IJPSR Vol. 2 Issue 2 Apr - Jun (2026) 88–91

eISSN: 3139-342X

International Journal of Primary and Secondary Research (IJPSR)

International, Double-Blind, Quarterly, Peer-Reviewed, Refereed, Edited and Open Access Research Journal
Journal homepage: ijpsr.co.in

Semiconductor-Based Photocatalysts for Wastewater Treatment

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DOI- https://doi.org/10.59436/ijpsr.v2i2.18.3139-342X

ARTICLE INFO

Article history:
Received 16 March 2026
Received in revised form
20 April 2026
Accepted 06 June 2026
Available online 16 June 2026

Keywords:
Semiconductor photocatalysts, Photocatalysis, Wastewater treatment, Titanium dioxide (TiO_2), Zinc oxide (ZnO), Nanomaterials, Advanced oxidation process (AOP), Water purification, Organic pollutant degradation, Environmental

ABSTRACT

Pollution of water has become one of the most pressing environmental issues due to the increasing amount of industrial, agricultural, and household waste dumping. Conventional treatment methods are usually ineffective in treating toxic organic pollutants and new contaminants. Semiconductor photocatalysts have received great attention as a modern and environmentally friendly option of wastewater treatment because of their ability to transform harmful pollutants into non-toxic products utilizing light. Common semiconductor photocatalysts (TiO_2, ZnO, g-C_3N_4, WO_3) have excellent photocatalytic activity, chemical stability, and compatibility with the environment. These materials are able to generate electron-hole pairs under illumination causing the formation of reactive oxygen species that may degrade dyes, drugs, pesticides, and other organic pollutants in wastewater. The advances in nanotechnology, doping, and heterojunction engineering led to the enhancement of the performance of these photocatalysts with visible light. The current paper reviews the functioning, methods of production and characterization, application, advantages and disadvantages, and ways of enhancement of semiconductor photocatalysts.

Introduction

Freshwater is crucial for agricultural activities, industrialization and health care. Unfortunately, fast-paced industrial growth, urbanization and an increased population have resulted in large quantities of industrial wastewater treated to make sure it is safe for the environment although it contains many dangerous substances. Wastewater from textile, pharmaceutical, paper, leather, petrochemical, food processing and dyeing industries is filled with highly poisonous, organic, technical substances, synthetic dyes, pesticides, pharmaceutical residues, phenols, etc. Dumping such substances into water bodies without proper treatment leads to catastrophic processes, loss of the water's quality, even degradation of water creatures and risks for human health. Conventional methods of wastewater treatment, such as flocculation, sedimentation, adsorption, biological and membrane treatment, are based on technologies that allow removing different contaminants from wastewater. Poor results in reducing stubborn organic contaminants are the barriers of conventional wastewater treatment. In most cases it only allows transferring pollutants from one phase into another without completely removing them. Moreover, a lot of conventional methods require much energy, resources and additional treatment. Those shortcomings have urged scientists to search for new and greener methods of wastewater treatment.

Photocatalysis with the use of semiconductors is one of the latest discoveries used in order to decompose pollutants using light.Photocatalysis is a process by which light energy is used to generate electricity from semiconductor materials. The technology works by exposing a semiconductor material to ultraviolet light in order to release the charge carriers (free electrons) responsible for the oxidative reactions on the surface of the semiconductor material. These reactions lead to the formation of various types of reactive species that can transform the organic pollutants into safe materials such as carbon dioxide and water.

Semiconductor materials are the best photocatalysts because of their properties such as chemical stability, high oxidative capacity, low toxicity, and low cost. Although titanium dioxide is the most popular photocatalyst, there are many semiconductor materials such as zinc oxide, tungsten trioxide, bismuth vanadate, iron oxide, cadmium sulfide, and carbon nitride having excellent photocatalytic properties.

To satisfy the growing need of the society for clean water and stringent environmental regulations, light assisted semiconductor photocatalysis technologies have been developed in the recent years. Present studies deal with the development of advanced semiconductor-based catalysts responding to sunlight.

Literature Review

Photocatalysis that is based on semiconductors has emerged as one of the most promising advanced oxidation techniques for wastewater treatment owing to its capability to degrade a variety of organic and inorganic pollutants under light exposure. In the last thirty years, tremendous research work has been undertaken to come up with efficient semiconductor photocatalyst with enhanced photocatalytic performance, visible light initiation, and sustainability. Researchers have been engaged in researching various semiconductor materials, preparation methods, and modification strategies to eliminate the shortcomings of the traditional wastewater treatment techniques.

Among all the semiconductor photocatalysts, titanium dioxide (TiO_2) has attracted maximum scientific interest from its inception in 1972 when Fujishima and Honda showed the photocatalytic splitting of water using TiO_2 under ultraviolet light. This discovery created a new trend in photocatalysis research, motivating scientists to find its application in environmental purification. TiO_2 has excellent chemical stability and has high oxidation potential, and it is not toxic, and has an affordable price. Because of these advantages, TiO_2 is widely used in photocatalysis for the decomposition of dyes, pesticides, pharmaceutical waste, and other toxic organic contaminants in wastewater.

Despite its high photocatalytic activity, TiO_2 cannot be fully utilized in practice because of the restricted range of its band-gap energy (about 3.2 eV), which permits the absorption of only UV light. Since UV light is only a small fraction of solar energy, researchers have developed different types of modifications of TiO_2 to enhance its activity in the visible light region. This will lead to increased absorption of light, decreased recombination of electrons and holes, and increased photocatalytic efficiency under sunlight.The significance of zinc oxide as a photocatalyst lies in its ideal characteristics like excellent electron mobility and oxidation power, and the affordable manufacturing process. Many researchers have found that zinc oxide nanoparticles possess photocatalytic capabilities equal or more effective than those of titanium dioxide when it comes to disposing of pollutants from industries and dyes applied in the textile sector. However, this material suffers from photocorrosion and instability during continuous illumination, which evoked the interest of researchers in the production of zinc oxide composites and hybrid photocatalysts.

In recent years, semiconductor materials that can utilize visible light, such as bismuth vanadate, tungsten oxide, cadmium sulfide, iron oxide, and graphitic carbon nitride have been tested more actively. These materials have lower band-gap energy than titanium dioxide and zinc oxide which gives them an opportunity to make better use of solar energy. The data prove that the combination of these semiconductor materials with titanium dioxide and zinc oxide can result in charge separation efficiency improvement due to the fact that more visible light can be used for its absorption and getting rid of dyes. Current literature shows that scientists are using nanotechnology for the production of photocatalysts. Nanostructured photocatalysts contain numerous active sites needed for photocatalytic reactions due to their high surface area. Various techniques applied enable the creation of nanoparticles, nanorods, nanotubes, nanosheets, and mesoporous photocatalysts. Nanostructured materials have shown to be effective in getting rid of colors, medicines, pesticides, substances that disrupt hormones, as well as other new pollutants in wastewater in comparison with traditional photocatalysts. Recent developments in photocatalysis based on semiconductors include making photocatalytic processes more effective, increasing the range of visible light absorption, increasing catalyst stability, and minimizing the recombination of free electrons and holes. While some traditional photocatalysts such as TiO2 and ZnO were capable of efficient oxidation, their potential to use solar energy was limited allowing scientists to look for the next generation of photocatalysts. Contemporary research integrates nanotechnology, materials science, and surface chemistry for the development of successful photocatalysts applicable for wastewater treatment.

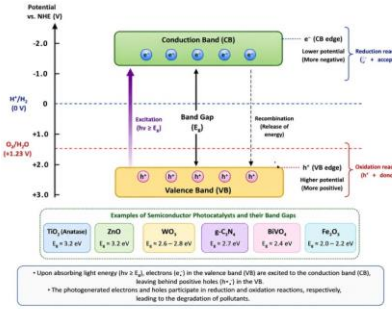
A new promising technological approach is represented by heterojunction photocatalysts formed by two or more semiconductor materials having different band structure thus allowing very effective separation of electrons and holes during the radiation process eliminating recombination, hence improving the performance of photocatalysts. Another significant innovation is that of element doping which implies introducing certain metal ions (for example, iron, silver, copper, and manganese) or non-metallic components (including nitrogen, sulfur, carbon, and phosphorus) into the semiconductor material to alter the electronic structure and reduce the band gap energy.

Nanostructured photocatalysts having controlled structure and size have been developed as well. These include nanoparticles, nanorods, nanotubes, nanosheets, and mesoporous materials which provide much larger surface area and many active sites for reactions taking place in comparison with the mentioned conventional photocatalysts. Hydrothermal synthesis, sol-gel technology, solvothermal approach, and green synthesis using plant extracts are the main techniques employed for manufacturing such nanomaterials. Graphitic carbon nitride or g-C3N4 has appeared as a promising metal-free photocatalyst because it has an appropriate band-gap size, visible light activities, and low cost as well as high chemical stability. The use of g-C3N4 in combination with titanium dioxide or other semiconductor oxides increases photocatalytic efficiency in the experiments. Moreover, Z scheme and S scheme photocatalytic systems have recently become very popular as they imitate natural photosynthetic mechanisms but keep high oxidation and reduction capabilities of these systems at the same time.

It becomes evident that semiconductor photocatalysis is on the way to undergo a serious transformation from academic experiments to the industry performance as there is a visible progress in the design of materials, catalyst recovery, and solar energy utilization.

Methodology

This review is the result of a systematic and thorough analysis of published scientific literature on semiconductor photocatalysts for



wastewater treatment. The study attempts to assess the recent advancements in photocatalytic materials, preparation methods, decomposition pathways, and their potential applications for pollutant removal from water. The literature review consists of information gained from peer-reviewed research articles, reviews, book chapters, proceedings, and other credible scientific publications in the field of environmental chemistry and material science. In the course of literature research, the following well-studied semiconductor photocatalysts were analyzed: titanium dioxide (TiO_2), zinc oxide (ZnO), tungsten trioxide (WO_3), graphitic carbon nitride ($g\text{-}C_3N_4$), bismuth vanadate ($BiVO_4$), iron oxide (Fe_2O_3), cadmium sulfide (CdS), as well as recently developed semiconductor nanocomposites. Research papers detailing structural properties, optical characteristics, photocatalytic processes, degradation efficiency, and applications for the environment were analyzed. Synthesis methods that were used to produce semiconductor photocatalysts were of special interest in the literature review. Among them are sol-gel synthesis, hydrothermal and solvothermal methods, precipitation, chemical vapor deposition, microwave-assisted, and green synthesis using plant extracts. The performed review focused on the strengths and weaknesses of each method in view of the particle size, crystallinity, surface morphology, purity, and photocatalytic activity. In addition to the analysis of semiconductor photocatalyst synthesis methods, the literature review analyzed the methods for characterization of photocatalysts to link their characteristics with the efficiency of photocatalytic activity. X-ray diffraction (XRD) was used for crystallographic characterization, while scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to assess the morphology and size of the materials. Fourier-transform infrared spectroscopy (FTIR) was used to detect surface functional groups, and UV-visible diffuse reflectance spectroscopy (UV-DRS) was employed to assess optical absorption and bandgap. The study also employed BET surface area and photoluminescence (PL) spectroscopy. Most studies described in the reviewed literature discuss photocatalytic degradation of various wastewater contaminants, such as synthetic dyes, pharmaceuticals, antibiotics, pesticides, phenolic compounds, EDCs, and heavy metals. The efficiency of the photocatalysts is discussed with regard to degradation efficiency, mineralization efficiency, stability, recyclability, as well as the efficiency of photocatalysts under UV and visible light. Some of the factors affecting photocatalytic efficiency were investigated, including catalyst concentration, pH, contaminant concentration, irradiation time, light intensity, and temperature.

The data collected through literature review allowed for determining the advantages and disadvantages of different types of semiconductor photocatalysts. The review considered recent advances in heterojunction photocatalysts, metal and nonmetal doping,

Photocatalyst	Band Gap (eV)	Light Source	Major Advantages	Limitations
TiO_2	3.2	UV	High stability, non-toxic	UV active only
ZnO	3.2	UV	High photocatalytic activity	Photocorrosion
WO_3	2.6-2.8	Visible	Good chemical stability	Weak reduction ability
$g\text{-}C_3N_4$	2.7	Visible	Metal-free, low cost	Fast e^-/h^+ recombination
$BiVO_4$	2.4	Visible	Strong visible-light absorption	Low charge mobility
Fe_2O_3	2.0-2.2	Visible	Abundant, inexpensive	Short carrier lifetime

nanostructured materials, Z-scheme photocatalysts, as well as solar photocatalysis. The paper wraps up by providing an overview of the obtained results while identifying the existing gaps and challenges in the field.

Results and Discussion

Based on the literature review, we can conclude that the application of semiconductor photocatalysts for the effective treatment of wastewater containing organic and inorganic pollutants looks very promising. Photocatalytic processes are advantageous compared to conventional treatment methods, as they allow for total mineralization of undesirable components into harmless substances such as carbon dioxide or water. The effectiveness of photocatalytic processes is determined by several factors, such as the type of semiconductor material used, the light source, the quantity of photocatalyst, parameters of pollutants, pH of the solution, treatment time, and characteristics of photocatalysts' surface.

Of all known semiconductor materials, titanium dioxide has always been attributed to the most effective ones in photocatalytic applications due to its high oxidation potential, stability, harmlessness, and affordability. Researchers have proved that titanium oxide can degrade large amounts of dyes (e.g. methylene blue, rhodamine B, methyl orange, Congo red) using ultraviolet light. Unfortunately, due to its wide bandgap, titanium dioxide cannot be activated by means of visible light. To solve this problem, scientists began modifying titanium dioxide with the help of metal and non-metal dopants and formation of heterojunctions.

Zinc oxide is very efficient in treating wastewater due to its high electron mobility and excellent photocatalytic properties.In any case, photocorrosion and lack of long-term stability remain two key problems. Some research suggests that the combination of ZnO materials with TiO_2, graphene or graphitic carbon nitride can increase their stability and efficiency of degradation in visible light conditions. Semiconductor materials which are responsive to visible light, such as graphitic carbon nitride (g-C_3N_4), bismuth vanadate ($BiVO_4$), tungsten trioxide (WO_3) and iron oxide (Fe_2O_3), have shown significant potential in the area of solar treatment of wastewater. These materials are known to have smaller band gap energy and thus make more effective use of solar spectrum. It has been reported in some studies that the heterojunctions created by these semiconductors make the process of charge separation more efficient, inhibit the electrons-hole recombination process and increase the number of reactive oxygen species used for degrading pollutants. Nanotechnology has fundamentally changed the effectiveness of photocatalysis. Nanostructures of photocatalysts, such as nanoparticles, nanotubes, nanosheets and nanorods provide higher surface area for processes of photocatalysis. At the same time, small dimensions of the particles make the distance, which charge carriers must pass shorter, minimizing the negative impact of recombination and increasing the process of degradation. Many studies have proven that nanocomposite photocatalysts are more effective than classical photocatalysts in terms of speed, durability and effectiveness. The materials reviewed in the sources show that semiconductor photocatalysts are very good at degrading various types of wastewater pollutants. Recently, different types of dyes used for fabric coloring, medical residues, antibiotics, pesticides, endocrine-disrupting chemicals, phenolic compounds and heavy metal ions have been successfully eliminated with the help of advanced photocatalysis systems. What is even more interesting, several studies have indicated the effectiveness of photocatalysis to destroy pathogenic microorganisms. However, the study points out that many challenges must be solved in order to use semiconductor photocatalysts on a large scale. Thus, problems of quick electrons-hole recombination, lack of certain visible light absorption by some materials, photocorrosion and recovery of catalysts among others exist. Therefore, future researches must concentrate on the creation and production of the photocatalysts which will remain stable during use, will be reusable, which will have the ability to work under the direct sun and are eco-friendly. In conclusion, the materials shown in this report prove that semiconductor photocatalysis might become one of the most promising technologies of wastewater treatment.

Conclusion

Semiconductor photocatalysis has become one of the most effective and environmentally friendly technologies for the treatment of wastewater. This is due to the fact that since many industries and households discharge waters containing toxic pollutants such as synthetic dyes, residues of medicinal agents, biocides, heavy metals, and so on, the demand for effective treatment technologies has been rapidly increasing. The publications cited in the present review show that semiconductor photocatalysis is able to solve these problems because it uses light energy for the destruction of poisonous pollutants without causing extensive pollution of the environment. Out of all semiconductor photocalysts, titanium dioxide (TiO_2) is by far the most widely studied photocatalyst due to its good chemical stability, its high oxidation potential, and the fact that it is non-toxic and cheap. Some other materials such as zinc oxide (ZnO), graphitic carbon nitride (g-C_3N_4), tungsten trioxide (WO_3), bismuth vanadate ($BiVO_4$), iron oxide (Fe_2O_3), cadmium sulfide (CdS), etc. have also revealed a great potential for wastewater treatment. Patented methods in nanotechnology and construction of heterojunctions, as well as elemental doping and the production of composite materials have already made photocatalysis process more efficient by improving the absorption of light in visible light spectrum and minimizing the recombination of electron-hole pairs. The review also refers to the fact that photocatalysis is a capable enough technique to degrade such pollutants as synthetic dyes, antibiotics, phenolic compounds, biocides, endocrine disruptors, and pathogenic microorganisms. The possibility of cutting down on contaminated water using the solar energy makes semiconductor photocatalysis an attractive and energy-saving technology. Despite the tremendous advancements made in photocatalysis in recent years, there are still quite a few difficulties which prevent the practical implementation of photocatalysts. The problems of durability of photocatalyst, its recovery and reuse, photocorrosion, low efficiency of utilization of solar light energy, and wastewater treatment still need to be solved in the further studies in the field. The main attention of the further research in photocatalysis should be given to the development of efficient and reusable photocatalysts which cost little and are harmless. All research done in photocatalysis should be conducted in real conditions with the use of the existing technologies. In conclusion, it should be stressed that semiconductors are one of the most promising technologies for wastewater treatment due to their effectiveness, compatibility with environment, and solar dependability.

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