
PHOTOCATALYTIC EFFICIENCY OF SULPHIDE NANOPARTICLE IN PHOTOCHEMICAL REACTOR

M.L. Meena

Department of chemistry
Government Girls College
Karauli (Rajasthan)

J. Meena

Department of chemistry
Government College
Karauli (Rajasthan)

A.S.Meena

Department of chemistry
University of Rajasthan
Jaipur (Rajasthan)

ABSTRACT

Toxic, non-biodegradable, and harmful organic pollutants have become an undeniable and global fact as a significant environmental problem in soils, wastewater, and the atmosphere. Because of the possibility of pollutants removal from water, heterogeneous photocatalysis, an advanced oxidation process (AOP) using semiconductor materials as catalysts, is a hot topic. The bandgap energy, phase composition, crystallinity, morphology, and surface area of the catalyst, electron-hole recombination rate, intensity of light, and adsorption capacity of the dye on the photocatalyst surface all influence photocatalytic degradation of organic contaminants (i.e. dyes, pesticides, phenolic compounds) present in water using semiconductor materials. The fast recombination of photogenerated electrons and holes is one of the major constraints on catalyst photocatalytic efficiency. As a result, various strategies for promoting charge separation have been employed, including the development of heterojunction between two semiconductor materials and the tailoring of photocatalyst properties.

Keywords: Organic, Material, Electron, Conductor, Dyes.

I. INTRODUCTION

The presence of organic dyes in industrial wastewaters from the textile, garment, and paper sectors pollutes the environment significantly. These dye-polluted effluents contain carcinogenic, non-biodegradable, and colourful pigments that can harm humans. Dyes are visible in water even at very low concentrations (below 1 ppm) can seriously degrade watery habitats. As a result, it is critical to remove coloured organic dyes from waste streams. Adsorption and coagulation are popular strategies for removing organic dyes from industrial effluent in conventional treatment. However, because dyes are merely transformed from a liquid to a solid phase, these activities result in secondary harmful contamination. As a result, additional treatments are required to address the issue of secondary contamination. Photocatalysis has been hailed as a viable alternative treatment in the field of water purification in recent years. The photocatalytic reaction is essentially heterogeneous catalysis, in which a light-absorbing catalyst is placed in contact with the target reactants in a solution or gas phase. This heterogeneous approach has been successfully used to degrade a variety of hazardous compounds, including air and aquatic organic pollutants, and it has a number of advantages over typical wastewater treatment techniques. At ambient temperature, for example, complete breakdown of organic contaminants employing active photocatalysts can take only a few hours. Furthermore, organic contaminants can be mineralized completely to comparatively non-toxic compounds (CO₂ and water) without producing secondary harmful products. Scheme 1 depicts the usual photodegradation procedure for organic dyes. When incoming photons strike the photocatalyst, electrons are stimulated to the conduction band (CB), while holes originate in the valence band (VB). The photoexcited electrons and holes can recombine to provide thermal energy, or they can diffuse to the photocatalyst surface and react with the adsorbed molecules. The photoexcited electrons and holes are then converted into reactive radical species such as superoxide radicals (O₂⁻) and hydroxyl radicals (OH).

Furthermore, the photosensitization of dye molecules can deliver additional electrons to photocatalysts, allowing them to generate radicals such as O_2 . Organic contaminants can be decomposed fast and non-selectively by these reactive entities. Operational parameters such as the pH of the solution, initial dye concentration, reaction temperature, and irradiation intensity affect the entire photodegradation process, from dye molecule adsorption on the surface of the photocatalyst to dye molecule destruction by reactive radicals. For example, Neppolian et al. found that the degradation of reactive yellow 17, reactive red 2, and reactive blue 4 over Degussa P-25 followed pseudo first-order kinetics, with decreasing photodegradation efficiency as the starting dye concentration increased. Shahwan et al. studied the photodegradation of methyl blue and methyl orange and discovered that the pH of the solution and the steric structure of the methyl blue and methyl orange were both strongly connected to photocatalytic efficiency. The band location and charge-carrier utilisation of photocatalysts, in addition to these operational characteristics, have an impact on the production of reactive radicals and subsequent photodegradation performance. Heterostructure photocatalysts with enhanced photocatalytic activity are presented and used to optimise carrier usage and hence achieve efficient reactive radical production.

II. EFFICIENCY OF PHOTOCATALYSIS

Photocatalysis' application in water purification and environmental protection is of particular interest. However, the limited accessibility of electron acceptor oxygen and low adsorption of organic compounds—crucial elements driving photocatalytic performance—can limit reaction kinetics. As a model photocatalyst, we use reaction interface microenvironment design to simultaneously ease these restrictions. The photocatalytic device exhibits a long-range hydrophobic force and an air–water–solid triphase interaction interface due to the low surface energy and rough surface microstructure properties of the nanoarrays. This concurrently modifies the organic compound adsorption model and the oxygen access pathway, resulting in significantly increased adsorption capacity and higher interfacial oxygen levels. In comparison to a regular diphasic system, these synergistic features result in over 30-fold greater reaction kinetics. This photocatalytic system is also stable after repeated cycles. Our findings emphasise the importance of reaction interface microenvironment design and point to a viable path for developing efficient photocatalysis devices.

III. DYES PHOTODEGRADATION—A GENERAL MECHANISM OVERVIEW

The majority of dyes, including cationic, anionic (acid, reactive, and direct dyes), and non-ionic dyes, are synthetic. They are categorised as azo, anthraquinone, indigoid, nitroso, and nitro dyes based on their chemical structure. Dyes are widely utilised in a variety of sectors (textile, leather, paper, rubber, printing, and plastics) and are chemically stable and resistant to degradation, allowing them to stay in water for extended periods of time. Because dyes can impede sunlight transmission and include harmful components such as heavy metals (lead, chromium) and aromatic compounds, a large quantity of dyes discharged in water poses a significant risk to the environment.

Dyes are the most used pollutant model for evaluating a catalyst's photocatalytic activity. Many organic dyes, such as azo dyes (methyl orange—MO, rhodamine B—RhB, congo red—CR, acid orange 7—AO7), thiazine, and cationic dyes (methylene blue—MB), have been examined for their light-assisted photodegradation.

Figure 1A summarises the photocatalytic degradation mechanisms of dyes utilising a photocatalyst as (I) dye sensitization via charge injection, (II) indirect dye degradation via oxidation/reduction, and (III) direct dye degradation via photolysis.

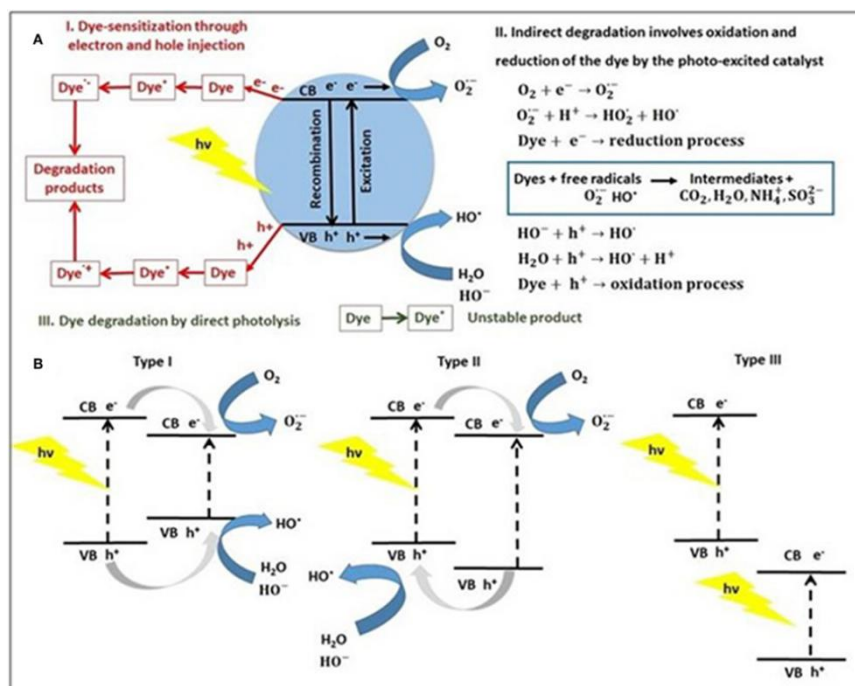


Figure 1. (A) The general photocatalytic degradation mechanisms of dye using a single semiconductor (e.g., metal sulfide) and (B) type of semiconductor heterojunctions based on metal sulfide, under light irradiation.

Charge carriers (electron-hole pairs) formed in the presence of light interact with dye molecules (Dye) via the chemisorption method to produce excited dye (Dye^*) that can be converted to cationic (Dye^+) and anionic ($Dye^{\cdot -}$) radicals, resulting in degradation products. Dye sensitization is an effective approach for modifying photocatalysts for several reasons: it increases light absorption to visible light irradiation, improves excitation efficiency, and promotes electron-hole separation, all of which lead to improved photocatalytic performance.

When a semiconductor photocatalyst absorbs photons with energy equal to or higher than its band-gap from solar light or an irradiation source, an electron (e) from the valence band (VB) is promoted to the conduction band (CB). This is linked to the development of holes (h^+) in the valence band, which results in the formation of pairs of electrons and holes that participate in reduction and oxidation reactions. The mechanism that deactivates the photocatalyst is electron-hole recombination on the surface. Additionally, electrons and holes trapped in surface states combine with molecular oxygen (O_2) to form anionic superoxide radicals ($O_2O_2^{\cdot -}$), while photogenerated holes react with water to form hydroxyl radicals (HO^{\cdot}), further oxidising the dye molecules. Photogenerated electrons and holes can produce the most important hydroxyl radical (HO^{\cdot}), a highly reactive radical. In wastewater photocatalysis, hydroxyl radicals act as reactants for dye oxidation, transforming contaminants into CO_2 and H_2O . When dye molecules contain heteroatoms (such as sulphur, nitrogen, halogens, or phosphorus), they are transformed into salt ions, which are environmentally beneficial substances that don't require any additional chemical or physical processing. The photolysis of dye molecules directly (mechanism type III) is a slow and catalyst-free process.

Many heterojunctions have been developed in recent years to improve the performance of semiconductors in photocatalysis. According to the distinct charge carrier separation methods, a heterojunction is described as an interface between two semiconductors with unequal band carriers. As a result, there have been three types of sulfide-based heterojunction photocatalysts reported to date: type I—straddling gap, type II—staggered gap, and type III—broken gap. Both heterojunction semiconductors could be stimulated to produce photogenerated electrons (e) and holes (h^+) by exposing them to light. The band energy levels of one semiconductor are

included in the band energy levels of the other, and electrons and holes travel in the same direction in a Type I heterojunction. When spatial charge separation occurs, electrons and holes from the heterojunction are free to move to other semiconductors (type II heterojunction).

IV. PHOTODEGRADATION OF DYES USING HETEROJUNCTIONS BASED ON COPPER SULFIDE NANOSTRUCTURES

In the last ten years, our lab has produced numerous heterojunctions based on copper sulphide nanostructures, with the primary goal of extending the photocatalytic response of the materials in the VIS region of the solar spectrum for industrial applications, resulting in significant cost savings. Thin films tandem structures, such as $\text{Cu}_x\text{S}/\text{SnO}_2$, $\text{ZnO}/\text{Cu}_x\text{S}-\text{CuO}/\text{SnO}_2$, and $\text{TiO}_2/\text{Cu}_x\text{S}-\text{CuO}/\text{SnO}_2$, obtained by the sequential deposition of individual semiconductor layers using Spray Pyrolysis Deposition (SPD), allow for high charge carriers mobility, allowing for the generation of oxidative species during photocatalysis. $\text{Cu}_x\text{S}/\text{SnO}_2$ and $\text{ZnO}/\text{Cu}_x\text{S}-\text{CuO}/\text{SnO}_2$ were investigated utilising a pollutant of 0.0125 mM methylene blue and a combination of UV (3 lx flux intensity) and Vis radiation (28 lx flux intensity). After 6 hours of irradiation, the $\text{ZnO}/\text{Cu}_x\text{S}-\text{CuO}/\text{SnO}_2$ tandem system has a higher contribution of cumulative charge creation, allowing it to achieve 78 percent photocatalytic efficiency, while $\text{Cu}_x\text{S}/\text{SnO}_2$ only manages 74 percent. The appropriate disposal of energy levels determines each component's contribution to total photocatalytic efficiency. Duta et al. (2016) investigated a tandem system based on $\text{TiO}_2/\text{Cu}_x\text{S}-\text{CuO}/\text{SnO}_2$ utilising the same irradiation situation but switching the pollutant. The pollutant in this example was phenol at concentrations of 4, 10, and 20 ppm, with the highest efficiency of 8.75 percent after 6 hours of irradiation for the 4-ppm pollutant concentration.

Our group also looked into the photocatalytic process of dyes (MB and MO) photodegradation using heterojunctions $\text{Cu}_x\text{S}/\text{TiO}_2$ tandem semiconductors, and found that heterojunction-based nanostructured materials have better photocatalytic activity than single-component nanomaterials or one-phase heterojunctions. The photochemical approach was used to produce copper sulphide powder, which had the major crystalline phases CuS and $\text{Cu}_{1.8}\text{S}$ (digenite), and the doctor blade technique was used to deposit thin films of Cu_xS , TiO_2 , and linked $\text{Cu}_x\text{S}/\text{TiO}_2$ on the glass. The irreversible charge separation, which generates kinetic restrictions as a result of dye pollutant interactions, explains the greater photocatalytic activity of $\text{Cu}_x\text{S}/\text{TiO}_2$ heterojunction structure Type II (Figure 1). The photocatalytic activity of $\text{Cu}_x\text{S}/\text{TiO}_2$ photocatalysts is dependent on the molar ratio of $\text{Cu}_x\text{S}:\text{TiO}_2$, with the best results obtained when $\text{Cu}_x\text{S}:\text{TiO}_2 = 3:7$ was used, with high degradation efficiency (almost 99 percent) achieved after 180 minutes for MB degradation and 300 minutes for MO degradation, respectively.

CuS/TiO_2 heterojunctions were created using an environmentally safe method that leverages the biomolecule L-cysteine as a sulphur source and chelating agent for in situ synthesis of CuS nanoparticles on the surface of 1D TiO_2 nanobelts, overcoming the problem of CuS nanoparticle aggregation. The photocatalytic activity of the CuS/TiO_2 samples was evaluated using MB degradation under Vis light (350 W Xe lamp with a UV cut-off filter, 420 nm) irradiation. The results showed that CuS/TiO_2 heterojunction based photocatalysts have degradation efficiencies in the range of 95–100%, which is more than double that of pure TiO_2 nanobelts (46 percent). The energy bandgaps match between CuS and TiO_2 , resulting in efficient separation of photogenerated electrons and holes, was linked to the increased photocatalytic activity. The photocatalytic characteristics of CuO/CuS core-shell nanowires, synthesised through thermal oxidation and two-step annealing, were exploited for the degradation of methylene blue under Vis light irradiation in recent research. In photocatalytic studies, the CuO/CuS heterojunction showed a nearly 25% improvement in MB degradation rate after 4 hours when compared to CuO nanowires.

It was also discovered that type II heterojunction ZnO/CuS had a higher visible-light photocatalytic efficiency in MB degradation. Using a wet-chemical technique at low temperature, the ZnO/CuS photocatalyst was created by decorating CuS nanostructure on the surface of ZnO nanotubes. The photocatalytic studies revealed that under Vis light irradiation, ZnO has no photocatalytic activity, the MB photodegradation rate with CuS reaches 63 percent after 30 minutes, and the photocatalytic efficiency with the ZnO/CuS catalyst improved to 87 percent, a nearly 28 percent increase. The increased photocatalytic activity is attributable to the ZnO/CuS p-n heterojunction formation, which supports the effective separation of photoinduced charge carriers, according to the mechanism analysis.

CuS/CdS and CuS/MoS₂ heterojunctions were produced using a simple and environmentally safe hydrothermal technique. According to the photocatalytic results, CuS/CdS and CuS/MoS₂ heterostructures outperformed pure CuS, CdS, and MoS₂ heterostructures in the degradation of MB dye under Vis light (250 W lamp with illumination intensity of 0.01 W/cm²) and simulated natural light (Xe lamp, 300 W) irradiation. After 10 minutes of exposure to Vis light, a CuS/CdS catalyst destroyed 99.97 percent of MB (10 ppm) in the presence of H₂O₂. After 60 minutes in the sun, the CuS/MoS₂ catalyst deteriorated the MB solution (10 ppm). CuS/CdS and CuS/MoS₂ photocatalysts have improved photocatalytic degradation efficiency due to a considerable reduction in electron-hole pair recombination.

V. CONCLUSIONS

Semiconductor(s) based photocatalysts have been identified as promising materials for industrial applications, combining the advantages of low cost with the fulfilment of the necessary requirements to improve photocatalytic efficiency.

Metal oxides with large bandgaps (e.g., ZnO, SnO₂, TiO₂) are photoactive in the UV light radiation domain, limiting their efficiency, whereas metal sulphides (e.g., CdS, CuS) have superior absorption in the Vis area but are photosensitive and have limited chemical stability. Copper sulfide-based heterostructures were prepared using simple, low-cost, and energy-efficient methods to improve photocatalytic activity in the VIS range of metal oxides: hydrothermal/solvothermal methods, sol-gel processes, in-situ synthesis, microwave irradiation, chemical precipitation, and so on. These materials are easy to prepare at the industrial level to transfer these materials in industrial applications. The higher photocatalytic performance (between 80 and 100 percent dyes degradation) of various heterojunctions based on copper sulphide nanostructures for dyes photodegradation highlighted in this mini-review show that these materials can act as VIS active materials, stable and low-cost photocatalysts with enhanced solar energy conversion efficiency for environmental remediation and green chemistry.

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