

## Advancement in Photocatalyst and Piezophotocatalyst Micromotor for Environmental Remediation: A Concise Review

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### ABSTRACT

This review analyses recent advancements in the synthesis and environmental applications of photocatalysts and piezophotocatalysts, pivotal for organic pollutant degradation and water remediation. Traditional semiconductor photocatalysts often face rapid electron-hole recombination and limited visible light absorption. Innovations have led to the development of semiconductor heterojunctions that enhance photocatalytic efficiency by improving charge separation and expanding light absorption. This review emphasizes semiconductor-semiconductor and semiconductor-metal interfaces, which significantly improve photocatalytic performance. Additionally, piezophotocatalysts have emerged, utilizing mechanical energy to augment chemical reactions, thereby increasing efficiency and applicability under various conditions. The review also highlights the role of photocatalyst-based microrobots in targeted water treatment, utilizing local chemical energy for precise operations. These advancements showcase the potential of photocatalytic and piezophotocatalytic technologies in environmental sustainability, highlighting current trends and future prospects for effective environmental remediation.

## 1. Introduction

Environmental pollution, especially from organic contaminants, poses a significant challenge to global health and the ecological balance. Photocatalysis, which leverages the power of light to initiate chemical reactions, has emerged as a promising technology for addressing such pollution. Recent advancements in photocatalytic materials have significantly enhanced their efficiency and effectiveness in degrading a wide range of pollutants. These materials, often composed of semiconductors like titanium dioxide, can break down harmful organic compounds into less toxic

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substances. Furthermore, the development of novel photocatalysts with improved light absorption and charge separation properties holds great potential for large-scale environmental remediation applications.

Traditional photocatalysts, such as titanium dioxide (TiO<sub>2</sub>), have been widely studied for their ability to utilize ultraviolet (UV) light to degrade pollutants. Despite their efficacy, their application is limited by quick electron-hole recombination and restricted ability to absorb visible light. This review discusses innovative modifications to traditional photocatalysts, including the development of semiconductor heterojunctions, with the aim of overcoming these limitations. Semiconductor heterojunctions, involving a combination of different semiconductors, have shown potential for enhancing charge separation and extending the light absorption spectrum to the visible range. This is achieved through the strategic alignment of the bandgaps, which facilitates improved photocatalytic activity under natural sunlight.

In addition to semiconductor-based solutions, this review explores piezophotocatalysts, a novel class of materials that integrate piezoelectric properties with photocatalytic functionalities. By utilizing both light and mechanical energy, piezophotocatalysts offer a dual-stimulus approach to enhance the chemical reactions necessary for environmental cleanup. Mechanical energy, derived from environmental vibrations or pressure changes, induces electrical charges in these materials, aiding in the separation of charge carriers and boosting the overall catalytic efficiency.

Another innovative area covered in this review is the application of photocatalyst-based microrobots for environmental remediation. These microscale robots are capable of autonomous movement and harness photocatalysts to drive localized chemical reactions for targeted pollutant degradation. Engineered on the nanoscale, microrobots can access confined spaces and perform precise operations, making them particularly suitable for applications such as water treatment, where they can directly interact with and degrade contaminants.

This review focuses on the advancements in the field of photocatalyst and piezophotocatalyst synthesis, particularly for environmental remediation. The primary objective of this review is to examine the recent developments in the synthesis of these materials, their mechanistic actions, and their environmental applications, with a focus on the degradation of organic pollutants and water treatment. This concise review aims to set the stage for a comprehensive discussion on the significant strides made in photocatalytic technology, highlighting innovative approaches that have the potential to revolutionize environmental remediation efforts. Through this review, readers will gain an understanding of key advancements, the underlying principles driving these innovations, and their implications for future research and applications in the field of environmental science. The remainder of this paper is organized as follows. It begins with a discussion of the limitations of traditional photocatalysts and the rationale behind the development of advanced heterojunctions. It then delves into the synthesis and mechanistic insights of semiconductor heterojunctions and piezophotocatalysts, followed by an exploration of emerging applications of microrobots in environmental contexts. Each section details the current state of research and critically evaluates the efficacy and practicality of these technologies for real-world applications.

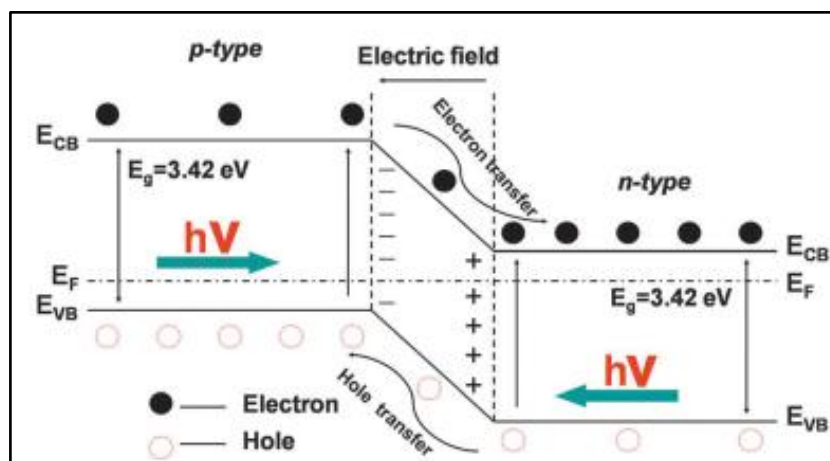
## **2. Photocatalyst Synthesis and Environmental Applications**

Photocatalysts have gained significant attention for their potential to decompose organic pollutants, as documented in various studies [1]. Specifically, semiconductor photocatalysts are valued for their environmentally friendly applications, such as splitting water into hydrogen and oxygen [2]. These materials absorb light energy, which leads to the generation of reactive oxygen species (ROS) and the creation of charge carriers including electrons and holes [3]. Electrons excited

to the conduction band react with oxygen to produce superoxide radicals, while holes in the valence band interact with water to generate hydroxyl radicals and protons ( $H^+$ ) [4]. These ROS then initiate surface redox reactions that degrade pollutants, ultimately resulting in the formation of carbon dioxide, water, and various lower-carbon organic compounds [5,6].

Despite the benefits of pollutant degradation, semiconductor photocatalysts face challenges such as the rapid recombination of charge carriers and limited absorption of visible light. Addressing these limitations has led to the development of photocatalyst heterojunctions, which often involve the combination of different types of photocatalysts [2]. For instance,  $TiO_2$ , an effective semiconductor, has a wide bandgap that requires ultraviolet or near-ultraviolet radiation for activation. The current trend is focused on the development of visible-light-driven photocatalysts to enhance their usability under broader light conditions. Nonetheless, challenges such as short-lived electron-hole pairs and limited visible light absorption continue to persist, emphasizing the necessity for further development in this area.

Various enhancements have been implemented to improve photocatalytic efficiency, including advanced textural design, doping, and the formation of semiconductor heterojunctions with metals or other semiconductors. Recent literature reviews by Wang *et al.*, have explored the rational design and fabrication of heterojunction photocatalysts, encompassing semiconductor-semiconductor, semiconductor-metal, semiconductor-carbon, and multicomponent heterojunctions [2]. Each modification offers distinct improvements in the photocatalyst performance. In particular, in semiconductor-semiconductor heterojunctions, enhanced charge collection and separation are achieved when p- and n-type semiconductors form a p-n junction, as illustrated in Figure 1 [2]. This junction establishes a space-charge region at the interface, creating a built-in electrical potential that directs the electrons and holes to travel in opposite directions. This setup not only facilitates effective charge separation, but also ensures rapid charge transfer to the catalyst, extends charge carrier lifetimes, and segregates locally incompatible reduction and oxidation reactions at the nanoscale, thereby significantly boosting the photocatalytic performance.



**Fig. 1.** Schematic diagram of energy band structure and electron pair in p-n heterojunction. Adapted from [2]

$TiO_2$ -based semiconductor-semiconductor heterojunctions have garnered considerable attention owing to their surface modification capabilities. These systems are particularly notable for their high dye adsorption capacity, extended range of light absorption, enhanced charge separation, and improved mass transfer, which collectively contribute to significantly increased photocatalytic efficiency. A notable example is the  $Bi_2WO_6-TiO_2$  heterojunction developed by Wang *et al.*, which demonstrated a remarkable enhancement in visible-light-driven photocatalytic activity. This

heterojunction was shown to decompose  $\text{CH}_3\text{CHO}$  with an efficiency eight times greater than that of  $\text{Bi}_2\text{WO}_6$  or  $\text{TiO}_2$  alone. This improved performance was attributed primarily to a reduction in electron-hole recombination and enhanced migration of photogenerated carriers [7].

Additionally, semiconductor-metal heterojunctions introduce a Schottky barrier that acts as another region for space-charge separation, effectively altering the movement of electrons from a higher to a lower Fermi level. The presence of this Schottky barrier significantly mitigates the recombination of electrons and holes, thereby enhancing the photocatalytic performance of the system [2]. For instance, Li *et al.*, developed  $\text{Ag}/\text{Bi}_2\text{WO}_6$  three-dimensional flow-like microspheres measuring approximately  $4\ \mu\text{m}$  in diameter using a straightforward hydrothermal method. The photocatalytic efficacy of these microspheres was assessed by the decolorization of rhodamine B under simulated sunlight. The results indicated a marked increase in the photocatalytic activity of the samples containing 1 wt% Ag-loaded  $\text{Bi}_2\text{WO}_6$ . This enhancement was largely due to the synergistic effects of the strong surface plasmon resonance of Ag and the efficient separation of photogenerated electrons and holes [8].

### 3. Piezophotocatalytic Materials and Water Remediation Application

Certain nanomaterials possess piezoelectric properties that enable the conversion of mechanical energy into chemical energy, offering a promising solution to the limitations faced by conventional photocatalysts, such as rapid electron-hole pair recombination and low charge carrier mobility [9-11]. The piezoelectric effect in these materials can significantly enhance photocatalytic activity by effectively separating electron-hole pairs through polarization, which directly influences the catalytic performance [12].

The piezoelectric catalysis technology utilizes this capability to harness environmental mechanical energy and convert it into electrical energy. The intense electric fields generated by piezoelectric materials produce reactive oxygen species (ROS), such as  $\bullet\text{OH}$ ,  $\bullet\text{O}^{2-}$ , and  $\bullet\text{HO}_2$ , which are highly effective in degrading organic pollutants, eliminating microbes, and reducing heavy metal ions in wastewater [13,14], highlighting the broad applicability of piezoelectric materials in environmental cleanup.

Reflecting on this wide usage, extensive research, including reviews by Pan *et al.*, has been conducted, focusing on the enhancement of photocatalysis and photoelectrocatalysis through piezoelectric and photoelectric effects. These studies underline how piezo-enhanced photocatalytic reactions and piezo-phototronics can modulate band bending and charge migration, thereby optimizing the photocatalytic process [15]. Similarly, Wang *et al.*, reviewed how mechanical energy variations, such as stress and temperature changes, in piezoelectric and pyroelectric materials can be harnessed to generate active species crucial for purifying pollutants [16].

Piezoelectricity involves the conversion of mechanical strain into electrical charge and vice versa. External mechanical stress induces dielectric displacement within these materials, affecting their surface charge density and altering the direction and magnitude of polarized electric fields. Such changes enhance the separation of electron-hole pairs or photo-induced charge carriers, reducing recombination and increasing the availability of electrons and holes for redox reactions [17,18].

Current research on piezoelectric catalysts has primarily explored three types of materials: zinc oxide (ZnO), transition metal dichalcogenides (TMDs), and  $\text{ABX}_3$  perovskite-type oxides. ZnO, known for its 1D structure, enhances the charge carrier mobility, with its bent nanowires creating a piezoelectric field that facilitates charge movement [19,20]. TMDs, including  $\text{MoS}_2$ ,  $\text{WS}_2$ ,  $\text{MoSe}_2$ , and  $\text{WSe}_2$ , are recognized for their high specific surface area and van der Waals gaps, offering unique properties such as an asymmetric structure, exceptional mechanical flexibility, high conductivity,

abundant active edge sites, large piezoelectric response, and extensive surface area, making them ideal for piezoelectric applications [21,22].

Perovskites, characterized by the general formula  $ABX_3$ , provide a versatile framework for piezoelectric materials, enabling a mix of different A, B, and X ions to produce materials with excellent optical, catalytic, and physicochemical properties. For instance,  $BaTiO_3$  exhibits spontaneous polarization and is highly effective in degrading organic pollutants, while  $BiFeO_3$  nanopowders, with their small bandgap energy and strong visible-light absorption, are also widely utilized for this purpose [9,23].

This extensive body of research underscores the potential of piezo-photocatalyst materials to achieve high degradation rates for a variety of organic pollutants, including dyes, antibiotics, and other organic substances, as summarized in various studies and reports in Table 1.

**Table 1**

Summary of piezo-photocatalyst degradation toward organic pollutants

No	Piezo-photocatalyst material	Types of pollutants	Degradation time	References
1	$Ag-Na_{0.5}Bi_{0.5}TiO_3$	Rhodamine (RhB)	98.6% degradation in 120 min	[24]
2	$Ag/ZnO$	Methyl orange	100% degradation in 25 min	[25]
3	$AuPt/BiOBr$	Rhodamine (RhB)	99.8% degradation in 30 min	[26]
		Tetracycline (TC)	36.5% degradation in 40 min	
4	$BiVO_4/BiFeO_3$	Rhodamine (RhB)	98% degradation in 120 min	[27]
5	$MoSe_2/Bi_2WO_6$	Rhodamine (RhB)	99.8% degradation in 60 min	[28]
6	$BaTiO_3@TiO_2$	Rhodamine (RhB)	99.5% degradation in 75 min	[29]
		Methyl Blue (MB)	99.8% degradation in 105 min	
		Indigo Carmine (IC)	99.7% degradation in 45 min	
7	$BiOI/ZnO$	Bisphenol Solution (BPA)	100% degradation in 30 min	[30]
8	$NiO/BaTiO_3$	Rhodamine (RhB)	93% degradation in 90 min	[31]
9	$In_2O_3/BiFeO_3$	Tetracycline (TC)	93.2% degradation in 120 min	[32]

#### 4. Photocatalyst-Based Microswimmer/Micromotor/Microrobot for Water Treatment

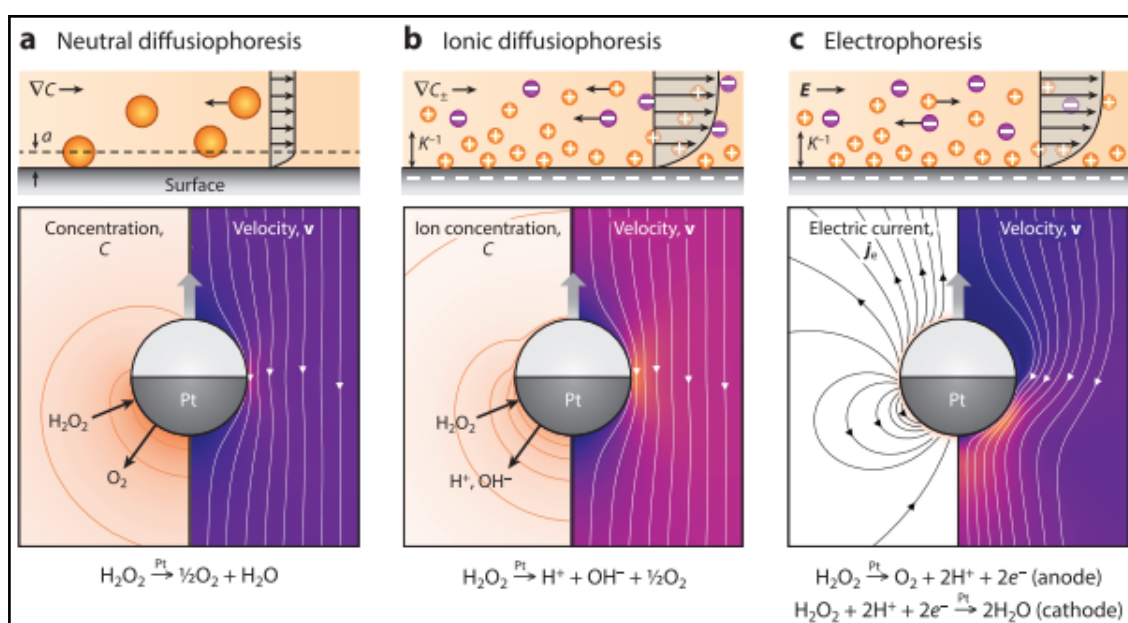
Microswimmers are micrometer-sized particles that convert local chemical energy into a propulsive force, mirroring natural phenomena observed in microorganisms, such as bacteria, algae, and spermatozoa, which are crucial in biological processes [33]. This biological inspiration has fueled the growing interest in developing micro- and nano-swimmers in recent decades, driven by the need for precise operation within complex and confined environments [34]. Micromotors and self-propelled particles epitomize this concept by extracting energy from their immediate surroundings to achieve directed motion [35].

Wirelessly operated microrobots are increasingly being used in various fields. These applications range from capturing microplastics and handling nuclear waste to purifying bacteria-contaminated water, engaging in precise chemical mixing, facilitating targeted drug delivery, conducting non-invasive microsurgery, and supporting various microfluidic applications [36-42]. Despite variations in size, shape, and propulsion mechanisms, all microswimmers operate at low Reynolds numbers, which enhances their ability to facilitate mass transfer [33]. However, a major challenge in the development of small-scale swimmers is the difficulty in incorporating internal batteries, given their limited volume [34].

To address this challenge, researchers have explored alternative energy sources, such as magnetic, electric, acoustic, and optical energy, although these approaches often face limitations, such as insufficient penetration depth, high costs, and the need for complex monitoring systems for effective feedback control [34]. Recently, advancements have been made in powering micromotors

with local chemical fuels (e.g.,  $\text{H}_2\text{O}_2$ ) as well as energy fields such as light or magnetic fields, and even using self-motile biological components such as algae and sperm. These developments are aimed at improving the functionality of non-motile objects for applications in water remediation, sensing, and medical therapies [43].

A landmark discovery in 2004 revealed the spontaneous swimming capabilities of a Pt Janus device in hydrogen peroxide fuel, achieving speeds up to  $10 \mu\text{m/s}$  [44]. This breakthrough demonstrated that the catalytic degradation of chemical fuels can effectively propel the motion of these devices. The propulsion mechanisms identified included neutral solute self-diffusiophoresis, ionic self-diffusiophoresis, and self-electrophoresis, contributing to a deeper understanding of how microswimmers can utilize chemical reactions for autonomous movement, as depicted in Figure 2.



**Fig. 2.** Phoretic mechanisms for self-propulsion of Pt-Janus Sphere. Adapted from [45]

In the mechanism of neutral solute self-diffusiophoresis, the surface of a Pt-Janus particle creates a local concentration gradient by generating oxygen because of the interaction between hydrogen peroxide and the Pt surface. This concentration gradient leads to particle motion, which is also known as diffusiophoresis. In ionic self-diffusiophoresis, the ion concentration gradient arises from the interaction between the  $\text{H}^+$  and  $\text{OH}^-$  ions produced from  $\text{H}_2\text{O}_2$ . This interaction drives the flow from the negatively charged surface to the positively charged surface, propelling the micromotor [45]. Furthermore, in self-electrophoresis, anodic currents are intensified near the equator of the Janus particle, whereas cathodic currents are concentrated at the poles. The resulting electric field induces an electroosmotic flow at the surface, which propels the motion of the Pt-Janus sphere.

Fuel-driven micromotors, also referred to as chemical or catalytic micromotors, utilize the reaction between a catalyst, typically platinum, owing to its efficiency in decomposing hydrogen peroxide, and chemical fuel to facilitate movement. This reaction often results in propulsion through bubble ejection or self-phoresis [46]. Externally driven microrobots, on the other hand, harness energy from external fields, such as light, acoustic, and electromagnetic fields. In particular, light-driven robots operate by generating electron-hole pairs in a photoactive material under irradiation. This process is often optimized by incorporating a metal-semiconductor junction to prevent the recombination of photogenerated carriers, thereby enhancing the motion through self-electrophoresis [47,48].

Magnetic fields also play a crucial role in enhancing the maneuverability of micromotors, thereby allowing them to operate in diverse media. These robots move either through magnetophoresis in a magnetic field gradient, or by converting rotational motion into translational movement via torque transfer in a rotating magnetic field. For example, helical propellers demonstrate translational movements under such conditions [49]. Recent advancements have showcased chalcogenide semiconductors as promising materials for the construction of light-driven microrobots. Notable studies include that of Zhan *et al.*, who observed strong dichroic swimming behavior in core-shell  $\text{Sb}_2\text{Se}_3/\text{ZnO}$  nanomotors under controlled light conditions [50]. Additionally, Chen *et al.*, demonstrated dynamic control over the assembly, disassembly, and reconfiguration of light activated  $\text{MoS}_2$  colloidal motor swarms, revealing capabilities beyond those achievable in static systems [51]. Moreover, de la Asuncion-Nadal *et al.*, highlighted the light-triggered photophoretic motion of  $\text{WS}_2$  micromotors, which displayed positive photophoretic motion and swarming-like schooling behavior [52]. These insights into propulsion mechanisms and the diverse applications of microswimmers and micromotors emphasize their potential in advancing technologies for targeted environmental and biomedical applications, reflecting significant strides in material science and robotic engineering.

## 5. Conclusion and Future Outlook

Advancements in photocatalyst and piezophotocatalyst technologies are significant milestones in the quest for efficient and sustainable environmental remediation solutions. The development of semiconductor heterojunctions has played a pivotal role in overcoming the intrinsic limitations of traditional photocatalysts, such as rapid electron-hole recombination and limited visible-light absorption. These heterojunctions enhance the charge separation and broaden the absorption spectrum, thereby maximizing the utilization of solar energy.

Piezophotocatalysts further extend the capabilities of traditional photocatalytic systems by incorporating mechanical energy harvesting, which boosts charge carrier separation and catalytic efficiency. This dual-stimuli responsiveness allows for the activation of photocatalytic processes under various environmental conditions, enhancing the versatility and effectiveness of these materials in practical applications.

Moreover, innovative integration of photocatalysis into microrobot systems opens new avenues for targeted and efficient pollutant degradation. These microrobots, equipped with self-propulsion capabilities and precise control, can access and treat pollution at their source, offering a promising approach for tackling environmental challenges on a microscale.

In the future, continuous refinement of these technologies is essential. Emphasis should be placed on enhancing the stability and scalability of these advanced materials to facilitate their transition from laboratory to real-world applications. Additionally, further research on the integration of multiple types of energy harvesting within single systems could lead to even more robust and effective environmental remediation technologies.

The convergence of materials science, nanotechnology, and environmental engineering in the development of advanced photocatalytic materials holds great promise in delivering practical, efficient, and sustainable solutions to combat environmental pollution. This field can significantly impact global sustainability efforts by addressing technical and scalability issues.



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