

**REVIEW**

Can Chalcogenide Alloys Replace Traditional Photocatalysts for Sustainable Dye Degradation: Review

Chandresh Kumari^{1,*}, Y. B. Saddeek², K. A. Aly^{3,4}, Ishu Sharma⁵, Pankaj Sharma^{6,*}, Sandeep Chhoker^{7,*} and Sunanda Sharda⁸

¹Department of Basic and Applied Science, Galgotias University, Greater Noida, India

²Physics Department, Collage of Science in Zulfi, Majmaah University, Al Majma'ah, Saudi Arabia

³Applied College at Khulais, University of Jeddah, Jeddah, Saudi Arabia

⁴Physics Department, Faculty of Science, Al-Azhar University, Assiut, Egypt

⁵Physics Department, Amity University, Dubai, United Arab Emirates

⁶Applied Science Department, National Institute of Technical Teachers Training and Research, Sector 26, Chandigarh, India

⁷Department of Physics and Material Science and Engineering, Jaypee Institute of Information Technology, Noida, India

⁸Department of Physics, Faculty of Applied and Basic Sciences, SGT University, Gurugram, India

*Corresponding Authors: Chandresh Kumari. Email: chandresh.kumari@galgotiasuniversity.edu.in;

Pankaj Sharma. Email: pks_phy@yahoo.co.in; Sandeep Chhoker. Email: sandeep.chhoker@jiit.ac.in

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ABSTRACT: Water contamination by synthetic dyes, a pressing environmental and health concern, is primarily attributed to industrial wastewater discharge. Traditional dye removal methods, while effective, often suffer from high energy consumption and secondary pollution. Photocatalysis, a green and energy-efficient approach, offers a promising solution by completely mineralizing dyes into harmless byproducts. Chalcogenide alloys have emerged as innovative photocatalysts for dye degradation. Their narrow bandgap allows them to absorb a broader range of sunlight, while their cost-effectiveness and superior photocatalytic activity make them attractive for practical applications. This review delves into the potential of binary, ternary, and quaternary chalcogenide materials, examining their mechanisms of dye degradation, the impact of dopants, and their effectiveness in various wastewater treatment scenarios. Despite their advantages, chalcogenide alloys face specific challenges and limitations. Addressing these issues will be crucial for their widespread adoption in large-scale water treatment systems. This review concludes by identifying key research areas and proposing future directions to optimize the performance of chalcogenide-based photocatalysts for sustainable dye removal.

KEYWORDS: Chalcogenide photocatalysts; dye degradation; water pollution; wastewater treatment; bibliometric analysis

1 Introduction

With an increase in current economic development and population growth, there is a need to protect water resources. On a daily basis, there is a discharge of nearly 2 million tons of waste pollutants to communal water supply that adversely affects both the environment and all life forms present on earth [1] and is one of the critical issues of today's world. Nearly 0.780 billion people do not have access to clean water, and one study reports nearly 5000 to 6000 deaths of children per day, which are mainly caused by water pollution [2]. Among various contaminants of the water system, the well-known contaminants in

terms of their toxicity include dyes, monoaromatic hydrocarbons, as well as antibiotics which are sourced from waste coming mainly from industries.

Dyes are defined as colouring substances that impart colour to any substance when used [3] due to the presence of chromophore groups in them [4–6]. Dyes are classified based on their source of origin, structure, and their uses for a variety of purposes, as shown in Fig. 1. Among all kinds of synthetic dyes, azo, direct, reactive, acidic, basic, mordant, disperse, and sulfur dyes find extensive applications to be used in textile industries such as wool, cotton, silk, polyamide, polyester, and acrylic [7–12]. Additionally, textile industries use toxic chemicals for softening, sizing, resizing, and brightening as a finishing agent [13]. Since the binding efficiency of different textile dyes to fabric is less, this leads to the untreated discharge of this waste in the form of textile wastewater into aquatic environments like rivers, lakes, streams, and ponds.

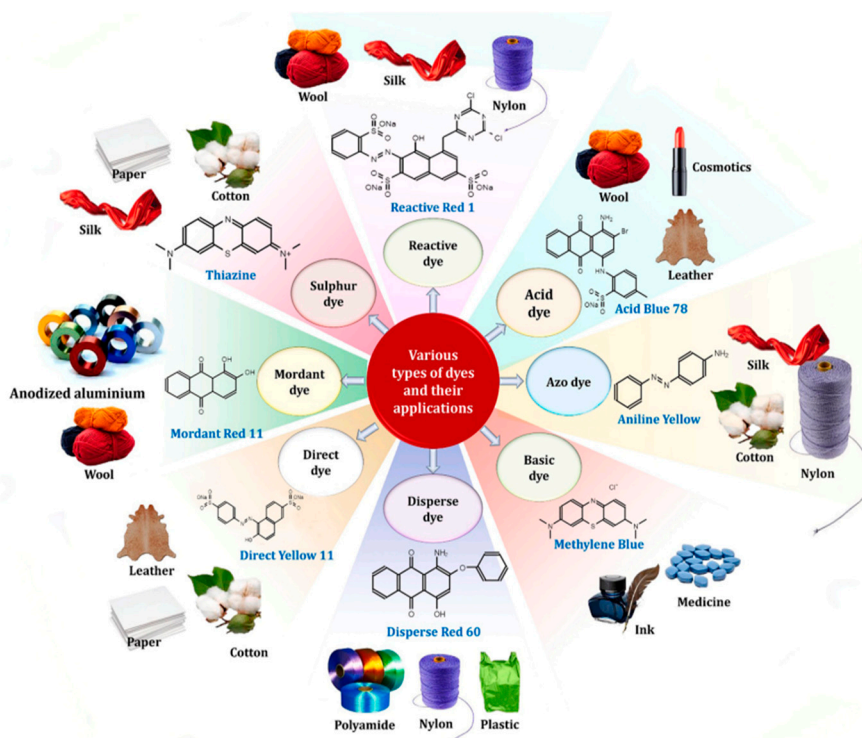
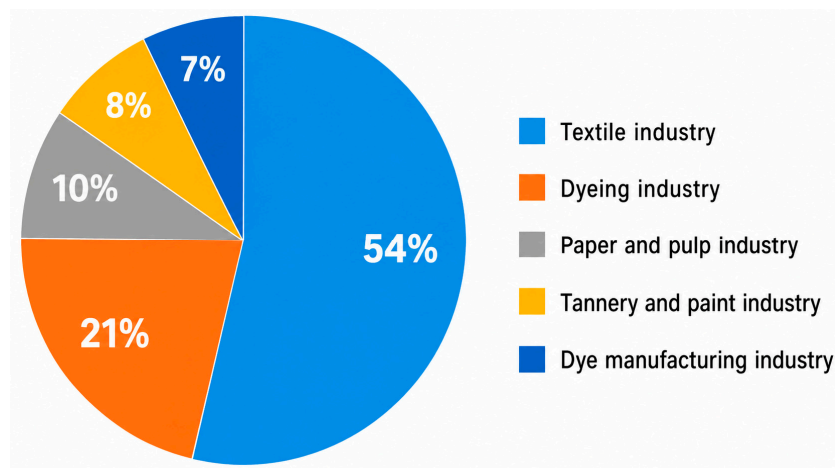


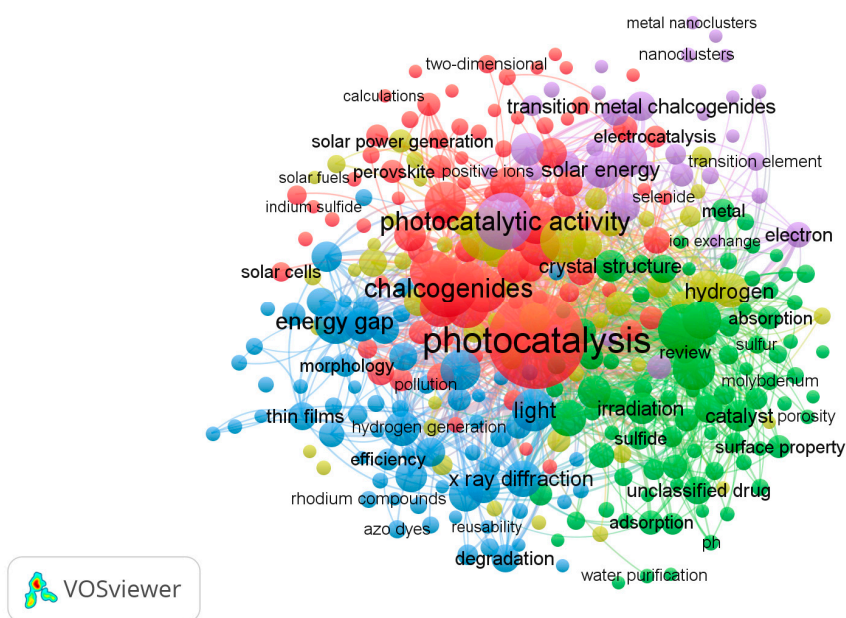
Figure 1: Different types of dyes and their uses [14].

Over 175,000 t of dyes are discharged into worldwide water resources annually. Fig. 2a shows the contribution of different industries towards dyes discharge into the environment as textile industries are accountable for 54% of the generation of dye effluents, and dyeing industries discharge nearly 21% of dyes into the environment. Further, 10% of dyes pollution is caused by paper and pulp industries, while tannery and paint industries result in 8% discharge of dyes. The remaining 7% of dye effluents are sourced from manufacturing industries [15,16]. Compared with the other sectors mentioned above, the textile industry is responsible for nearly two thirds of waste dye production, posing a serious threat to water resources and economic development. Globally, approximately 10,000 textile dyes are listed in the Colour Index, and their production and discharge have substantial environmental impacts, particularly on water quality [17–29]. To place this review within the broader research landscape, a bibliometric network was generated using Scopus metadata published between 1990 and 2026. The analysis used the keywords “chalcogenide,” “photocatalysis,” “dye,” and “water pollution.” The close association of “visible light,” “heterojunction,” and “chalcogenide” indicates growing interest in narrow band gap materials for improved solar light utilization. These trends

support the focus of this review on chalcogenide based photocatalysts for sustainable dye degradation (Fig. 2b).



(a)



(b)

Figure 2: (a) Industries responsible for water pollution [30] effluent and (b) bibliometric analysis via scopus database.

1.1 Need for Dye Removal

Certain synthetic dyes and their degradation products may exhibit carcinogenic, mutagenic, and other toxic effects, posing potential risks to human health and aquatic ecosystems. They are persistent towards degradation due to complexity in structure [31,32]. They adversely affect the aquatic life due to their intense colour by screening or inhibiting the sunlight penetration into the photic zone of the aquatic system, thus affecting the photosynthesis rate of the phytoplankton [33–38] even at their low concentration [39]. Methylene blue dye is well known for reducing photosynthetic rate in aquatic plants

when present in water systems and is carcinogenic in nature [40,41]. When dyes accumulate in a food chain, they resist the process of biological degradation of decaying matter obtained from organisms like bacteria, plankton, and fungi [42,43]. They also affect the rate of development and prevent the growth of aquatic macrophytes [44–48]. In humans, they are mainly responsible for causing serious health problems like skin rashes, headaches, nausea, diarrhea, fatigue, pain in muscles and joints, difficulties in breathing, heart issues, and unusual cancer (Fig. 3) [30,49]. Extensive studies have been carried out regarding dyes and their toxicity to the environment and human life [28,50,51].

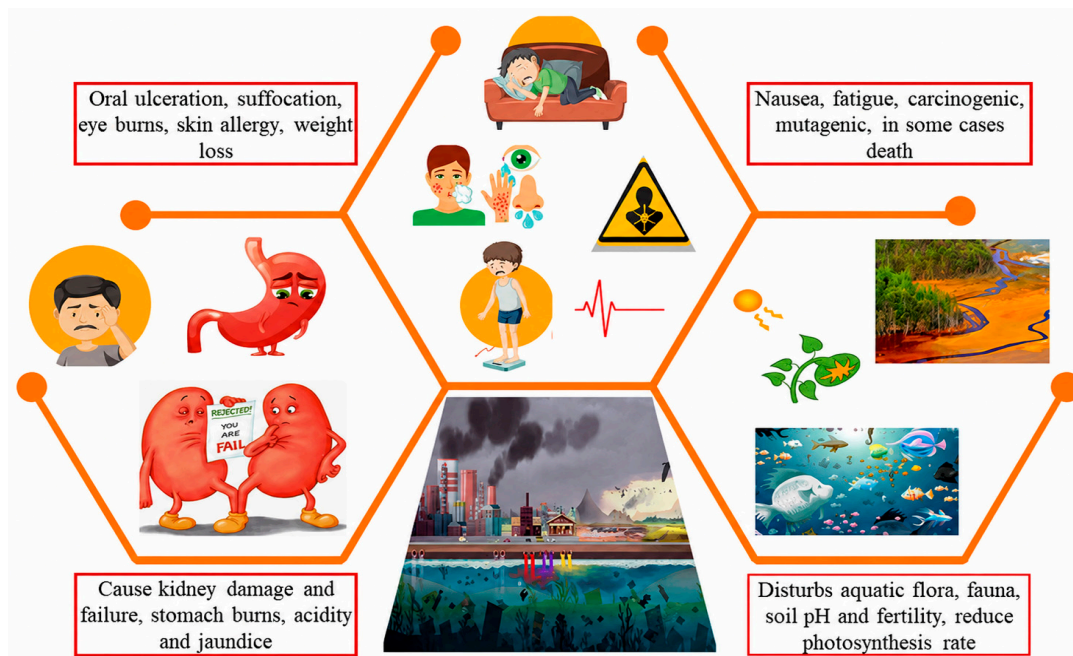


Figure 3: Schematic illustration of dye effluents discharged into water system from industrial.

One of the most toxic categories of dyes is azo dyes, which have extensive uses in textile industries [52–54] and are accountable for severe ecotoxicological problems that affect soil quality and crop germination rates. These dyes also affect aquatic life as they adversely affect life of aquatic fish and their predators [55]. Their greater stability, solubility, and the higher compositional ratio of aromatic rings in their structure make them resistant to degradation and, hence, removal from polluted water. The majority of these dyes are non-biodegradable under aerobic conditions [56–59]. In addition to azo dyes, many other dyes adversely affect human life and the environment. Disperse Red 1 dye is responsible for mutagenic changes in human hepatoma (HepG2) cells and human lymphocytes [60].

Further, damage to DNA is caused by Disperse Orange 1 dye, which is responsible for replacing base-pair and frameshifting mutations that alter the reading frame [61]. Azure B also resulted in causing variations in DNA helical structure [62] and is an inhibitor of monoamine oxidase A and glutathione reductase that, in turn, directly affects the central nervous system [63] and cellular redox equilibrium of humans, respectively [64]. This dye is also responsible for apoptosis when it comes in contact with HepG2 cells [65]. Similarly, the formation of carcinogenic amines take place due to Direct Blue 14 and Disperse Yellow 7 [66]. The carcinogenic and mutagenic nature of Basic Red 9 [67] and Crystal Violet dye also reported earlier [68]. Many other dyes, as Reactive Green 19, Disperse Red 1, and Reactive Blue 2, imparts genotoxic effects on human health [69]. Dyes present in water make water highly coloured, increase in

biological oxygen demand (BOD), total organic carbon (TOC) and chemical oxygen demand (COD) thus affecting both water quality and aquatic flora and fauna [14].

1.2 Conventional Techniques for Dye Removal

In view of dye toxicity, it is crucial to treat dye-loaded polluted water [70–72] using some efficient and promising techniques [6,73,74]. Numerous techniques for treating dye-loaded wastewater have been developed that belong to biological, chemical, or physical categories [29]. Electrodialysis [75], photocatalysis [39,71,76–79], nano filtration [80], electro-flotation [81], electro-oxidation [52,53], coagulation-flocculation, reverse osmosis [54], ozonation [82], colloidal manganese dioxide oxidation [83,84], ion exchange [85–88], anaerobic-aerobic [89], adsorption, membrane extraction [90] besides combined techniques [91] are some of the developed techniques that are put into action to resolve the issue of water pollution [92]. Although considerable efforts have been made to apply these techniques for polluted water treatment, their practical use remains limited because of the high costs of chemicals, infrastructure, and technical expertise [73,93–96]. Furthermore, some of these methods generate degradation products or secondary pollution in the form of sludge and require considerable energy input [73,97]. Some limitations of conventional techniques have been outlined in Fig. 4.

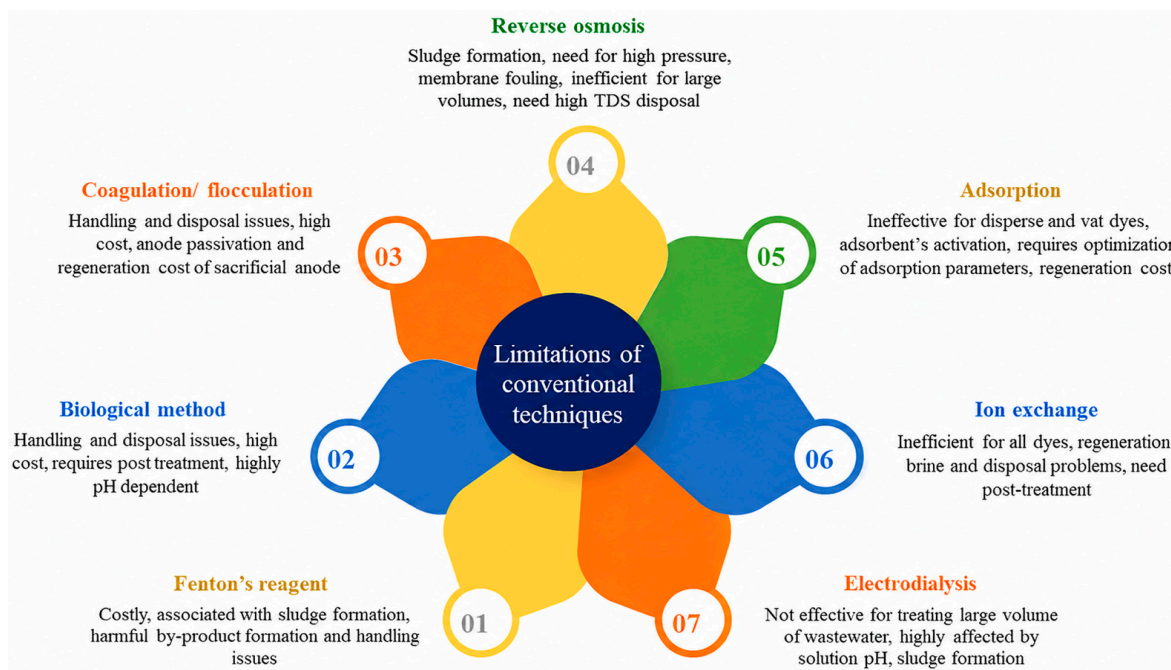


Figure 4: Limitations of some traditional dye removal techniques.

1.3 Why Photocatalysis?

Nowadays, the technology named photocatalysis has been discovered and studied by many researchers in detail and is of great consideration for efficient dye removal [43] owing to its low cost, less energy requirement, eco-friendly nature, and use of reusable and chemically stable catalysts (Fig. 5) [98–101]. Photocatalysis can promote the degradation and, under suitable conditions, the mineralization of organic pollutants into simpler products such as carbon dioxide and water; however, intermediate degradation products may also be formed during the process. This can be significantly enhanced by using some oxidizing agent like hydrogen peroxide [102,103].

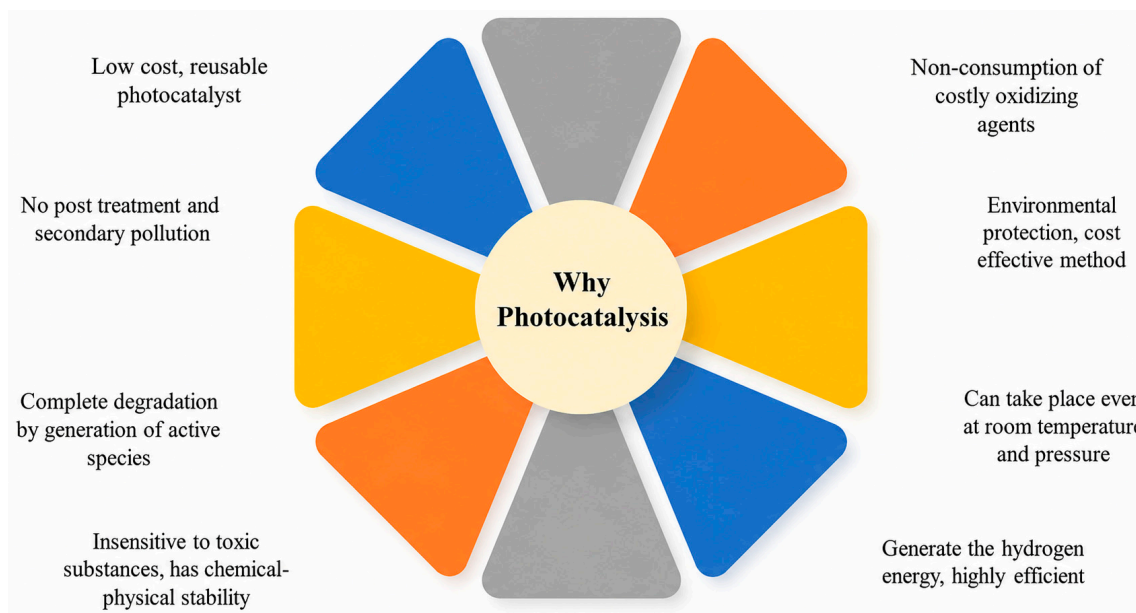


Figure 5: Advantages of photocatalysis over traditional dye removal techniques.

Several kinds of semiconductor catalysts like TiO_2 and ZnO are extensively employed as photocatalysts owing to their non-toxic, cost-effective nature and effectiveness in photo-corrosion [104]. Regardless of their merits, their uses as photocatalysts are limited because of their large band gap, which causes a greater absorption of only UV light (i.e., 4% of solar energy) [105–108]. Much research has been conducted to develop novel materials with narrow band gap energy. Among all kinds of catalysts used, chalcogenides glasses are of widespread interest owing to their extraordinary characteristics such as less hazardous nature, less band gap energy, and cost-effective nature (Fig. 6) [109,110]. Chalcogenides are synthesized using various methods, i.e., solvothermal, sol-gel, hydrothermal methods, etc. Meanwhile, the melt-quenching method of chalcogenides synthesis is widely employed [111–113].

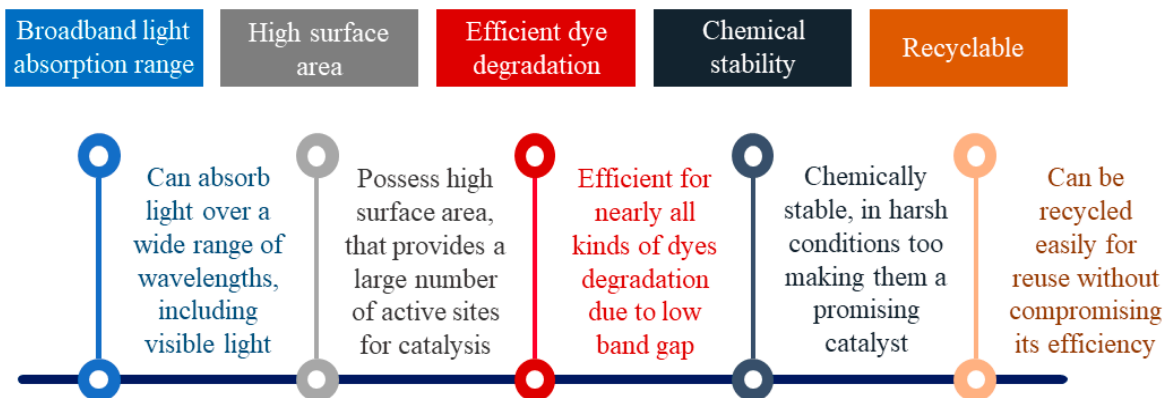


Figure 6: Characteristic properties of chalcogenide for their use as a promising photocatalyst.

Various kinds of chalcogenide combinations (ranging from binary to quaternary) were employed to treat contaminated water [114–119]. Each kind of combination has its own merits as well as demerits [120,121]. Chalcogenide compounds comprise one chalcogen anion and one electro-positive atom [122]. These are classified as binary (combination of one chalcogen and one electropositive element), ternary (combination of one electropositive atom with two chalcogens, i.e., $\text{S}^{2-}/\text{Se}^{2-}/\text{Te}^{2-}$), and quaternary (one electropositive

atom and three chalcogens or two electropositive atom and two chalcogens or three electropositive atoms and one chalcogen atoms). Different binary compounds are used for dye degradation, but their uses are limited due to the presence of floppy mode and large band gap. This floppy mode makes the system weak, and the system remains in a 2D network. The photocatalytic activity of ternary chalcogenide is greater than that of binary glasses because the presence of three elements causes a delay in the e^-/h^+ pairs' reunion, which is a limitation of binary chalcogenide. Photocatalytic activity of quaternary chalcogenide is more significant compared to binary and ternary glasses because the presence of three elements causes a delay in the e^-/h^+ pairs' reunion [107]. For best photocatalytic efficiency, doping with some kind of elements such as rare earth doped chalcogenides attracts researchers' attention owing to the narrow band gap (active in red-orange-green besides IR region) that makes them efficient for absorption of visible light within the range of 500–800 nm [114,123–125].

Under this context, an attempt is made in this review to provide detailed knowledge of dyes, their side effects on natural ecosystems along with some conventional techniques for dye removal, focussing mainly on photocatalytic degradation of dyes employing chalcogenide glasses as the best alternative to other catalysts. It was found that chalcogenide applications for photocatalysis have not been discussed properly previously [114]. Thus, there is a need to explore the efficiency of chalcogenides in a more effective way to treat dye-loaded wastewater [115]. This review paper will help in better management of textile wastewater with a view to working towards environmental safety. Previous reviews [107,126,127] have discussed crystalline metal chalcogenides for organic pollutant degradation and have provided broader accounts of chalcogenide photocatalysts and their water purification applications. Building on this literature, the present review adopts a more focused approach by comparing binary, ternary, and quaternary chalcogenide systems reported for dye degradation. Particular attention is given to the relationship between composition, band gap, irradiation conditions, degradation performance, stability, and practical limitations. Thus, this review complements existing publications by organizing the available evidence specifically around the suitability of chalcogenide alloys for photocatalytic dye treatment.

2 Photocatalysis and Its Mechanism

Photocatalysis is defined as the process that involves the absorption of light photons with energy equal to or greater than the photocatalyst band gap, resulting in the formation of electron-hole pairs. These pairs then take part in the oxidation-reduction reactions with species that get adsorbed on the surface of the catalyst, thereby resulting in dye degradation. Overall, the mechanism of dye degradation using photocatalysis mainly comprised of three key steps [128]:

Step 1: Electron-hole pair generation

In the first step, the photocatalyst absorbs light photons that possess energy higher than the energy of the bandgap in the catalyst. Once the light photons are absorbed, they result in exciting electrons from the valence to the conduction band (CB), resulting in the production of holes in the valence band (VB) behind.

Step 2: Oxidation-reduction reactions

The CB electrons and VB holes are in their active form and can actively react in different oxidation-reduction reactions with the pollutant or water species that get adsorbed on the catalyst.

Step 3: Pollutant degradation

Once the redox reactions take place on the catalyst surface, they result in the formation of highly reactive hydroxyl radicals. These radicals then react with the adsorbed pollutant molecules, leading to their conversion into simpler inorganic products.

The nature of the catalyst and its surface plays a key role in removing dyes by photocatalysis. As a general observation, the rate of photocatalysis is directly proportional to the catalyst surface. Generally, the degradation mechanism of dyes can be divided into two types, mainly direct and indirect photocatalytic mechanisms. Details of each mechanism have been summarized below.

2.1 Direct Mechanism of Photocatalysis

Two types of methods/models have been applied to explain the direct photocatalysis mechanism: Langmuir developed the adsorption isotherm in 1918. The Langmuir–Hinshelwood model subsequently incorporated Langmuir-type adsorption into a surface-reaction kinetic framework and is widely used to describe heterogeneous photocatalytic degradation [129] (Fig. 7). In the Langmuir Hinshelwood mechanism, dye molecules first adsorb onto the photocatalyst surface. Light irradiation then generates electrons and holes, which produce reactive radicals on the same surface. These radicals react with the adsorbed dye molecules and gradually convert them into simpler products. Thus, adsorption of the dye on the catalyst surface is an essential step in this mechanism [130]. The equation that best describes Langmuir-Hinshelwood model for dye degradation has been summarized below as [131]:

$$r = \frac{K_a K_c C_o}{1 + K_a C_o}$$

here, K_a refers to the constant of adsorption while K_c represents specific rate constant, and initial pollutant concentration can be expressed as C_o [132].

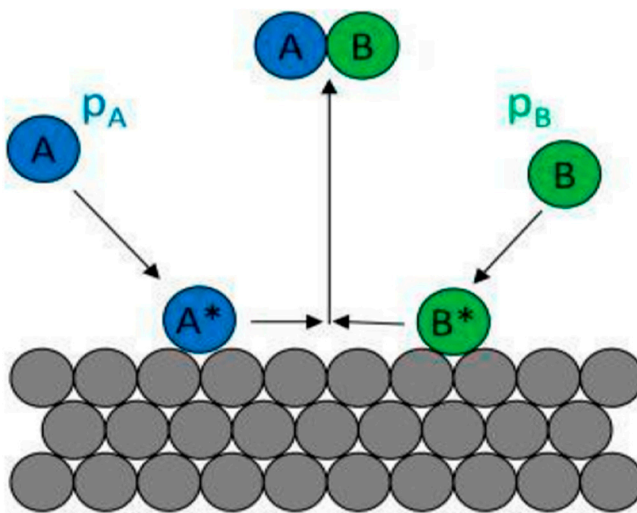
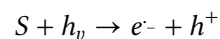
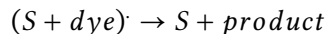
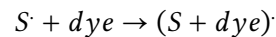
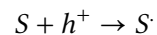


Figure 7: Illustration of adsorption process by Langmuir–Hinshelwood mechanism [132].

The Eley–Rideal mechanism, originally developed for heterogeneous surface reactions, has also been applied to describe photocatalytic degradation processes, Fig. 8. In the Eley Rideal mechanism, the dye does not need to be adsorbed on the catalyst surface. Instead, a dye molecule present in the solution reacts directly with a reactive species or hole generated on the illuminated catalyst surface. The resulting intermediate species are subsequently degraded into simpler products [132]. The key reactions involved in this method include [133]:





here, h_ν , S , e^- and h^+ represents light intensity, catalysts surface, electron as well as hole, respectively. The dot (.) in above equations refers to the radical species [134].

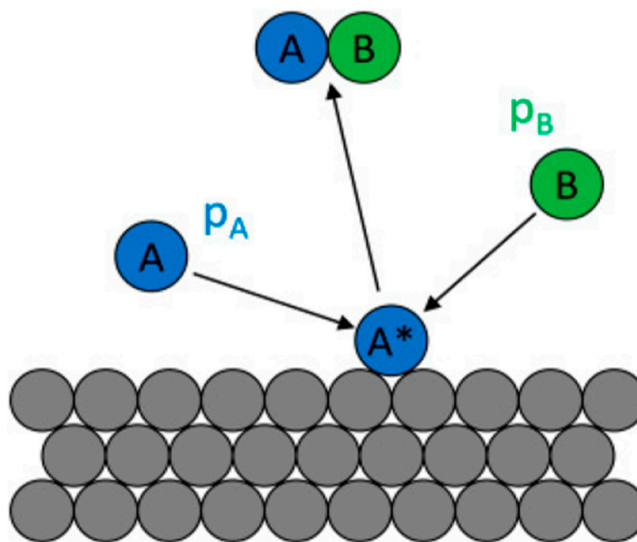
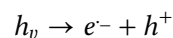


Figure 8: Illustration of adsorption mechanism proposed by Eley-Rideal [132].

Therefore, the main difference is that the Langmuir Hinshelwood mechanism requires dye adsorption, whereas the Eley Rideal mechanism allows dye molecules in the solution to react directly with surface species.

2.2 Indirect Photocatalysis Mechanism

In addition to the direct photocatalysis method, another method proposed for dye degradation is an indirect method, in which both electrons as well as holes are generated by the absorption of light photons on the catalyst (Fig. 9). Once the light photons (that possess energy higher than the band gap energy of the catalyst) get absorbed, it results in the generation of the electron-hole pair, as represented in the below equation [135]:



The first step of indirect photocatalysis is the excitation of electrons (after absorption of light photons) from VB to CB. This excitation leads to the generation of holes (h^+) on the VB, but a charge carrier (e^-) on CB. This was followed by dissociating water molecules by its reaction with generated holes yielding hydroxyl radicals. These radicals then undergo a reaction with pollutants that get adsorbed on the catalyst surface, resulting in the formation of a chain of radicals by using oxygen. These result in the formation of simpler and inorganic substances, mainly carbon dioxide and water. During photocatalysis, photogenerated

electrons in the conduction band are transferred to molecular oxygen adsorbed on the catalyst surface, reducing O_2 to superoxide radical anions ($O_2^{\bullet-}$):

$O_2 + e^- \rightarrow O_2^{\bullet-}$. The generated superoxide radical anions can undergo protonation to form hydroperoxyl radicals ($HO_2^{\bullet}$), which may subsequently lead to the formation of hydrogen peroxide (H_2O_2) [43].

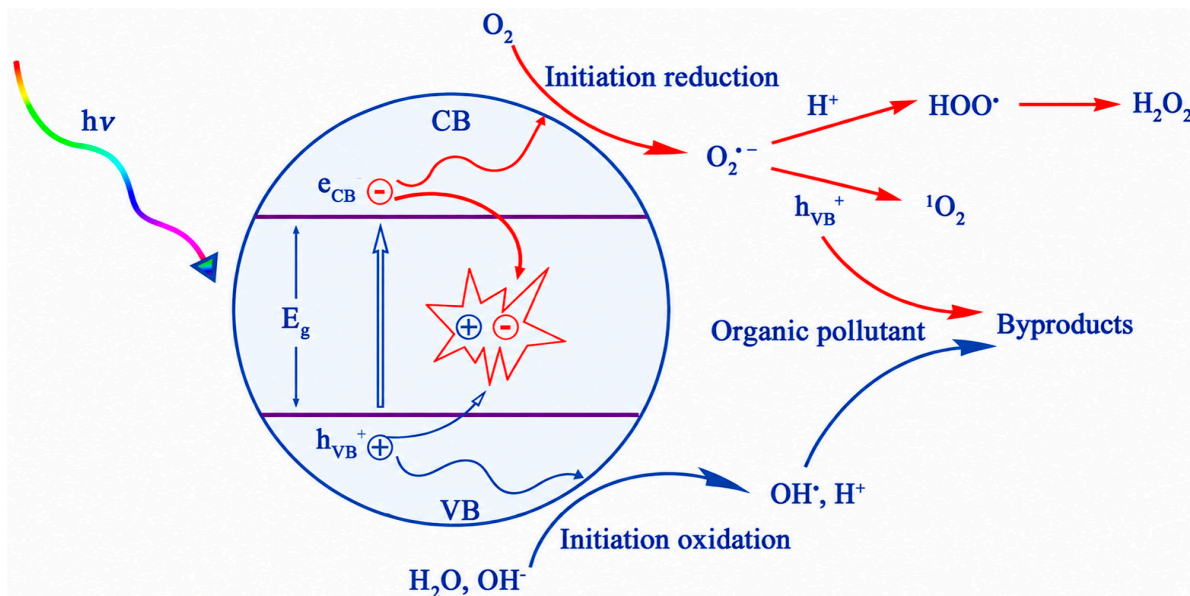


Figure 9: Mechanistic degradation of dye shows different types of oxidation and reduction reactions [43].

2.3 Factors Affecting Photocatalytic Degradation

Various factors may affect the degradation efficiency of the catalyst and, hence, the photocatalytic rate. These factors may include pH, temperature, light intensity, photo-catalyst dose, dye dosage, besides the shape of the catalyst (Fig. 10).

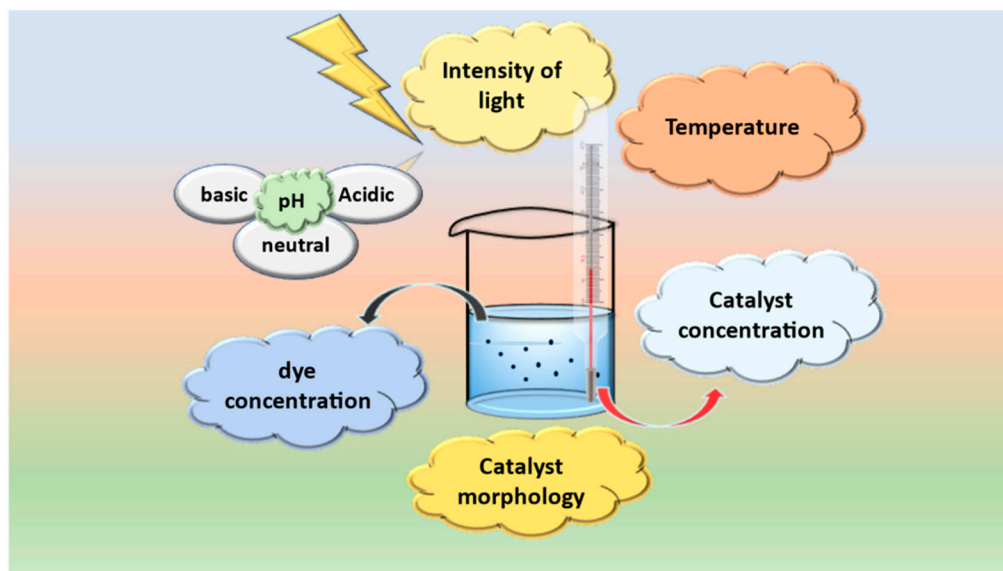


Figure 10: Schematic representation of the different factors influencing the rate of photocatalytic degradation [38].

2.3.1 Effect of Solution pH

Among these factors, the effect of solution pH is crucial as it affects the surface charge of the catalyst and dye molecules. Additionally, varying solution pH will affect the aggregate size of the catalyst along with the CB and VB position, thereby altering the ionic interactions taking place between substrate, catalyst, and generated radicals during the photocatalytic process [132].

2.3.2 Effect of Initial Dye Concentration

Photocatalysis is influenced by the adsorption of dyes onto the surface of the photocatalyst. Only the dye molecules adsorbed on the surface participate in the photocatalytic process, while those in the bulk solution do not contribute. The adsorption of dyes is dependent on their initial concentration, making it a crucial factor to consider in photocatalytic reactions.

Typically, the percentage of dye degradation decreases as the initial dye concentration increases, assuming a constant amount of photocatalyst. This can be explained by the fact that as the dye concentration increases, more organic substances are adsorbed onto the surface of TiO_2 . However, fewer photons are available to reach the catalyst's surface, resulting in the formation of fewer hydroxyl radicals ($\cdot\text{OH}$). This decrease in $\cdot\text{OH}$ production leads to a lower percentage of dye degradation [136]. A study conducted by Chen et al. in 2007 [137] revealed that malachite green (MG) dye adsorption on the catalyst surface decreased when the charge carriers recombination took place, while on the other hand, this efficiency increased due to the charge transfer process taking place at the interface of the catalyst [137].

2.3.3 Effect of Photocatalyst Dosage

Furthermore, the quantity of photocatalysts significantly impacts dye degradation. As the catalyst amount increases, so does dye photodegradation, a characteristic feature of heterogeneous photocatalysis. This enhancement is attributed to an increase in the number of active sites on the catalyst's surface, leading to a greater production of $\cdot\text{OH}$, which is essential for dye discoloration. However, beyond a certain catalyst concentration, the solution becomes turbid, obstructing UV radiation and hindering the reaction process, resulting in a decline in degradation efficiency [138]. The photodegradation of methyl orange dye was investigated at varying photocatalyst concentrations. The results demonstrated a direct correlation between the amount of photocatalyst and the percentage of dye degradation. As the catalyst dosage increased, so did the efficiency of methyl orange photodegradation [136].

2.3.4 Effect of Catalyst Surface Morphology

The surface morphology of a photocatalyst, including particle size and agglomerate size, is a critical factor in photocatalytic degradation processes. This is due to the direct relationship between organic compound adsorption and the surface area of the photocatalyst [139]. The number of photons that reach the photocatalyst's surface directly influences the reaction rate, emphasizing that photocatalysis occurs primarily in the adsorbed phase of the material [140]. The photodegradation of methyl red dye was investigated using both pure Titania and Cu-modified Titania nanocomposites. The results indicated that Cu-modified Titania exhibited significantly higher photodegradation efficiency compared to pure Titania. This enhanced performance can be attributed to the distinct surface morphology of Cu-modified Titania. Its rough and zigzag surface structure facilitates the adsorption of organic molecules onto the catalyst's surface, leading to improved photocatalytic activity [141,142].

Since the groundbreaking work of Honda and Fujishima in 1972 on water splitting using n-type TiO_2 electrodes, extensive research has been conducted to explore suitable photocatalytic materials [143].

Numerous semiconductors, including TiO_2 , CdS , and ZnO , have been developed for water treatment, particularly dyes degradation [144]. TiO_2 is widely regarded as the most extensively used photocatalyst due to its abundance, exceptional chemical stability, and non-toxicity [123]. However, TiO_2 suffers from several limitations, including insufficient visible light absorption due to its wide bandgap ($E_0 = 3.2 \text{ eV}$), rapid recombination of photoexcited charge carriers, and a high rate of reverse reactions [145].

To address these challenges, various strategies have been employed to enhance TiO_2 's photocatalytic activity [146]. One approach involves modifying TiO_2 with noble metals (e.g., Pt, Pd, Au, Ag), transition metals (e.g., Cu, Ni), their oxides (e.g., NiO , CoO_x), or by dye sensitization. Another strategy is to construct heterojunctions with other semiconductors. Many studies have utilized noble metals and their oxides as potential co-catalysts to improve TiO_2 's photocatalytic performance. However, the high cost of noble metals has led to a growing interest in exploring non-noble metal co-catalysts as a more affordable alternative [147,148]. Metal chalcogenides, including CdS , CuS , MoS_2 , and ZnS , have gained significant attention in recent years due to their impressive photocatalytic performance in water splitting and wastewater treatment. These materials possess narrow bandgaps, favorable physical and chemical structures, adequate thermal stability, and a strong response to visible light, which collectively contribute to their exceptional photocatalytic properties [147,149,150].

3 Chalcogenides as Promising Photocatalytic Materials

Chalcogenide glasses are amorphous inorganic materials composed primarily of elements from Group VI, including selenium (Se), sulfur (S), and tellurium (Te). These elements are known as lone-pair semiconductors and form the basis of chalcogenide (ChG) materials. Chalcogenides are compounds containing at least one chalcogen element and one electropositive element. They often include sulfides, selenides, and tellurides and can exist in crystalline, non-crystalline, or amorphous states. Chalcogenides exhibit remarkable electronic, optical, and semiconducting properties, characterized by unique features such as bending, self-organization, and photo-darkening [151].

Many types of research are conducted to develop novel materials having narrow band gap energy, and chalcogenides are compounds with narrow band gap energy [106]. These compounds comprise one chalcogen anion and one electro-positive atom [122]. They are of widespread interest owing to their extraordinary characteristics such as less hazardous nature, less band gap energy, and cost-effective nature [109,110]. Different kinds of synthesis procedures, like solvothermal [120], hydrothermal [113], and sol-gel [112] procedures, are employed for chalcogenide synthesis. Chalcogenide-based photocatalysts have a narrow band gap, and when they interact with light, they generate electron-hole pairs. These generated e^- move to the catalyst's conduction band, leading to the generation of h^+ . Reaction of e^- with adsorbed oxygen molecule at the catalyst surface generates reactive oxide radicals O_2^- . While in the valence band, the reaction of h^+ with oxygen generates hydroxyl radicals. Both hydroxyls, as well as oxide radicals, are accountable for organic/inorganic pollutants and biological pollutants degradation [152]. Fig. 11 shows the uses of chalcogenide as a photocatalyst.

When synthesizing chalcogenide-based photocatalysts for photocatalytic applications, several critical factors must be considered. Firstly, the substances must possess a high light-harvesting capacity, which can be achieved by tuning their bandgap energy to absorb visible light. Secondly, efficient separation of photo-induced charge carriers is essential to prevent recombination and maximize photocatalytic activity. Additionally, the charge carriers must be able to migrate effectively to the catalyst's surface to participate in chemical reactions. Furthermore, the growth and composition of the synthesized materials should be carefully controlled to ensure a high surface area-to-volume ratio, which increases the number of active

sites and enhances photocatalytic performance. Finally, the materials must exhibit stability under varying conditions to prevent photo-corrosion and maintain their photocatalytic properties over time [107].

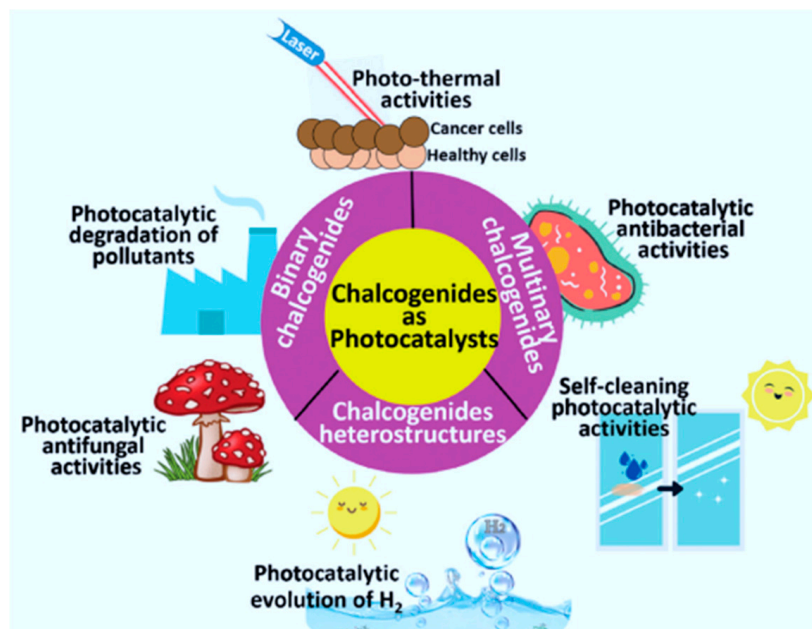


Figure 11: Applications of chalcogenides as photocatalyst [107].

3.1 Types of Chalcogenide Catalyst, Mechanism, and Their Applications

Chalcogenide glasses are classified into different categories based on their composition, including binary, ternary, and quaternary forms. The properties of chalcogenide glasses, such as their thermal, optical, and structural characteristics, are influenced by their specific composition.

Binary chalcogen glasses are composed of two elements: a chalcogen and an electropositive element. Pure selenium (Se) has a structural arrangement consisting of long helical chains and eight-membered rings. However, when an electropositive element is introduced into Se, the eight-membered ring structure is disrupted, forming a crosslinked structure with enhanced network strength due to the presence of the electropositive element. Raman and IR spectroscopy were used to study the structural properties of chalcogen glasses. Using these techniques, different authors studied the structure of chalcogenide glasses [153–164]. Thermal properties represent variation in material behaviour by changing temperature. Glass transition and thermodynamic properties of the glassy alloy were studied using DTA and DSC, which provide a detailed view of glassy alloys' thermal properties. The thermal properties of glass alloys have already been studied by various authors [165–186]. Optical properties describe the interactions between light and matter. These interactions can be quantified using the dielectric response, which is expressed in terms of the extinction coefficient, absorption coefficient, and refractive index. Numerous researchers have investigated the optical properties of chalcogenide glasses, focusing on these key parameters [187–200].

Binary chalcogenide glasses are widely used in wastewater treatment due to their photocatalytic properties [201]. Ain et al. synthesized hexagonal CuS nanoplates with a bandgap energy of 2.1 eV [202]. The photocatalytic efficiency of these nanoplates was evaluated using Congo red dye degradation under light irradiation. The results demonstrated optimal degradation of Congo red using CuS nanoplates with a contact time of 40 min. Additionally, Cu₂Se chalcogenide, possessing a bandgap of 2.25 eV, exhibited effective methylene blue dye degradation of approximately 98.2% when exposed to visible light for one

hour [107]. Khan et al. examined the efficacy of the Sono-chemically synthesized Ag_2Se glass system for photocatalytic treatment of A549 tumor cells in mice. Their findings revealed effective tumor cell reduction within a month [203]. Qiu et al. investigated the photocatalytic immobilization of *E. coli* using In_2S_3 (bandgap of 2.25 eV), achieving notable results. Upon interaction with light photons, the photocatalyst (in the valence band, VB) generates electron-hole (e^-/h^+) pairs. These generated electrons migrate to the conduction band (CB), leading to the creation of holes in the valence band. The reaction between electrons and adsorbed oxygen molecules (in the CB) at the catalyst surface results in the formation of reactive oxygen radicals. Simultaneously, holes in the valence band react with oxygen to produce hydroxyl radicals. Both hydroxyl and oxide radicals contribute to the photocatalytic activity of chalcogenides [152]. The conduction band (CB) and valence band (VB) of binary chalcogenides are significantly influenced by the metal orbital (d-orbital of transition metals) and the p-orbital of chalcogen, respectively.

Thomas et al. (2021) degraded malachite green (MG) dye under sunlight from wastewater by using ZnS nanostructures synthesized by hydrothermal method. XRD analysis confirmed the pure cubic zinc blende phase of ZnS nanostructures, with no impurities, and crystallite size and lattice strain were measured using the Debye-Scherrer and Williamson-Hall methods. The optical properties of ZnS nanostructures were successfully studied, revealing a temperature-dependent decrease in energy band gap, ranging from 3.513 to 3.386 eV. XPS analysis of the synthesized ZnS sample confirmed the chemical states of Zn and S within the structure. The XPS spectrum reveals peaks at 1021.5 eV and 1044.5 eV, due to $\text{Zn}2p_{3/2}$ and $\text{Zn}2p_{1/2}$, confirming the incorporation of Zn within the ZnS crystal structure. FESEM images exhibited agglomerated, irregular nanoparticles, while EDS confirmed Zn and S presence, along with minor oxygen impurities from unreacted salts. Photocatalytic degradation reached 74.25% efficiency after 240 min of solar irradiation, following first-order kinetics, with degradation rates improving with increased solar light intensity and reduced particle size. The ZnS photocatalyst shows strong reusability with minimal efficiency loss over three cycles, indicating good cyclic stability and suitability for repeated use in practical applications [204]. Further, Bhat et al. (2024) synthesized Ce-doped FeSe_2 nanomaterials with 5% and 7% Ce via a hydrothermal method to evaluate their photocatalytic efficiency observed for the removal of Rhodamine B dye under visible light. FE-SEM revealed a cauliflower-like morphology in pure FeSe_2 (~53.54 nm spheres), while XRD confirmed a pure orthorhombic phase with high crystallinity and successful Ce incorporation without impurities. UV-Vis spectrophotometry showed strong absorption at 345 nm, with band gaps of 1.78 eV (FeSe_2), 1.70 eV (5% Ce- FeSe_2), and 1.66 eV (7% Ce- FeSe_2). Electrochemical analysis (CV and EIS) showed oxidation-reduction peaks, with the 7% Ce-doped sample (FS-7) exhibiting the lowest charge transfer resistance, enhancing its charge transport and catalytic efficiency. FS-7 achieved a high Rhodamine B dye degradation rate of 95.21% within 120 min under a 70 W mercury lamp, making Ce-doped FeSe_2 a promising photocatalyst for textile wastewater treatment [205].

Chand et al. (2023) synthesized a Zinc Indium Sulfide (ZIS) photocatalyst using a simple aqueous solution method, Demonstrating its photocatalytic activity by degrading both cationic (Malachite Green, MG) and anionic (Congo Red, CR) dyes under sunlight. XRD analysis confirmed the predominant hexagonal phase of ZIS, while Raman spectroscopy showed bands at approximately 123, 300, and 350 cm^{-1} , supporting the formation of hexagonal ZnIn_2S_4 . EDX analysis verified near-stoichiometric composition with Zn, In, S, and trace O. FESEM micrographs revealed a porous microsphere morphology (1–4 μm) with petal-like structures. The highest degradation efficiencies achieved were 96.33% for MG and 99.79% for CR under sunlight, following pseudo-second-order kinetics. Reusability tests showed stability, with MG degradation efficiency declining from 94.97% to 85.62% over five cycles [206]. Khan et al. (2018) synthesized cobalt sulfide nanostructures (CoS NS) via facile precipitation. Its photocatalytic degradation of various dyes,

including methylene blue (MB), rhodamine B (RhB), Nile blue (NB), crystal violet (CV), and Congo Red (CR). Characterization techniques revealed distinct differences between two synthesized materials, CS-3 and CS-4. XPS analysis indicated that CS-3 primarily consisted of CoS with Co^{2+} ions, while CS-4 comprised Co_4S_3 with Co^{3+} and Co^{2+} ions, suggesting partial surface oxidation. Mott-Schottky plots revealed p-type behaviour for both materials. The degradation percentages of various dyes using CS-3 catalyst were as follows: Methylene Blue (MB) showed a degradation percentage of 99.8%, while Rhodamine B (RhB) and Nile Blue (NB) showed degradation percentages of 99.5% and 99.8%, respectively. Additionally, Crystal Violet (CV) exhibited a degradation percentage of 99.4% [207].

Furthermore, Kaur et al. (2017) synthesized Iron Disulfide (FeS_2) using an effective hydrothermal method for visible light-assisted photocatalytic remediation of two industrial dyes: Methyl orange and Novacron Yellow Huntsman from wastewater. The FeS_2 nanoparticles are crystalline, predominantly in the cubic pyrite phase, with high purity (39.42% sulfur, 60.57% FeS_2). XRD analysis revealed an average crystallite size of 26 nm. TEM images revealed that the FeS_2 nanoparticles are spherical, approximately 30 nm in size, and agglomerated. HRTEM analysis showed a lattice spacing of 0.25 nm, corresponding to [208] planes of FeS_2 . FTIR spectrum displayed O-H stretching at 3418 cm^{-1} and 3287 cm^{-1} , indicating water absorption, and S-O stretching at 1133 cm^{-1} and 1021 cm^{-1} . A peak at 624 cm^{-1} corresponds to the disulfide stretch of FeS_2 . The synthesized FeS_2 nanoparticles exhibited a band gap near the higher end of the reported range (0.7–2.6 eV), resulting in a shift of the absorption band toward higher energy (lower wavelengths), as confirmed by the UV-visible absorption spectrum. FeS_2 demonstrated strong photocatalytic activity, achieving 93.09% degradation of MO in 120 min and 98.15% removal of NYH in 80 min of visible light irradiation [209]. Muneeb et al. (2018) synthesized Sb_2S_3 (antimony sulfide) photocatalyst by hydrothermally and utilized it to degrade MO under visible light irradiation. Photocatalytic activity shows that the maximum degradation 90% of MO dye from water was achieved in the 4 h of sunlight irradiation [210]. Sun et al. (2008) synthesized Sb_2S_3 by a simple method and utilized it to degrade methyl orange dye under visible light. UV-Vis diffuse reflectance spectroscopy indicated that the band gap of Sb_2S_3 was approximately 1.66 eV, making it suitable for visible-light photocatalysis. The photocatalytic performance of Sb_2S_3 nanorods was evaluated by their ability to remove MO under visible light irradiation. The results displayed a 97% degradation of methyl orange in just 30 min of irradiation [208].

Ul Ain et al. (2020) developed a photocatalyst for solar-light-driven removal of Congo Red (CR) dye, an anionic dye. Hexagonal CuS nanoplates were synthesized through a thermolysis process using a single-source precursor and octylamine as solvent. UV-Vis spectroscopy revealed a broad absorption band at 406 nm, indicating a 2.1 eV band gap suitable for visible-light photocatalysis. Maximum degradation of dye CR was achieved within 40 min under solar light and 80 min in the dark [211]. Rafiq et al. (2020) synthesized pure and doped CdS nanoparticles by chemical method and used them to degrade methylene blue (MB) dye under visible light from wastewater. Complete degradation of MB was achieved in 45 min with pure CdS nanoparticles, while doped samples showed superior performance, with Co-doped and Ni-doped samples degrading MB in 20 and 25 min, respectively [212]. Ertis et al. (2017) synthesized metal-doped CdS photocatalysts (Co, Ni, Ce, Sb) using chemical precipitation to synthesize visible-light-active photocatalysts for methylene blue degradation. Metal doping notably enhanced the photocatalytic performance of CdS, with Co-doped CdS exhibiting the highest degradation efficiency of 87% within 4 h under visible light. Degradation efficiencies for Ni-doped, Ce-doped, Sb-doped, and pure CdS were 73%, 76%, 70%, and 68%, respectively, highlighting Co-doped CdS as the most efficient catalyst [213].

Ayodhya et al. (2016) synthesized photocatalysts (CuS nanoparticles) via green solvothermal method with xanthan gum (XG) as a capping agent. Photocatalytic experiments were conducted under three

irradiation sources: solar light, visible light from a 160 W mercury vapor lamp, and UV light from a 12 W UV lamp. The target organic pollutants for degradation were methylene blue (MB), rhodamine B (RB), eosin Y (EY), and congo red (CR). CuS nanoparticles exhibited superior photocatalytic activity under solar light, degrading MB, EY, RB, and CR by 90.29%, 91.97%, 69.23%, and 60.35%, respectively, within 4 h. The irradiation source significantly influenced the photocatalytic performance, with lower efficiencies observed under visible and UV light [214]. In another study, Dalal et al. (2023) synthesized a zinc-sulfide embedded reduced graphene oxide nanocomposite by combining ZnS nanoparticles with rGO through a simple precipitation method. The synthesized nanocomposite was employed for the degradation of Congo red (CR) from wastewater-assisted sunlight. TEM images revealed the formation of ZnS nanoparticles dispersed on the rGO surface. The ZnS-rGO catalyst achieved 98% degradation of CR under sunlight within 120 min [215].

Further, Manikandan et al. (2020) synthesized Graphene Oxide-Based Metal Sulfide (GO/NiS) Nanocomposite via the hydrothermal method, and Graphene Oxide was synthesized via the Hummers method, and NiS prepared by the Co-precipitation method. The photocatalytic performance of the prepared materials was evaluated by their ability to degrade crystal violet dye under sunlight. The nanocomposite (GO/NiS) exhibited enhanced light absorption and a reduced bandgap compared to the individual components shown by UV-Vis analysis. The GO/NiS nanocomposite showed successful integration of NiS nanoparticles onto the GO sheets. Under sunlight irradiation for 70 min, GO, NiS, and GO/NiS degraded CV dye by 90%, 86%, and 93%, respectively [216].

Ternary chalcogenide glasses exhibit superior photocatalytic activity compared to binary glasses due to the presence of three elements, which inhibits the rapid recombination of electron-hole (e^-/h^+) pairs, a common limitation in binary chalcogenides. Depiction of interfacial charge carrier separation and transfer (electrons and holes) in binary, ternary, and quaternary chalcogenides is shown in Fig. 12. Li and colleagues reported the synthesis and photocatalytic properties of $Zn_{0.5}Cd_{0.5}S$ ternary chalcogenide [217]. They observed a significantly higher hydrogen evolution rate of 7.42 mmol/h g, which was 24 and 54 times greater than that of CdS and ZnS, respectively. Ba_2ZnSe_3 (2.75 eV) demonstrated a 20% degradation of RhB dye under Xe lamp irradiation within 240 min [218]. Similarly, $BaAu_2S_2$ (2.49 eV) achieved a 45% degradation of RhB dye using a 1000 W Xe lamp [116]. Ternary $CuFeS_2$ glasses effectively removed tartrazine dye under 85 W fluorescent lamp, exhibiting maximum results after 40 min of contact time. Cu_2WS_4 (bandgap of 2.15 eV) demonstrated exceptional photocatalytic removal of Cr(VI) under a 250 W Xe lamp, achieving 99% metal removal within 150 min [219]. Fe-doped $ZnIn_2S_4$ ternary chalcogenide glasses exhibited photocatalytic activity towards 2,4,6-tribromophenol degradation under UV light (20 W Hg lamp) [220]. Citrate-modified $CuFeS_2$ ternary chalcogenide effectively degraded bisphenol A under 4 W fluorescent lamps, achieving a 97% degradation rate within 60 min [107].

Quaternary chalcogenide materials exhibit superior photocatalytic activity compared to binary and ternary chalcogenides due to the presence of four elements, which further delays the recombination of electron-hole (e^-/h^+) pairs. Additionally, the orbitals involved in the conduction and valence bands of quaternary chalcogenides, such as Cu_2ZnSnS_4 , differ from those in binary and ternary glasses. In Cu_2ZnSnS_4 , hybridized sulfide-p and copper d orbitals contribute to the valence band, while hybridized sulfide-s/p and Sn-s orbitals contribute to the conduction band [107]. Quaternary Cu_2FeSnS_4 thin films (synthesized by spray pyrolysis) demonstrated effective methylene blue dye degradation under both sunlight and Xe light. Thin films of Cu_2FeSnS_4 grown at 240°C achieved an 81% degradation of methylene blue dye in sunlight [119]. Cu_2ZnSnS_4 quaternary chalcogenides exhibited a 90% degradation of rhodamine B dye under a 300 W Xe lamp with a contact time of 2 h [107]. Yuan et al. investigated $MoS_2/Cu-ZnIn_2S_4$ chalcogenide

glasses for photocatalytic hydrogen production under a 300 W Xe lamp (wavelength greater than 420 nm). The results revealed a significantly higher hydrogen evolution rate of 5463 $\mu\text{mol/h g}$ under visible light, which was approximately 72 times greater than that of $\text{Cu-ZnIn}_2\text{S}_4$ alone.

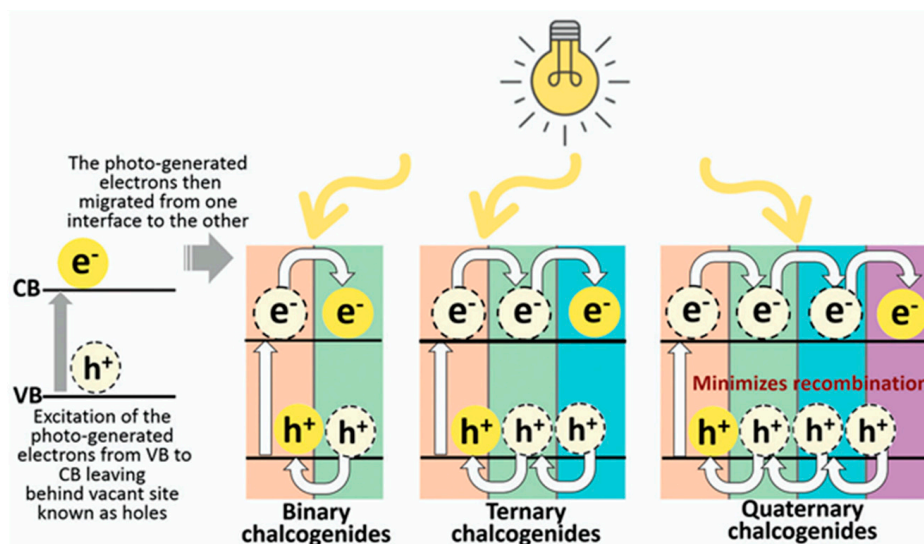


Figure 12: Depiction of interfacial charge carrier separation and transfer (electrons and holes) in binary, ternary, and quaternary chalcogenides.

Nefzi et al. (2020) synthesized $\text{Cu}_2\text{FeSnS}_4$ (CFTS) thin films via spray pyrolysis for photocatalytic removal of methylene blue (MB) dye. XRD analysis confirmed a stannite tetragonal structure with excellent crystallinity, while Raman spectroscopy confirmed the formation of pure stannite CFTS phase, with characteristic peaks at 252 cm^{-1} and 319 cm^{-1} . The peak at 319 cm^{-1} indicated high crystallinity. SEM analysis at 240°C revealed a uniformly covered surface with spherical micro-aggregates. The film synthesized at this temperature exhibited high visible-range absorbance ($\sim 78\%$), an optical band gap of $\sim 1.46\text{ eV}$, and a high absorption coefficient ($\sim 9.8 \times 10^4\text{ cm}^{-1}$). Electrical characterization showed p-type conductivity with improved mobility ($\sim 1.86 \times 10^2\text{ cm}^2/\text{V}\cdot\text{s}$), low resistivity ($0.18\text{ }\Omega\cdot\text{cm}$), and a carrier concentration of $\sim 0.74 \times 10^{17}\text{ cm}^{-3}$, attributed to enhanced crystallinity and surface morphology. Photocatalytic performance, assessed through MB degradation under solar light, demonstrated an 81% degradation rate within 4 h, highlighting the material's potential for water treatment applications [119].

Dileepkumar et al. (2020) synthesized sodium iron disulfide (NaFeS_2), a photocatalytic material, via a hydrothermal approach. The photocatalytic degradation of MB and IC using NaFeS_2 as the catalyst achieved efficiencies of 97% and 99%, respectively. The degradation kinetics revealed half-lives of 14.76 min for MB and 11.12 min for IC, with corresponding TOC removals of 82% and 84%, respectively [221]. Mugumo et al. (2022) synthesized a CuS/ZnS photocatalyst via a one-pot thermal decomposition method for visible-light-driven degradation of rhodamine B. The synthesized material was thoroughly characterized using various techniques. The high purity and crystallinity of the prepared nanoparticles were confirmed by XRD analysis. TEM analysis revealed that nanoparticles of ZnS, CuS, and CuS/ZnS showed the morphologies resembling clustered nanoplates and nanospheres. SEM analysis revealed nanoporous agglomerated morphologies characteristic of ZnS, CuS, and CuS/ZnS . EDX analysis revealed that the CuS/ZnS nanocomposite was composed of Zn (73.84%), S (10.58%), Cu (6.22%), and O (9.25%). CuS and ZnS nanoparticles exhibited photocatalytic degradation rates of 91% and 67%, respectively, under visible light. The CuS/ZnS composite demonstrated

superior performance, achieving complete degradation of rhodamine B within 24 h, showcasing its potential for wastewater treatment applications [222].

Seling et al. (2024) synthesized ultrathin $\text{Bi}_2\text{O}_2\text{S}$ nanosheets via a hydrothermal method, demonstrating their photocatalytic efficiency for degrading anionic Congo Red (CR) and Rose Bengal (RB), from aqueous media. The XRD analysis of $\text{Bi}_2\text{O}_2\text{S}$ nanosheet powder confirmed its orthorhombic phase. UV-Visible DRS spectra indicated a band gap of ~ 1.17 eV, confirming strong visible light absorption suitable for photocatalytic applications. FESEM images confirmed $\text{Bi}_2\text{O}_2\text{S}$ nanosheets with thin, sheet-like structures and lateral dimensions of ≥ 100 nm. EDS analysis verified the elemental composition of bismuth, oxygen, and sulfur in the nanosheets. TEM images revealed isolated nanosheets with weak interlayer forces, highlighting a layered structure that supports separation and reactivity, advantageous for catalytic applications. UV-visible spectra showed that $\text{Bi}_2\text{O}_2\text{S}$ nanosheets substantially improved the photodegradation of CR and RB dyes in visible light irradiation, increasing the degradation efficiency from $\sim 16\%$ and $\sim 49\%$ to $\sim 82\%$ and $\sim 80.6\%$, respectively [223]. Furthermore, Yasmin et al. (2022) successfully synthesized a selenide-based composite material (AgInSbSe_3) via the hydrothermal method for degrading anionic Congo red dye in aqueous media. XRD analysis confirms the crystalline nature of AgInSbSe_3 , identifying a ternary phase of AgInSe_2 and AgSbSe_2 . SEM micrographs show a homogeneous, grain-covered surface with a grain size of $0.58 \mu\text{m}$ and minimal inter-particle distance, while EDX analysis verifies the elemental composition. The FTIR spectrum confirms functional groups within the composite through distinct absorption bands. The photocatalyst demonstrated 77.8% degradation efficiency for Congo red under sunlight within 75 min, attributed to its small band gap for efficient sunlight utilization. The AgInSbSe_3 catalyst also exhibited notable stability and reusability; after three consecutive cycles, degradation efficiency decreased only slightly from 77.8% to 75% , indicating minimal deactivation. This stability underscores the composite's potential as a durable photocatalyst for sustainable wastewater treatment [224].

The synthesis and characterization of CuS hexagonal nanoplates for catalytic and photocatalytic applications is reported. These nanoplates, prepared using a single-source precursor and octylamine, exhibited excellent crystallinity, a narrow particle size distribution, and a suitable band gap for light absorption. Notably, this study represents the first demonstration of CuS nanoplates as dual-functional catalysts for the degradation of Congo Red (CR) under both dark and solar light conditions. The degradation kinetics followed a pseudo-first-order model, suggesting a Langmuir-Hinshelwood mechanism. Moreover, the recyclability of the CuS nanoplates was confirmed by the stability of their crystal structure after multiple degradation cycles. These findings highlight the potential of CuS nanoplates as promising materials for environmental remediation applications [211]. The synthesis and characterization of a novel visible-light-responsive photocatalyst, Ba_2ZnSe_3 , are presented. This one-dimensional chalcogenide material was prepared via a solid-state reaction. The band gap of Ba_2ZnSe_3 was determined to be 2.75 eV, enabling efficient absorption of visible light. Importantly, this material demonstrated excellent photocatalytic activity, thermal stability, and recyclability, making it a promising candidate for various applications in environmental remediation and energy conversion [218].

Incorporating noble metals into chalcogenide systems can improve visible light absorption and reduce electron and hole recombination [225]. In this context, the Au containing BaAu_2S_2 system provides a more relevant example of this strategy [116]. It exhibits superior photocatalytic activity and stability compared to $\text{g-C}_3\text{N}_4$. Its unique structural and electronic properties facilitate efficient electron-hole separation and high absorption, making it a promising material for photocatalysis. In another study, the modification of TiO_2 nanostructures with CuS and MoS_2 using hydrothermal and coprecipitation methods was carried out. The resulting nanocomposites were characterized and evaluated for photocatalytic hydrogen generation

and methylene blue degradation. Notably, 0.5 wt% CuS-TiO₂ prepared by coprecipitation exhibited an exceptional initial hydrogen evolution rate of 2.95 mmol h⁻¹ g⁻¹, while 3 wt% MoS₂-TiO₂ synthesized hydrothermally demonstrated a respectable performance. Both nanocomposites exhibited high degradation efficiency for methylene blue under UV-Vis and visible light irradiation. These results highlight the potential of metal chalcogenides as effective and versatile co-catalysts for enhancing TiO₂-based photocatalytic systems [147].

A study by Bhat et al. presents the synthesis and characterization of Ce-doped FeSe₂ photocatalysts for wastewater treatment. A simple, eco-friendly hydrothermal method was employed to prepare these nanomaterials, which were subsequently characterized using XRD, FE-SEM, EDS, CV, and UV-visible spectroscopy. The results indicated good crystallinity, desired morphology, and improved optical properties with increasing Ce doping. The photocatalytic activity of the Ce-doped FeSe₂ nanomaterials was evaluated for the degradation of Rhodamine B (RB) dye under UV-visible light irradiation. Notably, 7% Ce-doped FeSe₂ exhibited a remarkable 95.21% degradation efficiency within 120 min, following pseudo-first-order kinetics. These findings highlight the potential of Ce-doped FeSe₂ as a promising photocatalyst for effective and environmentally friendly wastewater treatment [205]. In the same context, Erti and Boz [213] synthesized metal-doped CdS nanoparticles via a chemical precipitation method. XRD and UV-visible reflectance spectroscopy confirmed the successful formation of cubic CdS nanostructures with crystallite sizes ranging from 4.0 to 4.5 nm. The band gap energies of the metal-doped CdS catalysts were estimated to be between 2.25 and 2.55 eV. Methylene blue degradation experiments under visible light irradiation ($\lambda > 420$ nm) revealed that metal doping significantly enhanced the photocatalytic activity of CdS nanoparticles. Among the various metal-doped catalysts, Co-CdS exhibited the highest degradation efficiency, reaching approximately 87% after 4 h of irradiation.

Sr-doped ZnSe nanoparticles were synthesized using a co-precipitation method. XRD analysis confirmed the cubic structure expansion due to Sr²⁺ doping. FT-IR, UV-DRS, FE-SEM, HR-TEM, EDS, and XPS analyses characterized the nanoparticles' surface properties, morphology, elemental composition, and oxidation state. The Sr-doped ZnSe nanoparticles exhibited excellent antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*. Additionally, the study demonstrated efficient photocatalytic degradation of methyl orange under visible light irradiation [226]. Recent studies [227,228] further demonstrate the effect of elemental doping on chalcogenide photocatalysts. Nd doped ZnSe with a band gap of 2.46 eV achieved 94.3% Congo red degradation within 80 min under sunlight and retained more than 95% efficiency after four cycles. Similarly, Mn doped CdS achieved 88.87% methylene blue degradation under direct sunlight, mainly because the secondary MnS phase promoted charge separation and reactive species generation.

Wang et al. [118] investigated the optoelectronic and photocatalytic properties of Cu₂SnSe₃-Au and proposed a mechanism to explain their superior photocurrent and photocatalytic performance compared with pure Cu₂SnSe₃. These novel heterostructures exhibited enhanced and extended optical absorption in the visible-near infrared (Vis-NIR) region. We investigated the optoelectronic and photocatalytic properties of Cu₂SnSe₃-Au and proposed a mechanism to explain their superior photocurrent and photocatalytic performance compared to pure Cu₂SnSe₃. In another study [219], CuFeS₂ powders were synthesized by conventional and microwave methods for their catalytic performance in photo-Fenton reactions. The microwave-assisted method produced samples with higher crystallinity and Fe²⁺ content. These samples exhibited superior catalytic activity for tartrazine dye degradation, achieving 99.1% decolorization and 87.3% mineralization. The hydroxyl radical was identified as the primary reactive species responsible for

degradation. The findings highlight the importance of the synthesis method in optimizing the catalytic properties of CuFeS_2 for environmental remediation applications.

$\text{Cu}_2\text{FeSnS}_4$ (CFTS) thin films were synthesized using spray pyrolysis at various substrate temperatures (Ts). Characterization studies revealed that the film grown at 240°C exhibited the best physical properties, including high crystallinity, optimal atomic ratios, and a spherical morphology. The band gap of this film was 1.46 eV, and the absorption coefficient was $9.8 \times 10^4 \text{ cm}^{-1}$. Additionally, electrical resistivity was low at $0.18 \Omega\text{cm}$. These results suggest that CFTS thin films could be promising absorber materials for solar cells and a more cost-effective alternative to TiO_2 in photocatalysis applications, as demonstrated by the 81% photodegradation rate of methylene blue under sunlight [119]. In another study, $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) nanoplates were synthesized using a one-pot thermal chemical method. The nanoplates exhibited a uniform morphology and a bandgap of approximately 1.4 eV. When used as a photocatalyst under visible light, the CZTSe nanoplates demonstrated high activity and stability in degrading Rhodamine B dye. The efficient light utilization of the nanoplates is attributed to their excellent dye removal performance [229].

Solar-driven pollution degradation offers a sustainable approach to addressing environmental issues. However, its practical application is hampered by low efficiency and poor stability. Yin et al. [230] introduced a novel CdS@MoS_2 core-shell nanorod heterostructure for efficient photocatalytic degradation of RhB. The well-defined heterostructure and photo corrosion-resistant MoS_2 shell contribute to the material's outstanding efficiency and long-term stability. These findings pave the way for overcoming the limitations of chalcogenides and advancing the development of practical solar-driven pollution degradation technologies. In a study by Zia et al. [231], the use of metal oxide (Co_3O_4), metal chalcogenide (CoTe), and their nanocomposites for photocatalytic degradation of Congo red dye was explored. The nanocomposite photocatalysts, synthesized hydrothermally, demonstrate superior photocatalytic activity compared to their individual components. These findings (96% congo red ye degradation) highlight the potential of nanotechnology and photocatalysis in addressing energy and environmental challenges. CuCo_2S_4 /reduced graphene oxide (RGO) nanocomposites were synthesized using a hydrothermal method, incorporating l-cysteine as a bio-sulfur source. A 3% RGO loading in CuCo_2S_4 matrix exhibited the highest degradation efficiency for malachite green. These findings highlight the potential of CuCo_2S_4 /RGO nanocomposites as a sustainable photocatalyst for environmental applications [232]. A highly efficient $\text{ZnIn}_2\text{S}_4/\text{MoO}_3$ Z-scheme heterojunction was synthesized for visible-light-driven photocatalytic degradation of organic pollutants (methyl orange, rhodamine B, etc.). The composite material exhibited superior photocatalytic activity compared to its individual components, attributed to enhanced light absorption and charge separation. The Z-scheme mechanism, involving the transfer of photoinduced charge carriers, was elucidated based on reactive species determination [233]. Table 1 summarizes the use of different chalcogenides as photocatalysts for dye degradation. Overall, these studies show that photocatalytic performance is controlled not only by band gap energy but also by surface morphology, charge separation, catalyst modification, and irradiation conditions. However, direct comparison remains difficult because different dyes, light sources, catalyst dosages, and reaction times were used.

Table 1: Chalcogenides as photocatalysts for dye degradation.

Chalcogenides	Band Gap Energy (eV)	Dyes	Light Source	Results	References
CuS	2.1	Congo red	Solar light	Complete degradation within 80 min	[211]
Sb ₂ S ₃	Indirect = 1.54 Direct = 1.72	Methyl orange	UV lamp (4 W) visible light (under direct sunlight)	Dark = 7.4% UV light = 22% Visible light = 47%	[210]
Ba ₂ ZnSe ₃	2.75	Rhodamine B	Xe-lamp	20% degradation within 240 min	[218]
BaAu ₂ S ₂	2.49		1000 W Xe lamp with 420 filters	45% degradation after 240 min	[116]
CuS-TiO ₂	2.83	Methylene blue	UV-visible	98% under UV-visible light within 2 h 96% with H ₂ O ₂ within 2 h	[147]
MoS ₂ -TiO ₂	1.82			98% under UV-visible light within 2 h 100% with H ₂ O ₂ within 2 h	
Ce-doped FeSe ₂	Not mentioned	Rhodamine B		95.21% degradation by 7% Ce-doped FeSe ₂ nanomaterial within 120 min	[205]
Ce-CdS	2.42 eV	Methylene blue		76% degradation in 240 min	[213]
Sr-doped ZnSe		Methyl orange	Visible light	88% degradation in 120 min	[226]
Cu ₂ SnSe ₃ -Au		Methylene blue	Xe lamp equipped with cut-off filter 400 nm	80% degradation after 90 min under visible light	[118]
CuFeS ₂	Not mentioned	Tartrazine dye	85 W fluorescent lamp	99.1% decolorization after 40 min 87.3% mineralization after 150 min	[219]
Cu ₂ FeSnS ₄	At variable substrate temperature 160°C = 1.62 eV 200°C = 1.05 eV 240°C = 1.46 eV 280°C = 1.58 eV	Methylene blue	Under sun and Xe light	Cu ₂ FeSnS ₄ thin film at temperature of 240°C show 81% degradation under sunlight	[119]
Cu ₂ ZnSnSe ₄	1.4 eV	Rhodamine B	300 W Xe lamp equipped with a 420 nm cutoff filter	90% degradation within 120 min	[229]
ZnSe/Co ₃ O ₄	2.2 eV	Congo Red	UV/visible	96% degradation in 60 min	[234]

Table 1: *Cont.*

Chalcogenides	Band Gap Energy (eV)	Dyes	Light Source	Results	References
CdS@MoS ₂ core@shell	CdS = 2.18 eV MoS ₂ = 1.61 eV	Rhodamine B	300 W Xe lamp as a light source with 420 nm light filter to obtain visible light	79.60% degradation	[230]
Co ₃ O ₄ /CoTe	Co ₃ O ₄ = 1.5–2.5 eV CoTe = 2.24 eV	Congo red	300 W Xe arc lamp with UV cut-off filter	Co ₃ O ₄ and CoTe (1:1) composite = 96% degradation	[231]
CuCo ₂ S ₄ /RGO nanocomposites	1.5 eV	Malachite green	500 W tungsten halogen lamp	3% of RGO loaded on CuCo ₂ S ₄ show 92% degradation in 360 min	[232]
ZnIn ₂ S ₄ /MoO ₃ heterojunction	MoO ₃ = 2.92 eV ZnIn ₂ S ₄ = 2.24 eV	Methyl orange, rhodamine B and paracetamol	500 W halogen lamp	ZnIn ₂ S ₄ /MoO ₃ composite show 98% degradation within 80 min	[233]
Ge ₁₇ Sb ₈ Se _{75-x} Er _x (Er; x = 0, 0.6, 1)	1.88 eV (for pure) to ~1.78 eV (for highest amount of dopant Erbium)	Methylene blue	Visible light	96% degradation in 160 min for Er; x = 0.6	[235]
Ge ₁₇ Sb ₈ Se _{75-x} Er _x (x = 0.4%, 0.8%)	1.8		UV-cut region	Degradation of 83% in 210 min	[236]
CuS nanoparticles	1.2 to 2.0 eV	Methylene blue, Rhodamine B, Eosin Y, Congo red	UV light from a 12 W UV lamp	MB (90.29%), (RB) 91.97%, (EY) 69.23%, and (CR) 60.35%,	[214]
Metal-doped CdS (Co, Ni, Ce, Sb)	2.25 and 2.55 eV	Methylene blue	visible-light-active	Co-doped CdS: 87% Ni-doped CdS: 73% Ce-doped CdS: 76% Sb-doped CdS: 70% Pure CdS: 68%	[213]
CdS nanoparticles	2.38 to 2.30 eV	Methylene blue	visible light	Pure CdS: MB reduced in 45 min. Ni-doped CdS: MB degraded in 25 min. Co-doped CdS: MB degraded in 20 min	[212]
Cu ₂ FeSnS ₄	~1.46 eV	Methylene blue	Solar light	81% (4 h irradiation)	[119]
CuS nanoplates	2.1 eV	Congo Red	Solar light	100% dye degradation in 40 min	[211]
Sb ₂ S ₃	1.66 eV	Methyl orange	visible light	97% in 30 min	[208]
Sb ₂ S ₃	1.54 eV	Methyl orange	Solar Light	90% in 4-h irradiation	[210]

Table 1: *Cont.*

Chalcogenides	Band Gap Energy (eV)	Dyes	Light Source	Results	References
Iron Disulfide (FeS ₂)	0.7–2.6 eV	Methyl Orange and Novacron Yellow Huntsman	visible light	Methyl Orange: 93.09% degradation in 120 min NYH: 98.15% removal in 80 min	[209]
Sodium iron disulfide (NaFeS ₂)	2.01 eV	MB dye and indigo carmine dye	UV light	MD dye degradation 97% in 105 min and indigo carmine dye degradation 99% in 45 min	[221]
ZnS nanoparticles with rGO	2.01 eV	of Congo red (CR)	Solar light	98% in 120 min	[215]
Cobalt sulfide nanostructures (CoS NS)	2.76 eV	methylene blue (MB), rhodamine B (RhB), Nile blue (NB), crystal violet (CV), and Congo Red (CR)	200 w tungsten lamp (Visible light source)	Methylene Blue (MB): 99.8% degraded in 10 min Rhodamine B (RhB): 99.5% degraded using CS-3; time not explicitly mentioned Crystal Violet (CV): 99.4% degraded using CS-3; time not explicitly mentioned Nile Blue (NB): 99.8% degraded using CS-3; time not explicitly mentioned	[207]
Graphene Oxide-Based Metal Sulfide (GO/NiS) Nanocomposite	Nickel sulphide (NiS): 3.29 eV Graphene oxide (GO): 5.14 eV Graphene oxide/nickel sulphide (GO/NiS) nanocomposite: 3.12 eV	Crystal violet dye	Sun light	Crystal Violet (CV): 93% degraded in 60 min	[216]
CuS/ZnS	ZnS: 3.72 eV CuS: 2.2 eV	Rhodamine B		100% dye degraded in 24 h	[222]
Bi ₂ O ₂ S nanosheets	1.17 eV	Congo Red (CR)	visible light	Congo Red (CR): Degradation 82% in 75 min Rose Bengal (RB): Degradation 80% in 150 min	[223]

Table 1: *Cont.*

Chalcogenides	Band Gap Energy (eV)	Dyes	Light Source	Results	References
Zinc Indium Sulfide (ZIS)	2.3 eV	(Malachite Green, MG) and anionic (Congo Red, (CR)	Sun Light	80% degradation of both dyes in 20 min under sunlight.	[206]
Ce-doped FeSe ₂ (7%)	1.66 eV	Rhodamine B dye	mercury lamp (Philips 70 W)	95.21% within 120 min	[205]
AgInSbSe ₃	1.97 eV	Congo red	Solar light	77.8% in 75 min	[224]
ZnS nanostructures	3.513 to 3.386 eV	Malachite green (MG) dye	Solar light	74.25% degradation in 240 min	[204]

Comparison of the reported systems shows that a narrow band gap improves visible light absorption but does not alone ensure faster dye degradation. For example, ZnS with a band gap of 3.39 to 3.51 eV achieved 74.25% degradation in 240 min, whereas Ce doped FeSe₂ with a band gap of 1.66 eV achieved 95.21% degradation in 120 min [204,205]. Binary chalcogenides are generally easier to synthesize, but charge recombination and photocorrosion may limit their performance. Ternary and quaternary systems provide better control over band structure and charge separation, although their synthesis and phase control are more complex. Reported efficiencies should also be compared cautiously because experimental conditions, including dye concentration, catalyst dosage, irradiation source, and treatment time, differ among studies. Photocatalytic efficiencies reported in different studies should be interpreted according to their experimental conditions. A higher initial dye concentration can reduce removal efficiency because active sites become saturated and light penetration decreases. Increasing catalyst dosage generally improves degradation up to an optimum level, beyond which particle aggregation and light scattering may reduce performance. Solution pH affects catalyst surface charge, dye speciation, and reactive species formation. Similarly, the irradiation wavelength, intensity, and exposure time influence charge generation. Therefore, degradation % obtained under different conditions should not be treated as direct measures of catalyst superiority [205].

3.1.1 Stability and Reusability under Practical Wastewater Conditions

The long term application of chalcogenide photocatalysts depends on their structural stability and ability to retain activity over repeated cycles. ZnS showed only a small efficiency loss over three cycles, while ZnIn₂S₄ retained 85.62% degradation efficiency after five cycles, compared with 94.97% in the first cycle [204,206]. Similarly, the degradation efficiency of AgInSbSe₃ decreased only slightly from 77.8% to 75% after three cycles [224]. However, practical wastewater contains salts, suspended particles, natural organic matter, and competing pollutants that can block active sites or promote photocorrosion and metal leaching. Therefore, future studies should evaluate catalyst recovery, elemental leaching, mineralization efficiency, and long term performance using real wastewater.

3.1.2 Challenges Limiting Commercialization

Despite their promising photocatalytic activity, several challenges restrict the commercial application of chalcogenide photocatalysts. Some materials contain toxic elements such as Cd, Pb, or Se, creating concerns about metal leaching and secondary pollution. Their large scale production may also require expensive precursors, complex synthesis conditions, and careful control of composition. Catalyst recovery, photocorrosion, reduced efficiency in real wastewater, and limited utilization of sunlight in large reactors further affect practical performance. Future studies should therefore focus on low toxicity compositions, simple large scale synthesis, immobilized catalysts, long term stability, and pilot scale testing under actual wastewater conditions [127,230,237].

4 Conclusion

This review highlights the promising potential of chalcogenide-based materials as efficient photocatalysts for water pollution remediation, specifically in the context of dye degradation. Compared to traditional catalysts like TiO₂ and ZnO, chalcogenide glasses offer superior photocatalytic performance, primarily due to their visible light activity and reduced electron-hole recombination. Binary, ternary, and quaternary chalcogenide compositions, especially when doped with rare earth metals, have been shown to significantly enhance the degradation of a variety of dyes under both solar and artificial light conditions. However, challenges such as scalability limitations, recombination issues, and long-term stability must

be addressed to fully realize their practical potential in large-scale water treatment applications. Future research should focus on overcoming the limitations of current chalcogenide-based photocatalysts by optimizing their structural and electronic properties. Enhancing their light absorption capacity in the visible spectrum and improving charge carrier separation are key areas for development. Additionally, coupling chalcogenides with other semiconductors or noble metals could further reduce electron-hole recombination and improve efficiency. More efforts should also be directed toward large-scale applications of these materials in real-world wastewater treatment systems. Moreover, exploring new synthesis methods to reduce costs and improve the recyclability and environmental stability of chalcogenides will be pivotal in making these photocatalysts commercially viable. Research into multi-functional catalysts that can simultaneously degrade a broader range of pollutants and developing systems that integrate solar energy to drive these photocatalytic processes more sustainably are also promising directions. Chalcogenide perovskites such as BaHfS_3 , BaZrS_3 , and CaZrS_3 may also be considered in future studies, although experimental evidence regarding their direct application to photocatalytic dye degradation remains limited.

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