circumstances of production, conduct p-type or n-type currents. 361,362 Chalcogenide material SnS has garnered significant interest due to its possible uses in several industrial applications, the range of applications include photodetectors (such as photodiodes and photovoltaic cells), optoelectronic devices, solar cells, gas sensors, wastewater treatment, and biological applications. 363-367 Although there have been claims of the presence of cubic-structured SnS, in most cases, the material exhibits a van der Waals force structure that is orthogonal to the c-axis, which holds the orthorhombic layers together. 368,369 Because of its layered structure, which facilitates ion intercalation, SnS has good electrochemical characteristics (e.g., Na⁺ and Li⁺), and it is also an efficient layer for photovoltaic absorption.³⁵⁶ Therefore, SnS shows promise as an electrode material for electrochemical energy storage methods. Several researchers have used SnS as anode components for Li-ion batteries and as electrode components for supercapacitors.³⁷⁰ Thermal evaporation, chemical misting and immersion, radiofrequency (RF) sputtering and spin coating are some of the physical and chemical methods that may be used to create SnS thin films. 368,371-375 Loferski calculated the bandgap efficiency to be 24%, which was the theoretical limit for the SnS absorber's power conversion efficiencies (PCE). Thus, SnS has become the best alternative material for solar cells of the future. So far, 4.36 % PCE has been recorded for SnS solar cells.³⁷⁶ The chalcogenide NSs semiconductor SnS has a small electronic bandgap (Eg) of 1.3-1.6 eV, a high absorption coefficient, hole mobility, and is both inexpensive and non-toxic, making it one

of the most appealing choices for organic pollutant degradation. 377,378 Because of its narrow Eg, which covers the whole visible spectrum, light shorter than one thousand nanometers (nm) may be absorbed by SnS. But, particularly for industrial applications, there is a pressing need to enhance SnS's photocatalytic efficacy, which is currently limited because of photogenerated electron and hole recombination. An intriguing avenue to enhancing photocatalytic efficiency is the fabrication of SnS semiconductor-based nanocomposite with precious metals. This might lead to a boost in the reduction process and charge separation at the interface.³⁷⁹ Gas sensors based on 2D sulfide might potentially respond quickly because of the fast charge transfer that happens when gas molecules meet substrates.380,381

Due to the S atom's decreased electronegativity and increased ability to absorb atmospheric oxygen, gas sensors based on sulfide nanosheets can function at far lower temperatures than their oxides semiconductor-based counterparts.³⁸¹ The SnS-based sensor does not show much selectivity when exposed to gaseous VOCs at room temperature.³⁸² The gas-sensing capabilities of 2D semiconductors have been improved using many realistic methods, including doping, nanocomposites, and modification with precious metals. 383-385 To improve gas sensitivity, a simple and successful method is to dope with impurity atoms. 384-386 Additionally, it has been shown that 2D nano sheets may be kept from aggregating or stacking when a hierarchical framework is built.³⁸⁷ High gas sensing responses are often achieved by loose hierarchical structures with huge active surface areas for gas adsorption/ diffusion.³⁸² Table 11 and Figure 12 display several synthesis

 Table 11: Present research on SnS synthesis, structure, crystallization system, dimensions of particles, and uses.

Materials	Precursors	Synthesis techniques	Crystal structure	Morphology	Applications
Nanosheets with spherical particle 2022	Tin chloride salt, thiourea		Orthorhombic		Anti-bacterial activity
Cubic NPs	Oleic acid, oleylamine, tri- octylphosphine, SnCl ₂ ,	Conventional	Orthorhombic		Photo detector
	SnS powder, sulfur powder, argon and hydrogen		Orthorhombic		Photodetectors with high sensitivity, fast response speed and wide spectrum detection
Nano films	Sn and S	Thermal	Orthorhombic		Photo detectors with specific detectivity of 6.89×10^{30}

Table 11: (continued)

Materials	Precursors	Synthesis techniques	Crystal structure	Morphology	Applications
Nanoflakes	SnCl ₂ ·2H ₂ O Ethylene glycol, thiourea,	Solvothermal	Orthorhombic		Gas sensing
Nanosheets	SnCl ₂ ·2H ₂ O Thioacetamide, PVP	Microwave- assisted Thermal	Orthorhombic		Photo-detector with excellent opto- electronic stability reproducible photo- switching for 200 cycles
SnSe/SnS	SnCl₂·2H₂O Na₂S, NaOH, SnSe		Orthorhombic		Anti-microbial activity
SnS thin film	SLG-substare and Mo-coated soda-lime glass substrate	RF magnetron sputtering	Orthorhombic		In solar cell at pressure 2 Pa with highest power conversion efficiency 0.58 %
Ag–SnS spherical 2020	SnCl ₂ ·2H ₂ O HAD, TOP, sulfur, Ag		Orthorhombic		Photocatalytic efficiency enhanced with increasing the amount of Ag and 100 %
Nanosheets	SnCl₂·2H₂O Ethylene glycol	Solvothermal	Orthorhombic		Highly sensitive methanol
Thin film	Sodalime glass and Mo-coated SLG	Sputtering	Orthorhombic		In solar cells with power conversion efficiency of 0.38 % along Jse of 3.56 mA/cm² and FF of 50 %
Nanosheets	SnCl ₄ ·5H ₂ O and S powders	Chemical bath	Orthorhombic		Gas sensor exhibited an excellent response of 14.86–100 ppm ethanol vapor when operating at 160 °C
SnS honey comb like structures	Thiourea, stannous chloride, methanol, 2-methoxy ethanol	Solution-based	Orthorhombic		Photovoltaic supercapacitors represented high specific capacitance of 42 ${\rm Fg^{-1}}$ At current density of 2 ${\rm Ag^{-1}}$

methods that have been used lately, together with CdS NS architectures, structures, and applications. Using hydrothermal and solvothermal processes, SnS nanosheets and nanoflakes were produced, respectively, and shown antimicrobial properties in gas sensing and photodetector systems. With an efficiency of 0.38 and 0.58 % in converting electricity, respectively, SnS thin films used in solar cells have been synthesized using the sputtering technique.

3.12 Lead sulfide

Cubic lead sulfide (PbS) possesses distinctive optical properties due to its cubic structure.³⁹⁵ At room temperature, bulk PbS exhibits a narrow energy band gap of 0.41 eV in the near-infrared range, which can be increased to approximately 2 eV in the visible spectrum when formed into nanoclusters. 396 Various morphologies of PbS, including

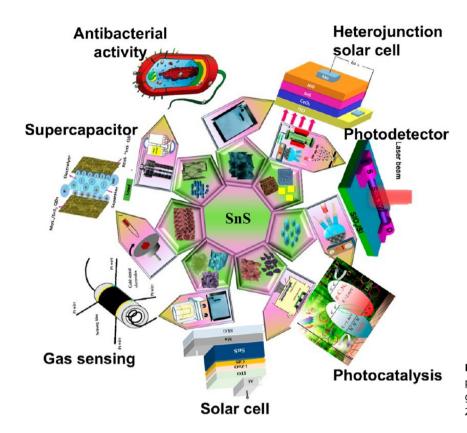


Figure 12: Diagrams showing SnS synthetic pathways, structures, and uses. Permission granted from. 264,381,389,392-394 Copyrights: 2019, 2022, 2020, 2020, and 2021.

nanoparticles (NPs), microflowers, thin films, nanosheets (NSs), quantum dots (QDs), and nanorods (NRs), have been reported using different synthesis methods such as hydrothermal, microwave, spray pyrolysis, diffusion-controlled, green, aqueous-based, and plasma chemical methods. 397-411

PbS finds potential applications in optical switching devices, infrared detectors, Pb2+ ion-selective sensors, and solar absorption due to its versatile properties. Colloidal PbS is utilized in solar cells, photodetectors, LEDs, and optical switches.

PbS nanoparticles exhibit intriguing optoelectrical characteristics such as tunable optical band gap, nonlinear optical behavior, enhanced electronic conductivity, and efficient multiple exciton generation (MEG) via single-photon absorption. The relatively small confinement radii of PbS nanoparticles, less than 20 nm, 412-417 make them highly desirable as they offer greater control over optical and optoelectrical properties. 418

Table 12 and Figure 13 describe some recent research on the uses and structures of PbS nanomaterials synthesized

 Table 12: Current investigation on lead sulfide synthesis, structure, crystalline system, particle dimension, and uses.

Materials	Precursors	Synthesis techniques	Crystal structure	Morphology	Applications
PbS NPs 2022	Lead acetate trihydrate, copper nitrate trihydrate and ammonium sulfide	Aqueous based	Cubic		Thermo electronics with charge carrier concentration $1.8 \times 10^{18} \text{cm}^{-3}$
PbS Thin film 2021	Lead acetate, thiourea, lanthanum acetate and methanol	Spray pyrolysis	Cubic		Gas sensing with small concentration of 200 ppm target gas
ZnO-PbS Hetero junc- tion 2020		Microwave	Cubic		Degradation of methyl orange dye (efficiency 96 %)

Table 12: (continued)

Materials	Precursors	Synthesis techniques	Crystal structure	Morphology	Applications
PbS (Quantum dots) QDs 2019	Sulfur, lead chloride, 3-mercaptopropionic acid, 1,2 ethanedithiol and tetrabutylammonium iodide	Diffusion- controlled	Cubic		Photocatalytic activity methyl or- ange dye shows 96 % efficiency
PbS NRS 2019	Lead acetate, trihydrate, carbon disulfide	Green synthesis	Cubic	1	
PbS Nanosheets 2019	Pb(II) dithiocarbonate, ethylenediamine	Microwave- assisted	Cubic	4	
PbS NPS 2019	Pb(NO ₃) ₂ ·Na ₂ S Cetyltrimethylammonium, silver nitrate	Microwave	Cubic		Optoelectronic
		Co-precipitation	Cubic	a (Optoelectronic devices
PbS NPS 2017	Lead nitrate, thiourea	Hydrothermal	Cubic		In semiconductor devices attributed to higher enband gap
PbS Flower like 2017		Ů	Cubic		

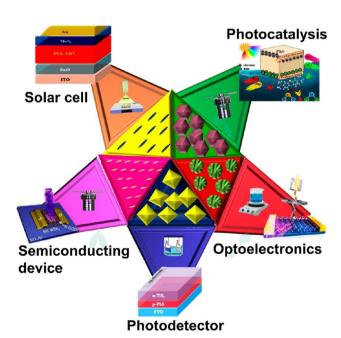


Figure 13: Diagram showing PbS production pathways, structures, and uses. Used with permission from. ^{70,409,423,424} Copies 2019, 2020, and 2022.

utilizing various methods. Cubic PbS NPs with structures appropriate for thermoelectric and optoelectronic applications were synthesized using microwave and water-based synthesis, respectively. A spray pyrolysis produced PbS thin film with a 40.32 nm diameter was used for gas sensing. An acceptable photocatalytic degradation of methyl orange was 96 % with QDs and hydrothermal, diffusion-controlled, and nanoflowers like PbS; acid brown was 95 %, acid violet was 75 %, and acid blue dye was 85 %.

4 Challenges and future prospects

MSs have great potential in fields such as biology, energy storage, environmental cleanup, sensing devices, and imaging and imaging. Further investigation, however, must overcome huge obstacles, such as the need to improve electrochemical performance and develop highly selective and sensitive MSs sensors. They are capable of cleaning industrial emissions of ${\rm SiO_2}$ and other dangerous contaminants. Future research into Fenton-like reactions and the

advanced oxidation process (AOP) should make use of highly active MSs catalysts and native carriers. The structure of the catalyst also determines its electrocatalytic performance. Better kinetic performances are a direct result of a bigger catalyst surface area, raising the total number of sites that are actively used. Although MSs have enhanced the competence of electrochemical supercapacitors in energy storage, their wide range of energy and faradic reactions during charging and discharging reduce their operating voltage, energy density, and cycle durability. Hybrid battery super-capacitors allow us to circumvent the problem of low energy density. Consequently, MSs would exhibit superior performance at low temperatures, quick charging time, high energy density, maintained long life cycle, and fast ionic diffusivity. Supercapacitor hybrid systems powered by Li/Na/K and Mg ion batteries also display impressive power and energy values. Another possibility is that doping or composites with different nanomaterials might increase electrochemical activity. By comparison to 2D NSs, 3D NSs have more surface-active sites, allowing them to produce a higher capacitance. Despite their limited direct application in the OER, layered MSs (such as MoS2 and WS2) have outstanding inherent electrocatalytic HER activity owing to their highly electrically conductive and well-exposed active regions. Due to their abundance, affordability, chemical stability, and exceptional activity, nonlayered MSs (FeS₂, Ni₃S₂, NiS₂, CoS₂, and Co₃S₄) have been extensively studied as electrocatalysts for water splitting. Researchers have looked at ways to increase electrical conductivity, inherent activity, and active sites in electrocatalysts by strain, facet, edge, and defect engineering, heteroatom doping, and composite design.

The mass transfer capability of the catalyst may be enhanced by water splitting, a process that produces gas. One promising approach to addressing energy scarcity, climate change, and environmental pollution is photocatalyst water splitting for hydrogen generation; however, this technique is limited due to photo corrosion of MSs photocatalysts. Nevertheless, constructing an interconnected network of porous structures with a large specific surface area and rapid mass transfer remains a formidable challenge. To build better MSs as catalysts/photocatalysts, to make them more stable when water is being divided and to protect them from photo corrosion attack, anticorrosion coatings must be added to their structure. They are not stable under high working circumstances, hence stronger MSs are needed. Within this framework, there is still much to learn about the surface chemistry of MS and how it is affected by experimental conditions. Another challenge is determining how stable these materials are for certain uses over the long run.

5 Novelty and significance

This comprehensive review article presents a novel and significant contribution to the field of metal sulfide nanoparticles by offering a thorough analysis of recent advancements in their synthesis and applications. By encompassing a wide range of metal sulfides, including MnS, FeS, CoS, NiS, CuS, ZnS, AgS, CdS, WS, SnS, PbS, and MoS₂, the article highlights their potential in addressing pressing challenges such as environmental contamination and sustainable energy storage demands. The article underscores the diverse applications of metal sulfide nanoparticles in various sectors, including health, biology, environmental remediation, and energy generation and storage, emphasizing their optical properties, specific capacitance, photocatalytic abilities, and light-absorbing capacities. Moreover, it discusses recent advancements in utilizing these nanoparticles as electrode materials for solar cells, supercapacitors, and ion batteries, as well as their roles in gas sensing, chemical sensing, electrocatalysis, and remediation of polluted areas. The article's unique focus on cost-effective synthesis methods and control over structures and compositions adds significant value, making it an essential resource for researchers and practitioners seeking to harness the full potential of metal sulfide nanoparticles across diverse applications.

6 Conclusions

There are several well-studied applications for MSs, which constitute a complex and diverse family of nanomaterials, and new concepts and examples of their use appear on a regular basis. MSs have great electrochemical activity, are environmentally friendly, and are inexpensive, making them ideal for application in energy conversion and storage systems. A synopsis of current knowledge on the efficient synthesis and regulated morphology, size, and crystal structure of MSs is given in this work. Using both top-down and bottom-up approaches, several monos- or bi-MSs have been produced. Hydrothermal, solvothermal, precipitation, and template methods are used to create MSs with nano- and microstructures. But combustion synthesis as a method for MS synthesis has seldom been investigated. Optimal control during production has allowed MSs nanocrystals to retain their chemical, physical, optical, and nano- and microstructural characteristics. The synthesis paths were dictated by factors such as the accessibility of raw materials, possible uses, and other monetary and ecological constraints. The existing literature was briefly linked to in terms of synthesis techniques, the dimension of particles, structure of crystals, and particular to the application geometries. Recent studies

have shown that MSs have many practical uses in various fields, in fields as diverse as biomedicine (including bioimaging, photothermal tumor treatment, and antibacterial agents), solar cells (for energy production), batteries (for energy storage, including supercapacitors and Li/Mg/Na ion cells), and photocatalytic dye degradation. The destruction of a wide variety of dyes using photocatalysis, including methyl orange, crystal violet, malachite green, rhodamine B, and MB, and others, has been shown in earlier research using a variety of MSs, including MnS, CoS, NiS, CuS, ZnS, MoS₂, Ag₂S, CdS, WS₂, and PbS.

By using CoS, the maximum degradation of MB dye was 89.5 %, whereas WS₂ achieved 90 %; CdS achieved 94 %. 96 %. and 99 %; and MnS achieved 56 % and 95.5 % destruction of malachite green dye, separately. On top of that, CdS had an efficiency of around 1.15 % in solar cell applications, whereas SnS had efficiencies of 0.3 and 0.5 %, respectively. Additionally, the most efficient materials for supercapacitors were CoS, NiS, MoS₂, and WS₂, with capacitance values of 1072 Fg⁻¹, 1745.50 Fg⁻¹, 348 Fg⁻¹, and 107.93 Fg⁻¹, respectively. Future study into the possible energy and environmental advantages of MSs nanoparticles with different morphologies and their applications in many areas may be made possible by this review.

In conclusion, this review highlights the significant potential of metal sulfide nanoparticles in addressing contemporary challenges in environmental remediation and sustainable energy storage. By exploring diverse synthesis methods and applications across various fields, it underscores the versatility and promise of these materials. However, further research is needed to optimize production methods and fully exploit their capabilities in practical applications.

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Data availability: The raw data can be obtained on request from the corresponding author.

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