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Recent advances in synthesis, structural properties, and regulation of nickel sulfide-based heterostructures for environmental water remediation: an insight review

Anuradha Sharma¹ · Peter R. Makgwane^{2,3} · Eric Lichtfouse⁴ · Naveen Kumar¹ · Ahmad Hosseini Bandegharai⁵ · Muhammad Tahir⁶

Abstract

Heterostructured nanomaterials exhibit pronounced potential in environmental science, including the water purification, pollutant monitoring, and environmental remediation. Especially, their application through advanced oxidation processes has been found capable and adaptable in waste water treatment. In semiconductor photocatalysts, metal sulfides are the leading materials. However, for further modifications, the progresses on specific materials need to be overviewed. Among metal sulfides, nickel sulfides are the emerging semiconductors due to relatively narrow band gaps, high thermal and chemical stability, and cost effectiveness. The aim of the present review is to conduct a thorough analysis and summary of recent progress in the application of nickel sulfide-based heterostructures in water decontamination. Initially, the review introduces the emerging needs of the materials for environment following the characteristics features of metal sulfides with emphasis on nickel sulfides. Subsequently, synthesis strategies and structural properties of nickel sulfide (NiS and NiS₂)-based photocatalysts are discussed. Herein, controlled synthesis procedures to influence their active structure, compositions, shape, and size for the enhanced photocatalytic performances are also considered. Furthermore, there is discussion on heterostructures formed by metal modification, metal oxides, and carbon hybridized nanocomposites. In the continuation, the modified characteristics are investigated which favors the photocatalytic processes for degradation of organic contaminations in water. The overall study highlights significant improvements in degradation efficiency of hetero-interfaced NiS and NiS₂ photocatalysts towards organics that are comparable to expensive noble-metal photocatalysts. Finally, we also added a little on prospects for future advancement of nickel sulfide-based photocatalysts for applications in sustainable environmental remediation.

Keywords Nickel sulfides · Heterojunctions · Photocatalysis · Photodegradation

Introduction

The accelerated rates of industrialization all over the world and over population are the two major sources of several kinds of contaminants in water that are deteriorating the environment (Kummu et al. 2016; Lichtfouse et al. 2021; Izzudin et al. 2021). As per European Community (EC) and the United States Environmental Protection Agency (USEPA), organic pollutants include different halogenated

pesticides, fertilizers, and biphenyls, monocyclic and polynuclear aliphatic or aromatic compounds, halogenated ethers, and phthalate acid esters along with some miscellaneous compounds (Wild and Jones 1991). In the contaminated wastewater treatment, some suitable methods are adsorption, membrane technologies, coagulation, and photocatalytic degradation (Kumar et al. 2019b; Akshatha et al. 2020; Alrobei et al. 2021). In this regard, photocatalysis has been intensely researched and widely applied in several areas including solar energy utilization, water splitting, medical and health care, pollutant degradation, and environmental governance (Anwer et al. 2019). This technology is driven by solar energy wherein simple operation, mild reaction conditions, and producing no secondary pollution make it

an effective strategy to solve global problems (Meng et al. 2019; Dhiman et al. 2022).

The photocatalysis process is a sort of advanced oxidative processes where a semiconductor material absorbs light of energy equal to or greater than its band gap energy, leading excitations of electrons from valence band to the conduction band (Soltani et al. 2012; Sharma et al. 2022). The generated electron–hole (e^-/h^+) pairs further produce different free radicals like hydroxyl, superoxide anion radicals in the reaction system to redox to activate the adsorbed compounds on the surface of the photocatalyst (Sharma et al. 2021b). Thus, photo-induced degradation of the organic compounds with the help of photo-chemically active semiconductor materials is one of the most interesting topics of environmental and global management (Adhikari et al. 2013). Therefore, the development of photocatalysts is the efficient strategy to overcome the issues of industrial wastewater remediation and energy crisis (Kumar et al. 2019a; Gan et al. 2021).

In advanced oxidation process, the frequently reported materials are transition metal oxides (Okpara et al. 2023), nitrides (Luo et al. 2023), carbides (Mabuea et al. 2022), phosphides (Han et al. 2021), sulfides (Wu et al. 2022), and selenides (Nawaz et al. 2023). Especially, the metal sulfides have emerged as promising candidates for water purification-relevant applications. In the metal sulfides, MoS_2 , CdS , SnS , and NiS are the frequently studied ones (Mishra and Chun 2015; Ong et al. 2016; Li et al. 2018; Wang et al. 2018; Mittal et al. 2019; Sharma et al. 2021a; Kumari et al. 2021; Passi and Pal 2021). Among the metal sulfides, nickel sulfides have attracted the attention due to ease of fabrication, low cost, and low toxicity and have widespread applications in environmental science (Wang et al. 2007).

These metal sulfides due to their narrow band gaps have capability to absorb in visible light regions and therefore have applied in the photocatalytic reactions extensively (Lopes et al. 2021). Further, the heterostructure interfaces of nickel sulfides with different materials like metal oxides, sulfides, and carbon-based structures improves the photocatalytic activity performances (Zhang et al. 2012; Wang et al. 2018; Zhao et al. 2019). Nickel sulfides exhibit low

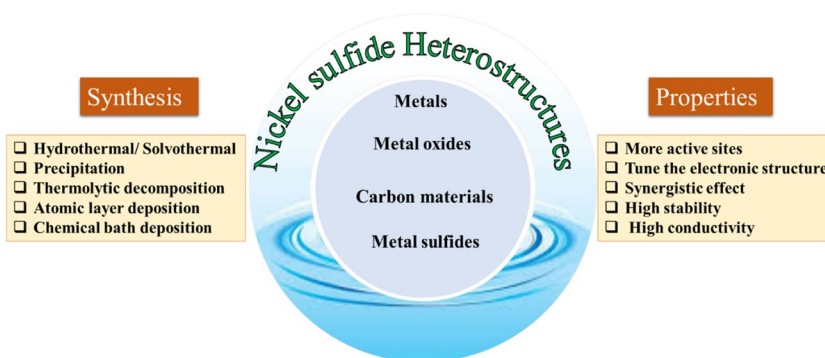
band gap value compared to tradition semiconductors such as TiO_2 , ZnO , SnO_2 , and CeO_2 (Rajamanickam et al. 2015). A properly matched p–n junction formation can significantly induce electric field at the interfaces, which in turn expands spectral response range and efficient generation, separation, and transference of the photoexcited charge carriers (Qian et al. 2018). However, there are a number of articles published on transition metal-based catalysts, but the main focus lies on electrochemical energy storage and photocatalysis with an emphasize on the catalyst synthesis methods, characterization techniques, morphology, and structure control. Despite the progress in heterogeneous catalysis for water purification, specially the study on nickel metal sulfide-based photocatalysis is still in its infancy, and the application in heterogeneous catalysis to treat contaminated water has never been reviewed till now.

The present review article emphasized on synthesis strategies and developments in characteristic properties for nickel sulfide and the assisted materials. In the modification pathways, special attention has been given on the heterostructures with metals, metal oxides, metal sulfides, and different carbon-based materials (Fig. 1). Finally, the nickel sulfide heterostructured materials are discussed scientifically for the photocatalytic applications towards decontamination of various organic pollutants for environmental remediation.

Properties of NiS and NiS_2 semiconductors

Transition metal sulfides have been reported to exhibit diverse stoichiometries compositions and structure morphologies. This is ascribed to the hybridizing of 3 s and 3p orbitals with the 3d orbitals that stabilize adjacent six cations and arranged in a trigonal–pyramidal configuration. The S–S bonds resulting in molecular anions and large dipole moments of the anions support the formation of layered structures (Rao and Pisharody 1976). In this regard, nickel sulfides reported generally in literature with the stoichiometries Ni_3S_2 , Ni_3S_4 , NiS , Ni_7S_6 , Ni_9S_8 , NiS_2 , $\alpha\text{-NiS}$, $\beta\text{-NiS}$, $\alpha/\beta\text{-NiS}$ composite, and structures of mixed phases with the

Fig. 1 A general layout of nickel sulfide heterostructures, properties, and synthesis strategies



films and nanosheets, nanospheres, nanotubes, nanorods, nanowires, and nanoplate-like (Dong et al. 2011; Zhou et al. 2013; Li et al. 2014, 2020; Tang et al. 2015; Shi et al. 2019; Shombe et al. 2020). Among the variety of nickel sulfide phases, most of the phases are found at lower temperatures. Out of the different nickel sulfide phases, two important ones are (i) low-temperature rhombohedral phase β -NiS and (ii) high-temperature hexagonal α -NiS phase. Each phase of nickel sulfide has its own physical and chemical properties and is useful when applied in particular field (Zheng et al. 2019). The synthesis of nickel sulfide nanocrystals with particular structural features for specific applications is very challenging. However, synthesis of phase selective materials enables the researchers to investigate the phase-dependent properties and extend the applicability of the respective materials and also provides new paths to design novel highly photoactive nanomaterials (Lim et al. 2006). It is well-known that the composition, phase, morphology, and size of any material are largely decided by the fabrication reaction kinetics and the related thermodynamics (Huang et al. 2015). Therefore, the structural characteristics of the synthesized material are probably altered by the control of experimental conditions. In addition, to synthesize nickel sulfide with specific structure and phase, understanding of the influencing factors for the crystal formation is necessary. The most important differences among the various classes of nickel sulfides are the stoichiometric ratios of nickel and sulfur and the different oxidation states of sulfur and nickel (S^{2-} , S_2^{2-} , Ni^{2+} , and Ni^{3+}) (Rhodes et al. 2017). It is documented that there are several factors which effect the composition and phase of the synthesized nickel sulfides (Manjunatha et al. 2020). The reactivity and concentration of the used precursors, solvent and its pH, reaction temperature, sources of nickel and sulfur, organic ligands, and reaction rate are the main decisive factors for the phase selective preparation of nickel sulfide materials (Hu et al. 2022a).

The fractal geometry-nickel sulfide dendritic structures were developed via chemical vapor deposition method (Shriber et al. 2022), and the growth mechanism of the crystals was examined. Different compositions were found during the nucleation including various stoichiometries of $Ni_{0.96}S$ (hexagonal phase), $Ni_{0.99}S$ (hexagonal phase), Ni_xS_6 (monoclinic phase), $(Ni_7S_6)_{3.25}$ (orthorhombic phase), and, finally, the Ni_3S_2 in rhombohedral phase were identified. The α -NiS is reported as the metastable phase at ambient conditions and gets transformed into the more stable β -NiS phase at lower temperatures exhibiting rhombohedral structure (Yousfi et al. 2010). Investigations of transformation mechanisms revealed that change in temperature and the sulfur content in the α -NiS significantly changes the structural transformation route. Also, the structural properties of nickel sulfide are determined by the source of sulfur taken in the reaction. Cubic polydymite (Ni_3S_4) were obtained (Balayeva

et al. 2017) when Na_2S was used as the source of sulfur (S), exploiting 0.5 M of nickel precursor in 24 h reaction time. On the other hand, when thiourea was used as S-resource, rhombohedral NiS nanocrystals were fabricated. A phase transition—orthorhombic Ni_7S_6 nanocrystals were observed when vacuum annealing was done for 8 h at 180 °C.

The structural composition can be varied by altering the atomic ratios of the precursors used for Ni and S respectively. For example, when various 2:1, 3:1, 1:2, and 1:3 atomic ratios of Ni and S were used to synthesize nickel sulfides (Khan et al. 2021), the corresponding crystal structure and phases were verified in the XRD patterns as shown in Fig. 2a. The fabricated samples were indexed to diffraction peaks at (002), (102), (101), (200), (110), (201), and (112) planes which supported the formation of NiS nanocrystals phase. Another work investigated the effect of reaction temperature on the phase compositions and reported that sulfur-rich nickel sulfides are obtained at higher temperatures (Gou et al. 2017). At 160 °C, the diffraction peaks were ascribed to the pure NiS rhombohedral phase, while mixed phases of cubic Ni_3S_4 and rhombohedral NiS were obtained at 180 and 200 °C, respectively (Fig. 2b).

Regulation of reactivity of precursors and ratio of metal ions to the sulfur source is also an important parameter. Sulfur-rich phases were obtained when weaker C—S bonds were present in the sulfur source (Rhodes et al. 2017), due to which more active sulfur species are released to react with metal ions and produce sulfur-rich sulfide product. In addition to it, there are some strategies which focus on the production of sulfur-deficient nickel sulfides. For instance, variation in the amount of coordination agent (Hu et al. 2022b) transformed the β -NiS/ α -NiS/ Ni_3S_4 composition to β -NiS/ α -NiS and finally to pure β -NiS. Another work (Hu et al. 2022a) reported the effect of solvent pH and found lower pH values suitable for S-rich sulfides. When 1 M HCl was used as the solvent, bulk structured pure NiS_2 phase was obtained, while layered structures of β -NiS were obtained with 2 M KOH solution as the solvent. Such types of observations are also supported with the DFT analysis. In acidic conditions, S atoms become more competitive for the Ni atoms as compared to the alkaline medium since the distance between the associated atoms is lesser, and the involved atoms can approach more easily. Moreover, the content of sulfur to nickel influences the association of the different atoms and, hence, the bond length between the atoms (Hu et al. 2022a). Therefore, the morphology and the respective structures are also altered. Figure 2c shows the correlation between the S -content and Ni-S bond distance and the obtained structures. The rate of feeding the starting materials during the synthesis introduces in homogeneity into the material. In a report, the effect of different feeding rates of the precursors was explained (Chandra Patel et al. 2021). It was observed that NiS_2 is favored only at low feeding rates since relative

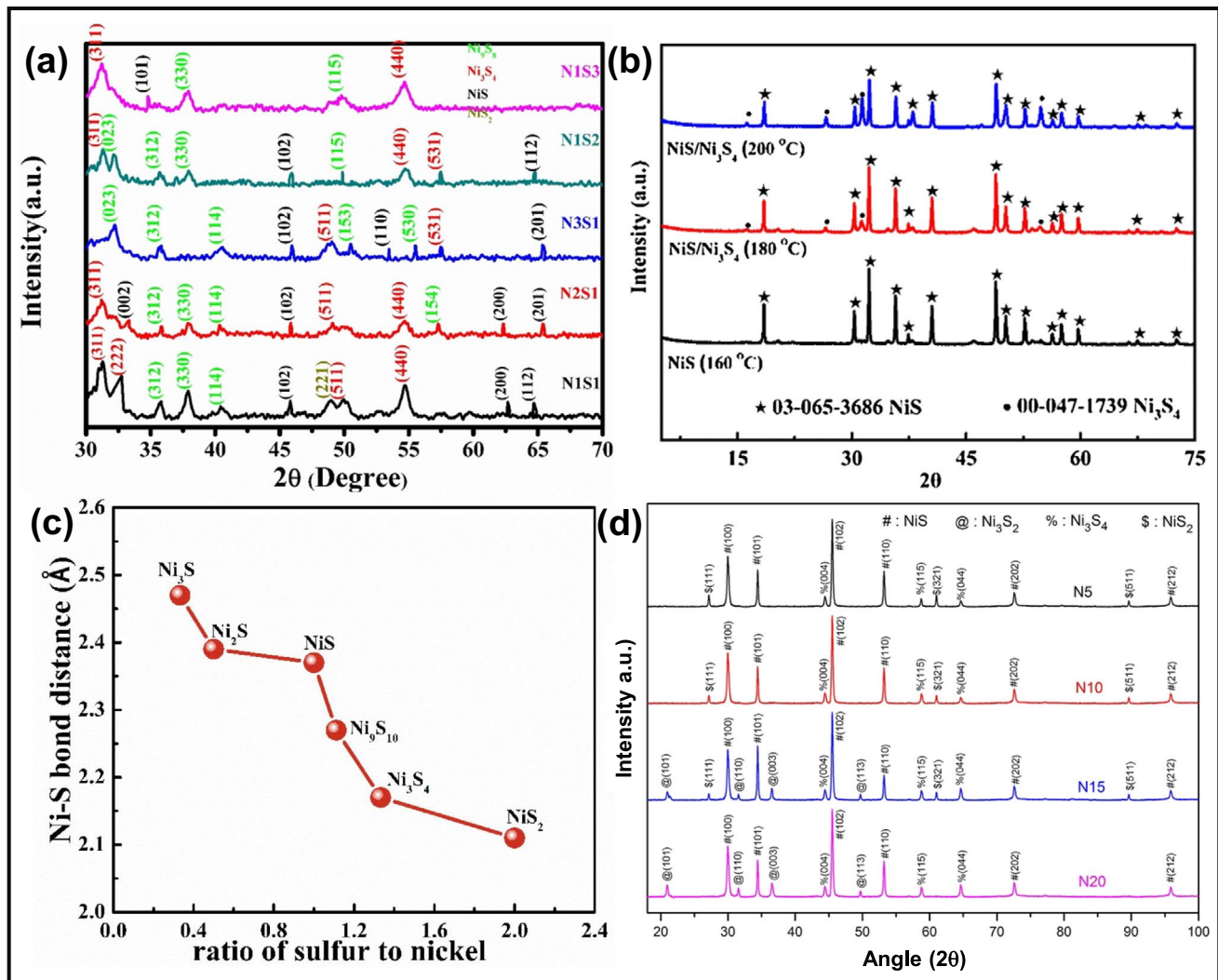


Fig. 2 **a** XRD spectra of the synthesized nickel sulfides at different atomic ratios of Ni and S (1:1, 2:1, 3:1, 1:2, and 1:3). Reprinted with permission from ref. (Khan et al. 2021). Copyright 2021 Elsevier. **b** Effect of temperature (160, 180, and 200 °C) on the different phase ratios of nickel sulfides. Reprinted with permission from ref. (Gou et al. 2017). Copyright 2017 Elsevier. **c** Correlation of the S- content

and Ni-S bond distance obtained from (Materials Project (<https://materialsproject.org/>)). Reprinted with permission from ref. (Hu et al. 2022a). Copyright 2022 Elsevier. **d** Effect of feeding rates of the Ni and S precursors on the existence of nickel sulfide phases. Reprinted with permission from ref. (Chandra Patel et al. 2021). Copyright 2021 Elsevier

amount of the NiS₂ phase goes on decreasing with increase in the flow rates from 5 to 15 ml/min and becomes absent at 20 ml/min flow rate (Fig. 2d). On the other hand, at the flow rate of 10 ml/min, maximum content of α-NiS was obtained. Thus, it is concluded that the rate of adding the precursors greatly affects the existence of phases in nickel sulfides.

Nickel sulfide composites with other metal sulfides have been reported that successfully form heterojunctions of the two materials and allow sufficient band offset for electron-hole separation (Zhao et al. 2022; Yendrapati et al. 2022). ZnS/Ni_xS_y heterojunctions were obtained via one-pot synthesis and exhibited proper band alignment (Khan et al. 2020). The band structures and electron density of

states for NiS and NiS₂ were investigated with the theoretical DFT study as shown in Fig. 3a–e. Using the calculated positions for NiS and NiS₂ Fermi levels as well as a Schottky-type junction with downward band bending was generated (Fig. 3e).

Synthesis strategies of nickel sulfide-based photocatalysts

The nickel sulfide network is highly interesting owing to the numerous phases that it exhibits; including β-Ni₃S₂, Ni₃S₄, α-Ni_{3+x}S₂, Ni₄S_{3+x}, Ni₉S₈, Ni₇S₆, Ni₆S₅, NiS₂, and α-NiS,

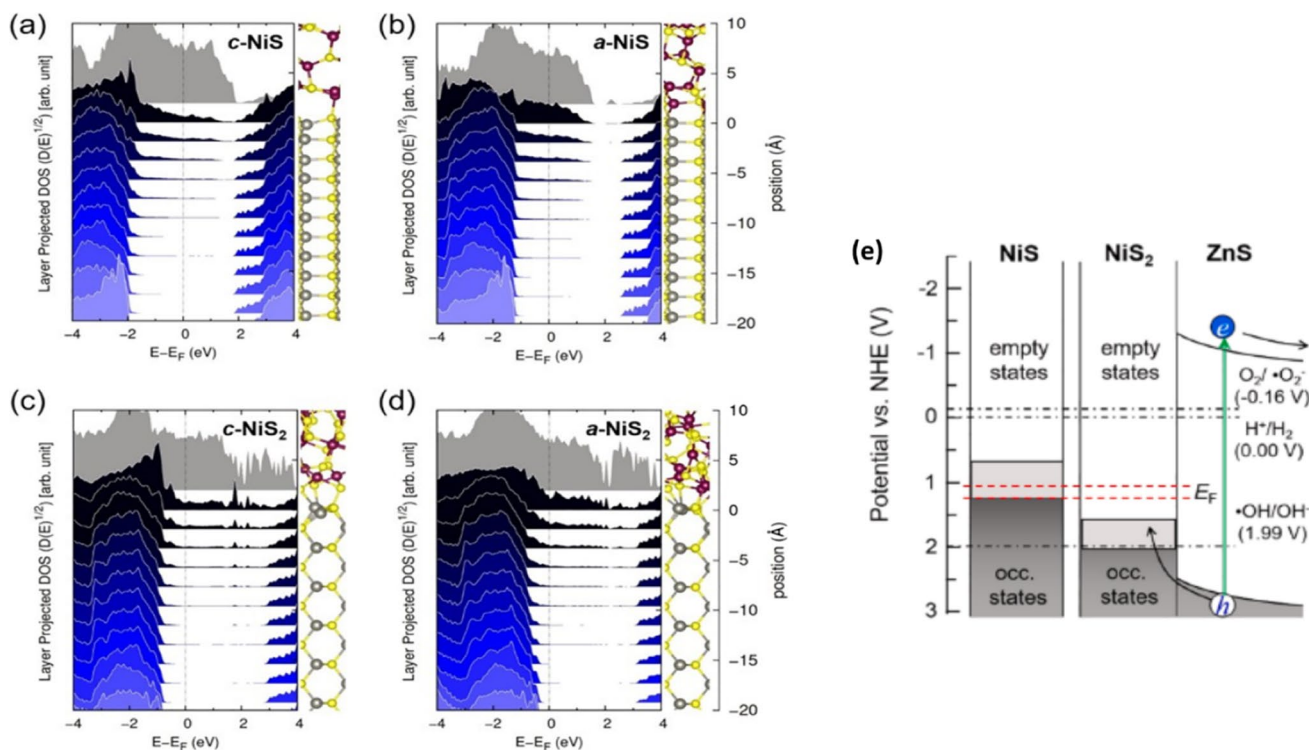


Fig. 3 Electron density of states (DOS) projected onto each layer of **a** c-NiS, **b** a-NiS, **c** c-NiS₂, and **d** a-NiS₂ with a c-ZnS (1 1 0) surface. Note that VBMs of ZnS locate at **a** 1.80, **b** 1.27 eV, **c** 0.91, and **d** 0.50 eV below the Fermi level. **e** Band diagram drawn using the

valence band level of ZnS relative to Fermi level from DFT simulations and measured band edges of NiS. Reprinted with permission from ref. (Khan et al. 2020). Copyright 2020 Elsevier

β -NiS (Emadi et al. 2017). Since, in the present article, we are dealing especially with NiS and NiS₂, various synthesis methods and the resulting morphologies are listed in Table 1. The constituent elements itself declare that the preparation of nickel sulfide materials are affected by Ni precursor and sulfur source than the conditions being used in their respective synthesis procedures. The most prominent nickel salts that are used in the preparations of NiS or NiS₂ are nickel (II) nitrate, nickel (II) chloride, and nickel (II) acetate tetrahydrate. For sulfur source, the widely used are ammonium sulfide, sodium sulfide, and thiourea. Other important matter of synthesis is the procedure or method adopted to get the desired Ni sulfide.

NiS-based photocatalysts

NiS is reported to possess two phases: (i) hexagonal and (ii) rhombohedral phase (Sun 2003; Ghezlbash et al. 2004). The synthesized phase and the corresponding morphology of sample are largely determined by the precursor used, reaction route, or method selected along with the synthesis conditions employed. For example, NiS with β -phase and nanoflakes morphology was obtained (Zhao et al. 2009) when reaction was carried out for 12 h, while NPs

morphology instead of nanoflakes were obtained for the reaction time of up to 3 h. Pristine NiS can be prepared via solvothermal approach using nickel nitrate as Ni source and thiourea (CH₄N₂S) as the sulfur source in ethylene glycol solvent. Literature reveals that during the synthesis of nickel sulfides, obtaining single phase of either β -NiS or α -NiS is difficult task. Generally, the formation of mixed phases is obtained in case of NiS. Up to date various synthesis methods have been utilized to prepare controlled phases of nickel sulfides including solvothermal, microwave, and hot injection method (Idris et al. 2011; Yang et al. 2014; Karthikeyan et al. 2015). NiS preparation using square planar nickel bis (dithiocarbonate) complexes [Ni(S₂CNR₂)₂] exhibited α -NiS to β -NiS with phase transformation at high temperature of 280 °C (Roffey et al. 2016). Band gaps for NiS can be tuned by adjusting the temperature and changing capping agents such as citric acid, polyvinylpyrrolidone, and β -cyclodextrin (Molla et al. 2016). Similarly, another study reported α and β phases of NiS synthesized by green synthesis protocol using water and ethanol under solvothermal conditions (Muniyappa et al. 2022). When the precursors of (Ni(CH₃COO)₂·4H₂O, (NH₂)₂CS, and NaCl₂H₂SO₄) were dissolved in pure ethanol, α -NiS was obtained whereas β -NiS phase was observed with 1:2 ratio of ethanol to water.

Table 1 Synthesis method, morphology, and precursors used for the preparation of nickel sulfides and their heterostructures

Catalyst	Nickel precursor	Sulfur source	Synthesis method	Morphology	Reference
NiS	Ni(NO ₃) ₂ ·xH ₂ O	C ₁₂ H ₂₅ SH	Thermolytic decomposition (190 °C, 5 h)	Nanorods	(Ghezelbash et al. 2004)
NiS and NiS ₂	Ni(NO ₃) ₃	Na ₂ S ₂ O ₃	Hydrothermal (180 °C, 12 h)	Hollow microspheres	(Luo et al. 2017)
α/β-NiS	Ni(CH ₃ COO) ₂ ·4H ₂ O	Thiourea	Solvothermal (200 °C, 8 h)	Elongated oval-shaped particles	(Muniyappa et al. 2022)
CuS-NiS-TiO ₂	Ni(NO ₃) ₂ ·6H ₂ O	Thiourea	Hydrothermal (160 °C, 12 h)	Microspheres	(Wang et al. 2014)
ZnO/NiS@NiO/rGO	Ni(CH ₃ COO) ₂ ·4H ₂ O	CH ₄ N ₂ S	Solvothermal (150 °C, 4 h)	Nanoparticles	(Liu and Li 2021)
NiS/rGO	NiCl ₂ ·6H ₂ O	Na ₂ S	Hydrothermal (170 °C, 5 h)	Nanoparticles	(Arumugam et al. 2020)
Ni(OH) ₂ /NiS _x /BiVO ₄	Ni(NO ₃) ₃	Na ₂ S	Precipitation (-)	Nanoparticles	(Huang et al. 2022)
NiS/CdS	Ni(NO ₃) ₂ ·6H ₂ O	Thiourea	Solvothermal (150 °C, 12 h)	Nanoparticles and flower	(Liu et al. 2021)
AC-NiS/CoS	NiCl ₂ ·6H ₂ O	Na ₂ S	Precipitation (-)	Spherical-nanosheets	(Artagan et al. 2021)
NiS ₂ /g-C ₃ N ₄	NiCl ₂ ·6H ₂ O	Thiourea	Hydrothermal (120 °C, 24 h)	Nanosheet dispersed quantum dots	(Qin et al. 2020)
β-NiS/ ZnIn ₂ S ₄	NiC ₄ H ₆ O ₄ ·4H ₂ O	Thiourea	Solvothermal (180 °C, 4 h)	Nanosheets	(Ding et al. 2021)
NiS/NU-1000 (MOF)	Bis(N,N'-ditert-butylacetamidinato) nickel(II)	nickel(II) sulfide	Atomic layer deposition (120 °C, 5 min)	–	(Peters et al. 2016)
NiS-CuO@ ZnFe ₂ O ₄	Ni(NO ₃) ₂ ·2H ₂ O	Na ₂ S	Chemical bath deposition (-)	Nanoarrays	(Chen et al. 2020b)
CoNiS _x -C ₃ N ₄	Ni(NO ₃) ₂ ·6H ₂ O	Thiourea	Thermal polymerization and Hydrothermal (120 °C, 5 h)	Polyhedrons and nanoparticles	(Jiang et al. 2019)
NiS/CuInS ₂ /NiO	Ni(CH ₃ COO) ₂ ·4H ₂ O	C ₂ H ₅ NS	Successive ionic layer adsorption and reaction (25 °C)	Nanosheets	(Liu and Zhou 2020)
Ni ₃ S ₂ -NiS ₂ -g-C ₃ N ₄	Ni(OAc) ₂	CH ₃ CSNH ₂	Hydrothermal (130 °C, 12 h)	Particles distributed over C ₃ N ₄	(Xi et al. 2022)

A solvothermal technique is well known to achieve the nanostructures of different dimensions with controlled morphologies. Recently, multicomponent sulfides materials are receiving tremendous attention owing to their excellent optical properties and adjustable band gaps (Su et al. 2019). A one-pot solvothermal method was used to synthesize NiS/Mn_{0.3}Cd_{0.7}S with p-n heterojunctions (Han et al. 2020). The NiS nanoclusters were highly dispersed onto surface of Mn_{0.3}Cd_{0.7}S nanorods. Heterostructured composites of NiS with metal organic framework (MOF) have been prepared by the deposition of NiS on NU-1000, Zr (IV)-based MOF scaffold with the bis (N, N'-di-tert-butylacetamidinato) nickel- (II) and H₂S as the nickel and sulfur sources, respectively (Peters et al. 2016). A unique, one step method is reported in which MOF based on MIL-101 (Fe/Ni) was used as metallic source and calcined in the presence of Na₂S to prepare the NiS/γ-Fe₂O₃/C type-II heterojunction (Rashid et al. 2021). The MIL-101 (Fe/Ni) was used as a

sacrificial template. Loading NiS on graphite-like carbon nitride (g-C₃N₄) nanosheets is also an effective strategy to prepare NiS heterojunctions. This can be achieved either directly loading or some intermediaries. The strategy using intermediary compounds has advantages over direct loading method involving (i) more efficient contact is possible between NiS and C₃N₄ nanosheets and (ii) proper orientation of the co-catalyst takes place due to the introduction of intermediaries. This reason may be the proper d-spacings existing in the intermediary material corresponding to both the species going to form heterojunctions. CuWO₄ was used as the intermediaries to prepare NiS/g-C₃N₄ photocatalyst (g-C₃N₄/NiS-W) (Xue et al. 2021). The overall synthesis procedure followed is depicted in Fig. 4a with the help of a schematic diagram. Moreover, carbon nanotubes (CNTs) consisting of cylindrical tubes are also considered as potential materials in forming nickel sulfide heterojunctions and utilized in several fields (Wang et al. 2019). Apart from these, MoS₂ is

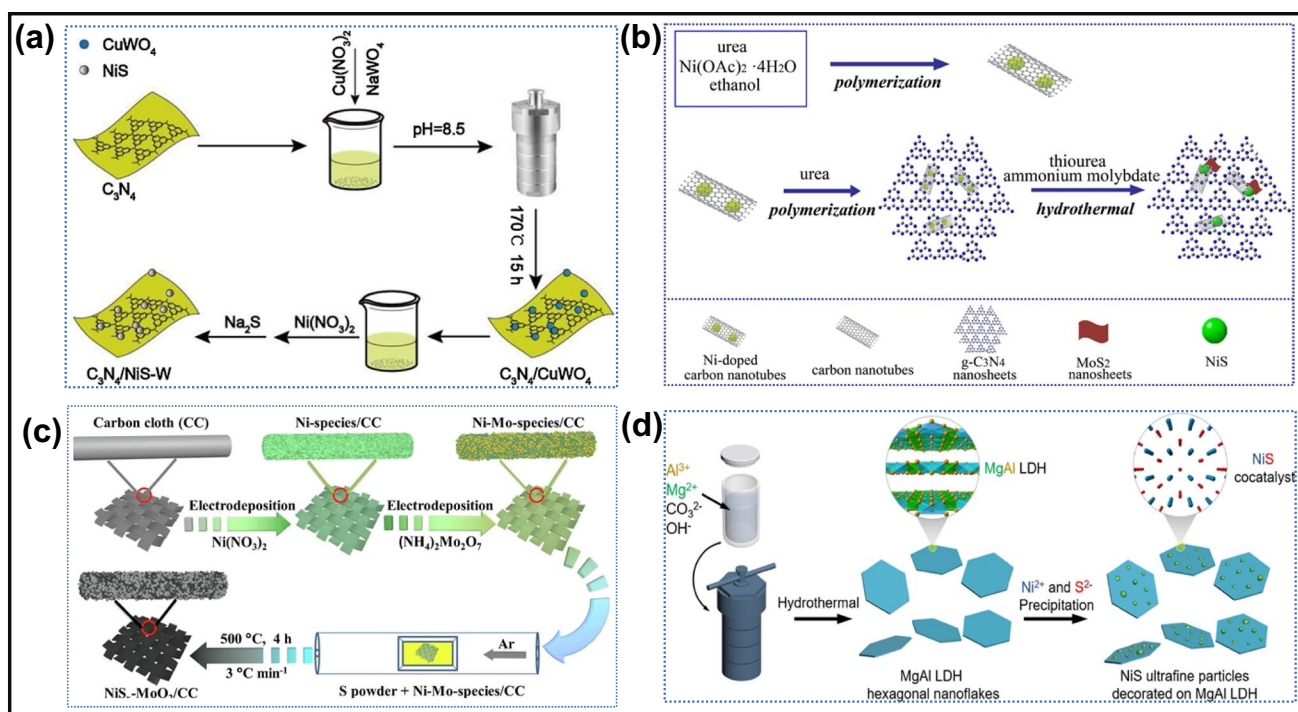


Fig. 4 Synthesis process of **a** g-C₃N₄/NiS-W. Reprinted with permission from (Xue et al. 2021) Copyright 2020 Elsevier. **b** NiS-MoS₂/CNTs/g-C₃N₄ hybrid. Reprinted with permission from ref. (Zhang et al. 2018b). Copyright 2018 Elsevier. **c** NiS_x-MoO₂/CC. Reprinted

with permission from ref. (Wang et al. 2020a). Copyright 2020 Elsevier. **d** MgAl-LDH/NiS heterostructures. Reprinted with permission from ref. (Chen et al. 2020a). Copyright 2019 Elsevier

also a low-cost and attractive material that when integrated with nickel sulfides that exhibited enhanced photocatalytic reactions. NiS-MoS₂/CNTs/g-C₃N₄ composite was synthesized by hydrothermal and polymerization treatment (Zhang et al. 2018b). Nickel (II) acetate tetra hydrate was used as the source of Ni²⁺ ions and NiS was generated by the reaction between nickel ions and thiourea. Firstly, Ni-CNTs/g-C₃N₄ was prepared via thermal polymerization and after that ammonium molybdate was used as the source of molybdenum followed by a hydrothermal treatment (Fig. 4b) to construct NiS₂-MoS₂/CNTs/g-C₃N₄. Layered double-metal hydroxides (LDHs) also act as good catalytic supports for NiS photocatalyst. NiS nanoparticles were decorated over pre-prepared 2D hexagonal nanoflakes by the precipitation method. Figure 4d shows the diagram illustrating the procedure for preparing MgAl-LDH/NiS heterostructure (Chen et al. 2020a). It is well known that the efficiency of a catalyst in any application is closely determined by the constitution as well as their morphological characteristics. The porous sponge-like structures provide a number of active sites, confinement effect, high surface area, and sufficient mass transfer and also prevent catalyst agglomeration (Peng et al. 2016; Li et al. 2019). A highly active carbon cloth decorated with NiS_x-MoO₂ nano-sponge was prepared and exhibited excellent electrocatalytic activity (Wang et al. 2020a). The

synthesis involved a two-step electro-deposition and was followed by vulcanization. NiS_x were grown directly on the surface of MoO₂, and the coating process was eliminated in this synthesis route (Fig. 4c).

NiS₂-based photocatalysts

NiS₂ exist in two main phases, cubic and triclinic (Luo et al. 2017). Several heterostructure composites photocatalysts based on NiS₂ of various morphologies have been fabricated. A heterostructure of NiS₂ QDs with g-C₃N₄ using NiCl₂ and thiourea as Ni and S source respectively was fabricated. In the QDs-NiS₂/g-C₃N₄ heterojunction, NiS₂ was obtained with 200 plane having 0.20 interplanar spacing (Qin et al. 2020). In the other study, a hollow NiS₂ microspheres were synthesized by hydrothermal approach, and after annealing the prepared NiS₂ under mixed atmosphere (H₂ and Ar) conditions, mesoporous NiS was obtained by the reduction (Luo et al. 2017). The hollow microsphere structures of respective NiS and NiS₂ possessed large surface sites, which improved the photocatalytic activity properties (Fig. 5a–h). NiS₂ applicability as photocatalyst is limited due to its low charge transfer and high aggregation. To overcome these limitations, NiS₂ is employed with other semiconductor materials.

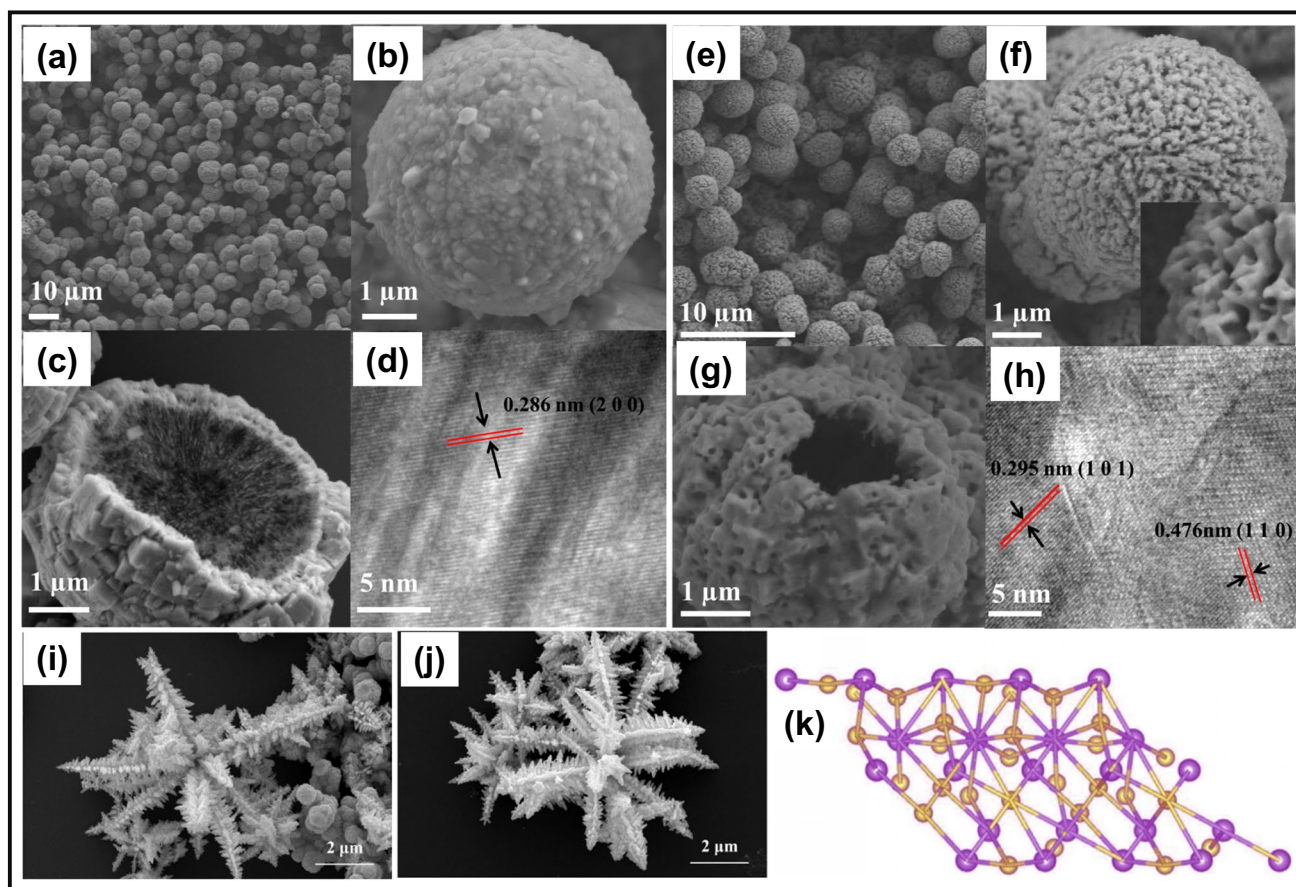


Fig. 5 Microspheres FESEM and TEM images of NiS_2 (a–d) and NiS (e–i). Reprinted with permission from ref. (Luo et al. 2017). Copyright 2016 American Chemical Society. i–j SEM images of pure CdS and NiS/CdS (Ni/Cd ratio of 0.4) nanoflowers. Reprinted with permission from ref. (Zhang et al. 2018a). Copyright 2019 Elsevier. k

NiS_2 {111} crystal facets atomic structure from top and side view respectively (purple sphere represents Ni and orange sphere represents S atom). Reprinted with permission from ref. (Liang et al. 2020). Copyright 2019 Elsevier

Although metal-associated materials are originated with high activity, research view is towards metal-free materials to avoid secondary environmental issues. In this regard, carbon nitride found an advanced material which possesses not only good electrical properties but also remarkable photostability. Hybrid interface of $\text{g-C}_3\text{N}_4$ with NiS_2 improve the charge transfer, but the aggregation of the NiS_2 particles is achieved by the adoption of some suitable synthetic routes. A novel $\text{NiS}_2/\text{g-C}_3\text{N}_4$ is reported prepared by a simple hydrothermal method with the use of a low cost $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ as Ni source and CS_2 as carbon source (Zhu et al. 2016). Engineering crystal facets is a hot research topic in photocatalysis. It has been observed from the reported works that synthesis of a particular facet is determined by the precursors used, solvent, and reaction parameters employed in the synthesis procedure (Zhang et al. 2022). For example, NiS_2 was prepared in two crystal

facets, i.e., {111} and {100} where a hydrothermal treatment was given for 12 h at 150 °C to the reaction contents (Liang et al. 2020). When $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (96 mg) and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ (266 mg) along with 220 mg of polyvinylpyrrolidone (PVP) were used in deionized water, NiS_2 {111} was obtained, whereas NiS_2 {100} was observed on using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.4 g), $\text{CN}_2\text{H}_4\text{S}$ (1.6 g), and 1.2 g PVP with 2 mg of NaOH. Figure 5k shows the atomic structure of NiS_2 {111} facet from both top and side views. In the other study, NiS/CdS heterostructures were prepared by adjusting the feed molar ratios of Ni/Cd from 0 to 1.2 and also varying the amounts of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and lactic acid (Zhang et al. 2018a). NiS and CdS were obtained in β -rhombohedral and hexagonal phases respectively. The synthesized samples mainly composed of nanoflowers, and no appreciable change in the morphology was observed on changing Ni/Cd ratio as shown in Fig. 5i–j.

Applications of nickel sulfide-based photocatalysts

NiS and NiS₂-based photocatalysts for the degradation of organic compounds

NiS and NiS₂ nanostructures are the superior semiconductors and various photo-active materials took advantage of their semiconductor features in constructing composite catalysts and vouchsafed excellent photocatalytic activity towards organic compounds degradation (Zhu et al. 2016; Huerta-Flores et al. 2018; Ardebilchi Marand et al. 2020; Khan et al. 2021; Mohtar et al. 2021). Table 2 presents the survey scan summary on NiS and NiS₂-based photocatalytic degradation activities of different organic contaminants. The photocatalytic efficiency of nickel sulfide microstructures with different atomic ratios of Ni and S can be explained with the help of ANSYS simulation and field emission studies (Khan et al. 2021). It was observed that the sample having highest atomic ratio of Ni to S, i.e., 3:1, exhibited best performance in photodegradation (Khan et al. 2021). The probable reason may be associated with the morphologies of the samples. With increase in the atomic ratio of Ni, rod-like blocks increased and each rod behaves like an individual emitter. On the other side in S-rich samples, the single particles are not effective emitters; in fact, the whole tube behaves as the cold cathode, thus leading to higher emission properties. The obtained results are also supported by the ANSYS simulation and turn-on fields as shown in Fig. 6.

Several materials including organic and inorganic have been explored as supports for NiS and NiS₂-based photocatalysts with improved suppression rates of the recombination of e⁻/h⁺ pairs, thus resulting in higher photocatalytic efficiencies. Integrating NiS and NiS₂ with metal oxides is an effective approach towards designing active photocatalysts for the removal of organics (Saboo and Quadrelli 2019). Although nickel sulfide is of a high ability to harvest visible light due to their narrower band gaps, bare nickel sulfide suffers from the rapid recombination of charge carriers and photo-corrosion which affects its photocatalytic efficiency. Therefore, in this regard, nickel sulfides interfaced with other semiconductors behave like a co-catalyst, matching band edge positions lead to an efficient separation of e⁻/h⁺ pairs, thereby boosting the photocatalytic effect (Lee and Chang 2019). A remarkable adsorption and degradation of methyl orange was reported for heterostructure TiO₂/NiS₂ photocatalyst (Zhu et al. 2012). The higher surface area, porosity, and polarity match between the adsorbate and the adsorbent were found to be the major contributing factors. Similarly, in another report (Mahmood et al. 2019), incorporation of NiS₂ into TiO₂ increased the photodegradation efficiency from 17

to 80% for rhodamine B under visible light. Recently, a highly stable α-Fe₂O₃/NiS₂ composite achieved up to 93.7% degradation efficiency for humic acid which was higher than both the α-Fe₂O₃ and NiS₂ (Mohtar et al. 2021). The proposed degradation mechanism is depicted in Fig. 7a. Among the different proposed supports, magnetic materials like Fe₃O₄ are of prior importance because of large surface area and simple separation of the catalyst from the reaction system due to their paramagnetic behavior (Habibi-Yangjeh and Akhundi 2016). In the same direction, different conducting polymeric compounds are also regarded as promising materials due to their ease of preparation, high surface area and conductivity, and good environmental stability (Marimuthu et al. 2015). A polypyrrole@Fe₃O₄ core/shell as the support for NiS photocatalyst was fabricated and examined its photodegradation activity in cephalixin antibiotic removal under both direct sunlight and simulated UV irradiations (Torki and Faghihian 2017). The degradation efficiencies were determined to be 65 and 82% in sunlight and UV light respectively. The effect of irradiation time on cephalixin degradation by NiS and Fe₃O₄@PPY-NiS is shown in Fig. 7b.

Hybrid NiS/rGO composite formed by the adjacent interface of NiS and rGO stimulate the formation of charge carrier with higher life times and thus displayed the higher photocatalytic performance in degradation removal of methylene blue dye (Arumugam et al. 2020). A high photoactivity observed for the NiS/rGO was 87%, which was significantly higher than the NiS of 70% activity for the dye degradation. The electrochemical impedance spectroscopy (EIS) studies also confirmed the higher charge transfer efficiency for the NiS/rGO in comparison to NiS and reduced graphene oxide, respectively. In the NiS/rGO composite, rGO can act as electron acceptors which enhance the charge separation. Another work reported a highly active NiS/CNTs photocatalyst for methylene blue degradation within 50 min (Haider et al. 2021). The enhanced photoactivity of the hybrid photocatalyst than the individual NiS or CNTs was explained on the basis of generation of more reactive free radicals, surface defects, formed Ni-S-C bond, and availability of a greater number of active sites.

While dealing with NiS₂ photocatalyst, aggregation of the NPs is the main problem in the system. In this direction, g-C₃N₄, acts as a fascinating material owing to its s-triazine structure and visible light response (Zhu et al. 2016). This is due to the reason that heptazine rings of g-C₃N₄ serve as a good support for loading NiS₂ NPs and more importantly prevent the agglomeration of NiS₂ particles, thus improving the specific surface area and hence the photoactivity of the material. It is reported that the loading of NiS₂ over g-C₃N₄ is beneficial in improving the photoactivity especially because of the electron

Table 2 Photocatalytic removal of organic contaminants in the presence of nickel sulfide catalysts under different experimental conditions

Photocatalyst	Synthesis method	Morphology	Contaminant solution	Catalyst (mg)	Light source	Removal rate	Reference
NiS	Hydrothermal	Sponge-like	Methylene blue ($\sim 10^{-5}$ M) in 14 ml aqueous	5	Direct sunlight	99% (10 min)	(Molla et al. 2016)
NiS ₂	Hydrothermal	Spherical	Indigo carmine (30 ppm) in 200 ml aqueous	200	450 W Xenon Lamp	51% (240 min)	(Huerta-Flores et al. 2018)
NiS	Sol-gel	Microtubes	Rhodamine B (10^{-5} M in 40 ml solution) Phenol (20 ppm, 40 ml solution)	30 22	40 W UV (Philips) tubes	96.72% (7 h) 88.84% (120 min)	(Khan et al. 2021)
NiS/SnS ₂	Ball milling	Dispersed particles	Metronidazole (2 ppm, 10 ml solution)	25	60 W Tungsten lamp UV lamp	69.2% (240 min) 93.2% (240 min)	(Derikvandi and Nezamzadeh-Ejehieh 2017)
NiS-SiO ₂	Ultrasound-microwave	Spherical particles	Methyl red	–	11 W UV lamp	85% (50 min)	(Hosseini et al. 2019)
Ni _x S _y /NiO	Solution combustion	Particles	Methylene blue (5 ppm, 100 ml)	35	Two 100-W Xenon lamps as visible light	52% (5 h)	(Ardebilchi Marand et al. 2020)
NiS/TiO ₂	Sol-gel	Spherical particles	Sunset yellow (3×10^{-4} M, 50 ml)	200	Direct sunlight	98.90% (80 min)	(Rajamanickam et al. 2015)
NiS-TiO ₂	Hydrothermal	Nanoflowers	Methyl orange (10 ppm, 30 ml)	30	500 W Xenon lamp	98% (20 min)	(Luo et al. 2020)
NiS/LaFeO ₃	Hydrothermal	Nanoparticle-nanosheets	Methyl orange (20 ppm, 100 ml)	50	Direct sunlight	90% (120 min)	(Wang et al. 2020b)
MoS ₂ /NiS ₂	Hydrothermal	Spherical shape-like sheets	Rhodamine B (20 ppm, 100 ml)	–	400 W Xenon lamp	90% (32 min)	(Harish et al. 2021)
AC-NiS/CoS	Chemical precipitation	Nanosheets	Methyl violet (10 ppm, 100 ml)	500	9 W LED lamps	98% (90 min)	(Artağan et al. 2021)
NiS/BiOBr	Hydrothermal	Nanoflakes	Rhodamine B (15 ppm, 200 ml)	20	450 W Xenon lamp	99% (50 min)	(Hu et al. 2020)
α -Fe ₂ O ₃ /NiS ₂	Precipitation	Stacked plate-like	Humic acid (30 ppm, 100 ml)	10	300 W Xenon lamp	93.7% (100 min)	(Mohtar et al. 2021)
NiS ₂ /g-C ₃ N ₄	Hydrothermal	Particles dispersed over sheets	Rhodamine B (10 ppm)	50	350 W xenon arc lamp	86% (210 min)	(Zhu et al. 2016)
NiS ₂ /RGO	Hydrothermal	Spherical particles dispersed over sheets	Cong red (10 g/L, 50 ml)	15	Direct sunlight	97.03% (40 min)	(Borthakur and Das 2018)
NiS/rGO	Hydrothermal and modified Hummer's method	Spherical particles over rGO layers	Amido Black dye (10 ppm, 100 ml)	100	500 W Tungsten halogen lamp	99% (120 min)	(Muninathan and Arumugam 2021)
NiS _x /FeOOH/BiVO ₄	Hydrothermal	–	Phenol (0.43 mM, 100 ml)	100	400 W metal halogen lamp	53.4% (5 h)	(Huang et al. 2022)

Table 2 (continued)

Photocatalyst	Synthesis method	Morphology	Contaminant solution	Catalyst (mg)	Light source	Removal rate	Reference
NiS-PPY-Fe ₃ O ₄	Polymerization and hydrothermal	Globular particles	Cephalexin (50 ppm)	-	UV	82% (30 min) 65% (30 min)	(Torki and Faghihian 2017)
Co-doped/NiS/S-g-C ₃ N ₄	Self-assembly method	Nanorods	Methylene blue	-	Visible light Xenon lamp	99% (32 min)	(Hakami 2022)
NiS/CNTs	Hydrothermal	Nanotubes dispersed over nanoparticles	Methylene blue (5 ppm, 50 ml)	5	200 W visible bulb	96% (50 min)	(Haider et al. 2021)

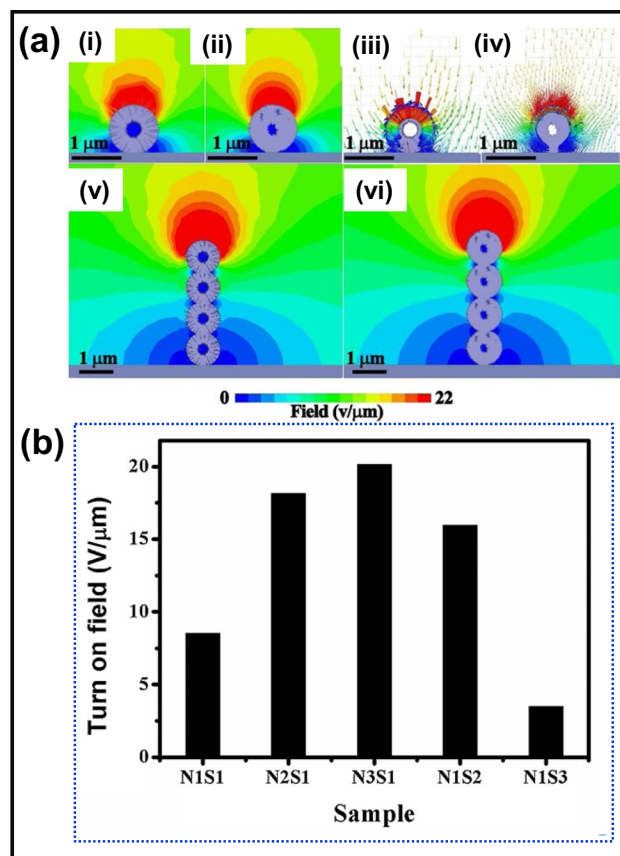


Fig. 6 **a** ANSYS simulations for output field magnitude of nickel sulfide; individual rod-made sphere (i), particulate sphere (ii); field vectors for individual rod-made sphere (iii), particulate sphere (iv); and output field magnitude for micro tube with rod-made sphere (v), particulate sphere (vi), and **b** turn-on fields for varying Ni to S atomic compositions (1 to 3). Reprinted with permission from ref. (Khan et al. 2021). Copyright 2021 Elsevier

transference from g-C₃N₄ to NiS₂ and decreasing the charge recombination rate (Zhu et al. 2016). NiS₂/g-C₃N₄ composite with improved absorption, less aggregation, and more charge transfer showed enhanced photocatalytic activity (Zhu et al. 2016). A 13.7 wt% NiS₂/g-C₃N₄ composite demonstrated the highest photocatalytic performance on rhodamine B underneath visible light illumination. Furthermore, doping g-C₃N₄ with non-metallic elements (O, B, S, P, and halogens) and then forming heterojunctions with metal doped-NiS is also an efficient way to improve the catalytic efficiency of NiS photocatalyst. A co-doped NiS/S-g-C₃N₄ heterojunction was synthesized and demonstrated an improved photocatalytic performance towards methylene blue degradation when compared to single photocatalysts (Hakami 2022). The results showed that the interface contact between Co-NiS nanorods and S-g-C₃N₄ nanosheets increased the formation and separation effectiveness of the photoexcited charge carriers, thus preventing their recombination.

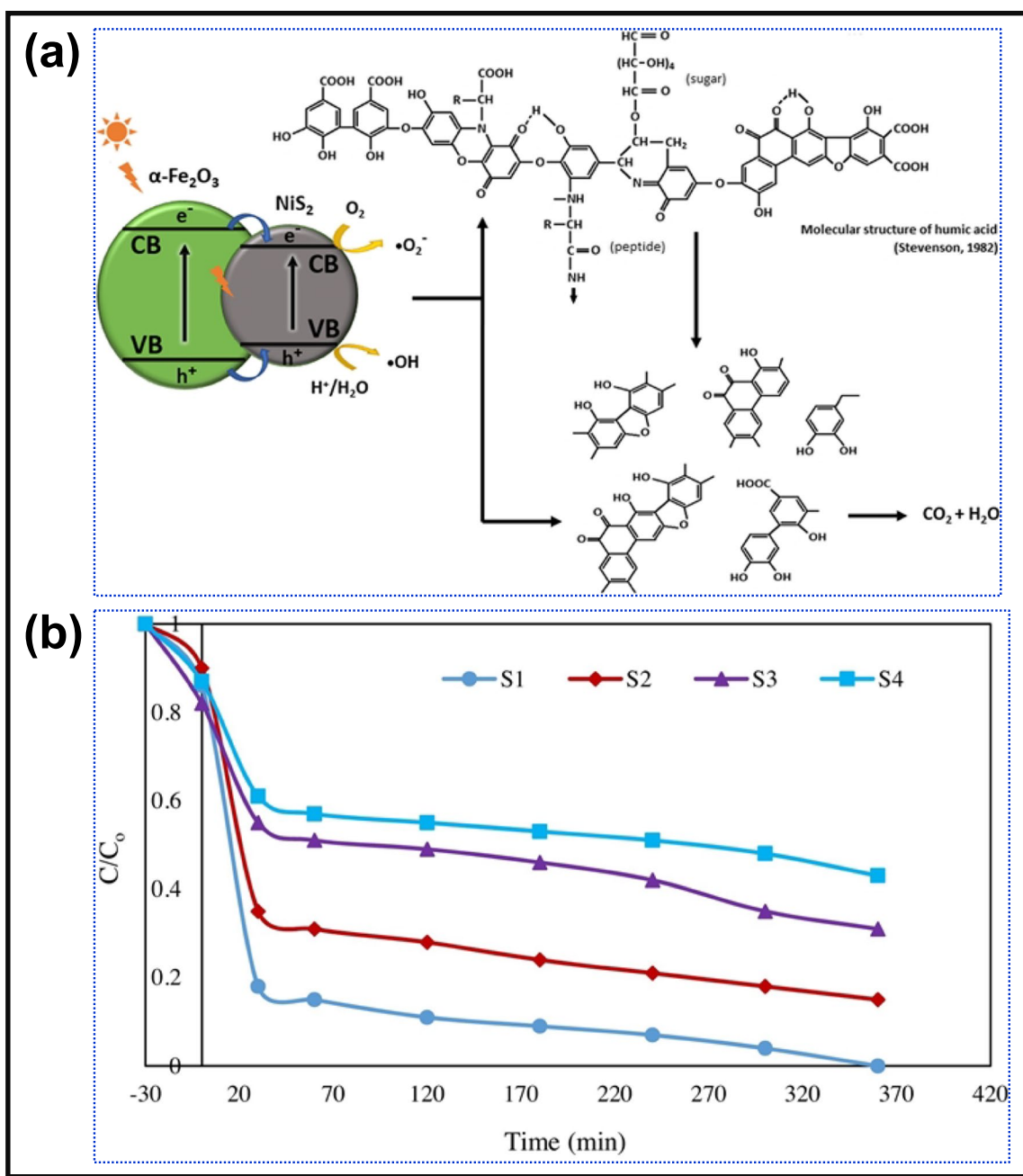


Fig. 7 a Photocatalytic mechanism of humic acid degradation by $\alpha\text{-Fe}_2\text{O}_3/\text{NiS}_2$ photocatalyst. Reprinted with permission from ref. (Mohtar et al. 2021) Copyright 2021 Elsevier. **b** Cephalexin degradation

tion by NiS and $\text{Fe}_3\text{O}_4/\text{PPY-NiS}$; S4 and S2 (sunlight) and S3 and S1 (UV) irradiations respectively. Reprinted with permission from ref. (Torki and Faghilian 2017). Copyright 2017 Elsevier

Amorphous polysulfide, NiS_x , also acts as a good co-catalyst. Both $\text{Ni}(\text{OH})_2$ and NiS_x have been reported as highly active co-catalyst with bismuth vanadate (BiVO_4) in the photodegradation of phenol due to effective electron transfer (Huang et al. 2022). As already described, phase and size of the synthesized nanoparticles (NPs) can be regulated by varying the initial ration of the concentrations of the used sources. Single-phase nickel sulfide NPs

including NiS , Ni_3S_4 , NiS_2 , and Ni_7S_6 were obtained utilizing a temperature-controlled precursor injection procedure (Karthikeyan et al. 2015). The synthesized NiS -phase NPs exhibited metallic characteristics and highest reduction efficiency towards 4-nitrophenol when compared with the other nickel sulfide phases. A complete reduction of 4-nitrophenol into 4-aminophenol was achieved in 300 s (Karthikeyan et al. 2015). On the other hand, the removal efficiencies of

other sulfur-rich phases were found lesser than that of the NiS phase being in 400 and 500 s for (NiS₂, Ni₃S₄) and Ni₇S₆ respectively. In recent times, crystal facet-dependent materials are receiving tremendous attention in the field of photocatalysis. It is found that a particular faceted nanocrystals exhibit greater photoactivity than the other facets of the same material. Liang et al. found NiS₂ {111} nanocrystals exhibiting better photocatalytic activity in degrading of methyl orange and methylene blue organic dyes than {100} faceted nanocrystals (Liang et al. 2020). Moreover, integrating NiS₂ {111} with (rGO) further enhanced the photocatalytic efficiency where complete removal was achieved in 150 and 180 min respectively.

Conclusion and future perspectives

This review presents the recent progress and developments in nickel sulfide (NiS and NiS₂)-based photocatalysts, focusing on the applications in environmental degradation of model organic wastewater pollutants by photocatalytic process. Undoubtedly, both NiS and NiS₂ can be considered as superior active visible-light semiconductors, due to their narrow indirect bandgap, which have demonstrated promising inherent photocatalytic properties.

NiS and NiS₂ both possesses the characteristics to be an efficient photocatalyst with a limitation of fast recombination rates of photogenerated charge carriers which need to be improved for a better performance. Hence, much effort has been directed to towards co-catalyst in constructing heterostructures interfaces with enhanced photocatalytic properties. The analyzed properties of NiS and NiS₂ can be extended to make the perception of inherent effects of heterostructure composite photocatalysts easy, paving the course of designing photocatalysts with improved photocatalytic activity and higher performance in the degradation of various organic wastewater pollutants. NiS and NiS₂ hybridized with metal oxides, metals, and carbon-based materials and further leads multicomponent from binary to ternary heterostructures which causes band edge alignments and improved heterostructures and surface characteristics with enhanced photocatalytic properties. The overall survey scan of the literature highlighted significant improvements on hetero-interfaced photocatalysts based on NiS and NiS₂ that are comparable to expensive noble-metal photocatalysts and degradation activity of organics. This compiled literature advancements in NiS and NiS₂ photocatalysts for the environment will provide a comprehensive insight for developing new approach of designing superior visible-light photoactive catalysts based on cost-efficient nickel metal cocatalysts.

Although current studies have reported significant improvements in the catalytic efficiency of the heterostructures in water treatment, the active components of the

catalyst will inevitably be lost or poisoned after multiple cycles. Therefore, there is need to improve the stability and reusability of the catalysts. In the future, more optimized synthetic methods should be developed for the stable heterostructured materials.

There are fewer studies on the eco-toxicity of nickel sulfide-based materials. Analysis of eco-toxicity is favorable for establishing more environmentally friendly catalytic systems.

DFT computations can provide in-depth view of the transformation of target pollutants and help us to accurately elucidate the active catalytic centers.

Overall, the study on nickel sulfide-based heterostructures is still at an early stage; it is far from the large-scale practical application. Studies on stability for long-term performance, incorporation on structural modelling of pure structures of NiS and NiS₂, and their heterostructures are encouraged for further advancements in comprehending these photocatalytic materials for potential industrial implementations.

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Data availability Complete data has been included in the manuscript.

Declarations

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Consent for publication We have reviewed the final version of the manuscript and approved it for publication.

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