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Review Article

Heterogeneous Photocatalysis for Environmental Pollutant Removal: Reaction Mechanisms, Advanced Materials and Environmental Applications : A Review

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Abstract
In order to address persistent pollutants from the environment, heterogeneous photocatalysis is an effective and sustainable method for removing such contaminants through a variety of water systems. In this review, we have critically examined the fundamental reaction mechanisms of heterogeneous photocatalysis and provided an overview of the most recent advances in photocatalytic materials, including doped titanium dioxide, zinc oxide, tungsten dioxide, bismuth vanadium oxide, and metals-organic frameworks and their environmental applications. We will discuss the manner in which the application of nanostructured photocatalysts can enhance the number of active surface sites, reduce charge carrier recombination rates, and increase the amount of UV light absorbed in the visible region. Further, we will describe current challenges and future opportunities with respect to the optimisation of photocatalytic material, development of photocatalytic reactor design, and commercial-scale application of photocatalytic technologies as a comprehensive reference for the anticipated developments in photocatalytic treatment.

INTRODUCTION

Water pollution is still a significant environmental problem and it has many negative effects on the environment and on all aspects of human health. Water pollution also threatens water security[1]. Traditional treatment methods such as coagulation (clumping of small particles), sedimentation (settling), filtration and activated carbon adsorption do not sufficiently remove persistent organic pollutants, heavy metals from wastewater or newly-discovered contaminants (e.g., pharmaceuticals) or endocrine disruptors[2]. Advanced Oxidation Processes (AOPs) have emerged as promising alternatives due to their ability to generate highly reactive species capable of degrading complex organic molecules. Among these, heterogeneous photocatalysis has attracted significant attention[3]. The incorporation of nanotechnology into photocatalytic systems has further enhanced treatment efficiency by increasing surface area, improving charge separation, and accelerating reaction kinetics[4].

Photocatalysis: There has been a tremendous amount of research investigating photocatalysis over the last few decades, producing a great deal of data on the processes involved[20]. Photocatalysis is essentially the production of electron-hole pairs by means of oxidation and reduction reactions occurring on the surface of the catalyst, typically below the intensity of incoming light. The organic pollutant can undergo direct oxidation via a hole produced through this mechanism, or an organic pollutant may undergo oxidation indirect by a reaction involving specialized reactive groups (Reactive Oxygen species, ROS) produced in the solution, in conjunction with a photocatalyst[5].

Photocatalyst Materials: Photocatalyst materials utilized for water treatment and environmental remediation encompass conventional metal oxides, visible-light-responsive semiconductors, metal-free photocatalysts, and advanced hybrid systems. Titanium dioxide (TiO_2) and zinc oxide (ZnO) are widely employed due to their chemical stability, low cost, and high oxidative potential under UV irradiation, although both are constrained by wide band gaps and rapid electron-hole recombination. Narrow band gap semiconductors, such as tungsten trioxide (WO_3), bismuth vanadate ($BiVO_4$), and hematite (α-Fe_2O_3), demonstrate efficient visible-light absorption, yet their photocatalytic performance is often limited by poor charge carrier mobility. Metal-free materials, including graphitic carbon nitride (g-C_3N_4) and cadmium sulfide (CdS), offer visible-light activity, with CdS being susceptible to photocorrosion and potential toxicity. Emerging photocatalysts such as silver-based materials (A_g3PO_4), metal-organic frameworks (MOFs), and perovskite-type oxides present tunable electronic structures and enhanced surface properties, although challenges related to stability, scalability, and synthesis complexity remain[6-12].

Dyes: The textile industry produces the highest volume of liquid effluents that contaminate water due to the significant amount of water consumed during the dyeing process. Additionally, the various characteristics of the effluent such as pH, DO, chemical (organic/inorganic) contents are based on different dyeing process steps and the types of synthetic dyes used in this conversion[14]. Textile dyes are typically the most prevalent types of organic contaminants in water and azole dyes are by far the main number of synthetic dyes available, followed closely by anthraquinone dyes, which do not degrade under visible and UV light irradiation, and are resistant to aerobic degradation; however, they may convert into carcinogenic aromatic amines when anaerobically treated or in vivo[1,15]. Azo dyes are the most frequently used synthetic colorants in everyday operations one or more azo bonds (N=N) and which also have many different alkyl that are usually of an aromatic nature, and have auxochrome groups (-OH, -SO3, and others) that contain compounds that cause poisonous, mutagenic, carcinogenic, biodegradable pollution of the aquatic environment, and have become an environmental health risk to the communities in which they are discharged[16]. Some of the most common techniques available for eliminating azo dyes from water include methods such as adsorption, coagulation, photo-catalysis, ozonation, and biosorption. Although these techniques have been employed successfully in many instances, they are frequently costly and labour-intensive to implement. As such, these methods are often not considered viable alternatives to current methods for the removal of azo dyes from aquatic systems[17]. There are Various kind of dyes utilized for the dyeing of varies appear in (Table 1)

Advanced Oxidation Processes (AOPs): Advanced Oxidation Processes (AOPs) represent a class of technologies that oxidise numerous distinct organic contaminants found in contaminated waters to generate scientifically acceptable-quality drinking waters (and/or for all purposes[18]) by oxidising these compounds. The breakdown of antibiotics appropriate at the time-due largely to the costs and efficiencies of the Fenton process-has induced many research

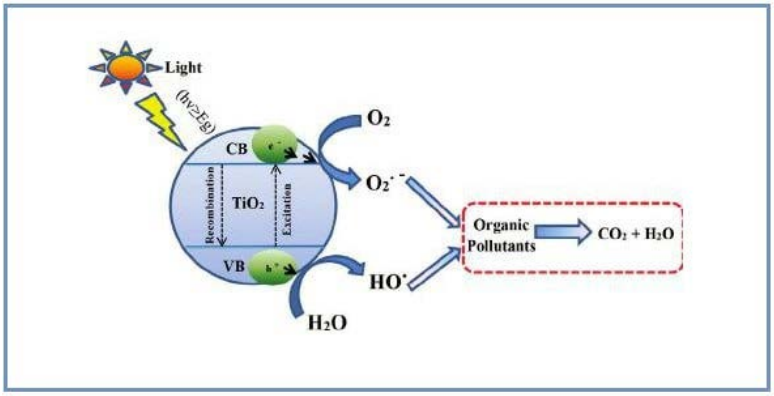

Fig. 1. Schematic representation of the photocatalytic degradation process

interests in this topic[19]. Advanced oxidation processes are a group of technologies similar but not identical in nature, and although they are mostly (but not limited to) generated through the formation of highly reactive hydroxyl radicals, they can also be generated by heterogeneous and/or homogeneous photocatalysis; by Fenton processes (and/or its derivatives); through ozonation; via ultrasonics; microwaves; gamma radiation; through electrochemical methods; and by the process of wet oxidation[20]. AOPs have been used to effectively eliminate pollutants in the manufacturing of drinking waters and in the removal of biorecalcitrant, micro-pollutant concentrations from bioprocessing systems, as well as for the disinfection of drinking waters, including processes that are photo-assisted. These processes rely on the formation of highly reactive intermediates, which are typically free-radicals, that may mineralise virtually any compound that can be oxidised[21]. Abstract of disadvantages and advantages of these ways appear in Table 2.

Principles of Heterogeneous Photocatalysis: Heterogeneous reactions are becoming increasingly popular and widely studied among the many different types of chemical reactions. In particular, the industrial use of heterogeneous reactions highly depends on the use of solid catalysts. Currently, approximately 80% of commercially available catalytic processes use heterogeneous environments. One of the most studied forms of heterogeneous reactions is how reactions at the surface of solid materials occur[22-24]. During the last decade, however, many other types of heterogeneous reactions have not been studied at the macroscopic level because of the limitations imposed by technology. In the case of liquid-liquid heterogeneous materials, for instance, it is very challenging to perform phase separation and very difficult to investigate these types of systems with optical spectroscopy due to the enormous amount of light-scattering from the heterogeneity of the material[25-27]. Heterogeneous photocatalytic processes utilizing semiconductor oxides, metal oxides, and solar lamps have been developed in the last ten years to remove both organic and inorganic pollutant from carbon dioxide and water. One of the most commonly used semiconductor materials is titanium dioxide (TiO_2), which is a highly stable and inexpensive metal oxide that is also nontoxic and environmentally safe[27-30]. These materials can be used in water purification, hydrogen production, partial and/or complete oxidation of organic compounds, and removal of various types of gaseous pollutants. Heterogeneous photocatalytic reactions involve semiconductor materials that produce electron-hole pairs. The photocatalytic activity of a material is determined by its bandgap, which describes the difference in energy between the valence and conduction bands of the material[30-33]. When a photon hits a material and has an energy level equal to or greater than the material's bandgap, electrons are able to move frame and create holes. In this case, the photoexcited electrons and holes can participate in redox reactions with adsorbed reactants unless they recombine on their way to the catalyst's surface[20,31,33]. In the last few decades, researchers have dedicated their efforts to finding new ways to improve the heterogeneous photocatalytic process since TiO_2 was the first photocatalyst discovered to be photocatalytically active. It is well established that this process generates some hydroxyl radicals and superoxide ions, which are responsible for oxidizing organic pollutants into carbon dioxide and water[34,37,40].

Applications in Pollutant Degradation: Photocatalysis has demonstrated considerable effectiveness in the degradation of various environmental contaminants. In the context of water treatment, it has been successfully employed to break down a wide range

Table 1: Comparative Overview of Major Photocatalysts[13].

Material	Band Gap (eV)	Light Response	Key Advantages	Key Limitations
TiO_2	~3.2	UV	High stability, non-toxic, low cost	Limited visible-light absorption, charge recombination
ZnO	3.2–3.3	UV	High electron mobility, strong photocatalytic activity	Photocorrosion, instability under acidic conditions
WO3	2.6–2.8	Visible	Absorbs visible light efficiently	Weak reduction potential, poor electron transport
BiVO4	~2.4	Visible	Strong visible-light absorption	Limited charge carrier mobility
a-Fe2O3	~2.1	Visible	Abundant, environmentally benign, low cost	Short carrier diffusion length, low conductivity
g-C3N4	~2.7	Visible	Metal-free, chemically stable, low cost	Rapid charge recombination
CdS	~2.4	Visible	Strong reduction ability	Photocorrosion, potential toxicity
Ag3PO4	~2.4	Visible	High quantum efficiency	Photoreduction instability
MOFs	Tunable	UV/Visible	High surface area, tunable porosity	Water stability, scale-up challenges
Perovskites (SrTiO3, LaFeO3)	2.0–3.2	UV/Visible	Adjustable band structure, tunable composition	Complex synthesis, stability issues

Table 1: Several kinds of textile dyes[22].

Dye	Example
Dyes Acid	Acid red 57, Acid-blue 25, Congo-red, methylene orange
Dyes Basic	Basic yellow 28, basic red9 ,Basic red 46, Malachite green, basic brown, methylaene blue
Dyes Disperse	Disperse orange, disperse yellow, disperse reddisperse blue
Dyes Reactive	Reactive red, remazol, ,reactive yellow 2, reactive black5
Vat	Vat blue, indigo ,Vat green 6,
Dyes Direct	Black direct, violet direct, orange 34 direct, direct blue

Table2: Techniques of the Separation disadvantages and advantages[22].

Techniques Separation	Disadvantages	Disadvantages
Chemical methods		
Ozonation	Some photocatalyst degrades intotoxic by-products	No sludge generation
Photocatalyst	Working cost is very great, halflife is short (20 min)Some photocatalyst degrades intotoxic by-products.	Working cost is littleand economicallyfeasible
Fenton reagent	Disposal issues and sludgeproduction	Little-priced reagentand afficient process
Biological methods		
Degradationanaerobic	conditions aerobic requireLarge treatment and yield ofhydrogen sulphide and methane	By-products may beutilized as energy resources
Aerobic degradation	Provide suitable environment forgrowth of microorganisms andvery slow process	Operational cost is lowand effective inremoval of azo dyes
Physicochemical methods		
Adsorption/sorption	Low surface area for some adsorbents, high cost ofadsorbents.	High adsorptioncapacity for all dyes.
Ion exchangeElectro kineticcoagulation	Need to dispose of adsorbents .Need further treatments byflocculation and filtration andproduction of sludge	No loss of sorbents Economically feasible
Membrane filtration.	Suitable for treating low volumeand production of sludge	Effective for all dyeswith high qualityeffluents

of pollutants, including organic dyes (e.g., methylene blue and rhodamine B), pharmaceutical residues, pesticides, herbicides, and persistent organic pollutants (POPs)[35-36]. Enhanced photocatalysts, inclusive of doped titanium dioxide (TiO_2) and next generation semiconductor materials, are suitable candidates for converting complicated organic molecules into harmless byproducts; photocatalysts can also be used to remove metals from water by means of photocatalytic reduction reactions. Toxic metal ions may be reduced to less harmful or easily removable compounds via photocatalytic reduction reactions[38-39]. Photocatalysis was established as a recognised and commercially viable technology at the end of the 20th century. Typically, photocatalytic technology is used in the following areas: wastewater treatment, air purification, self-cleaning surfaces, photovoitaic systems and solar energy systems. The design and development of photocatalytic materials is still in early stages and will continue to evolve, resulting in more effective, selective and scalable solutions to today's challenges[40-42].

CONCLUSION

Heterogeneous nanophotocatalysis is a very effective and environmentally sustainable method for removing persistent pollutants from a given Advances in photocatalytic materials-such as doped TiO_2, ZnO, WO_3, $BiVO_4$, and MOFs-have significantly improved photocatalytic efficiency and expanded activity into the visible light region. Despite these advancements, challenges related to catalyst stability, charge recombination, and large-scale implementation remain. Future research should focus on material optimization, reactor design, catalyst recovery, and industrial-scale applications to fully exploit the potential of photocatalytic water treatment technologies.

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