



Review

Review on the criteria anticipated for the fabrication of highly efficient ZnO-based visible-light-driven photocatalysts

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ABSTRACT

Among the popular photocatalysts, ZnO is one of the most potent photocatalysts considering its green properties, cheap price, and durability. However, the practical application of ZnO is limited because of its large band gap energy and rapid recombination of the photoinduced electron–hole pairs. This paper reviews the main advancements in overcoming the barriers accompanied by pure ZnO and the criteria for fabrication of effective visible-light-responsive ZnO-based photocatalysts. Herein, the binary ZnO-based nanocomposites with p–n heterojunctions, n–n heterojunctions, and ternary ZnO-based nanocomposites based on different heterostructures, and their mechanism for enhanced light harvesting and charge separation/transfer were thoroughly discussed.

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Introduction

Water is one of the most important substances on the earth, which is critical for life-sustaining of all living creatures. Although about 71% of the earth surface is covered by water, only about 2.5%

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is fresh water [1,2]. On the other hand, water consumption in various sectors has been dramatically overdone in the past decades, which caused diminution in fresh water required for wildlife and human life. In addition, billions of people access to limited clean water resources, that makes them vulnerable to water-borne infections [3]. It is estimated that prior to 2015, approximately 70% of the globally generated wastewater was not properly treated so that their discharge caused the pollution of receiving natural water-bodies. Correspondingly, by 2025, it is predicted that 50% of the people will face clean water crises [4].

In light of this, there is an urgent need to develop effective, dependable and economically viable methods to deal with the emerging contaminants and address the safety problems caused by them [5]. In the last decades, several technologies have been established for wastewater treatments [6–8]. The well-known methods are coagulation [9], sedimentation–flocculation [10], ion exchange [11], molecular sieves [12,13], reverse osmosis [14], membrane filtration [15], adsorption processes [16], ozonation [17], chlorination [18], chemical precipitation [19], and chemical and electrochemical techniques [20,21]. The conventional treatment technologies are reportedly not cost- and energy-efficient and inadequate for complete degradation of recalcitrant contaminants in wastewater [22]. Accordingly, novel advanced treatment methods are needed to destroy organic portion of wastewaters. Over the past two decades, we have been witnessing an unprecedentedly large number of research on the wastewater treatment through advanced oxidation processes (AOPs) [23]. The in-situ generation of energetic oxidizing agents, mainly hydroxyl radicals ($\cdot\text{OH}$), superoxide anion radical ($\cdot\text{O}_2^-$), and photogenerated electron/hole (e^-/h^+) pairs through AOPs lead to the complete degradation and mineralization of contaminants in polluted water [24]. Heterogeneous photocatalysis has been recognized as one of the most appealing and potentially efficient AOPs owing to its relative low-cost and high stability, nontoxicity, no resistance to mass transfer and no secondary pollution, operation under ambient conditions, and more importantly the potential for decomposing the recalcitrant organic pollutants at

short reaction time into less harmful compounds [25–28]. In this regard, the application of semiconductor-based photocatalysis has received much attention across various disciplines as it offers an efficient and green solution for environmental problems (Fig. 1).

Fundamentals and applications of heterogeneous photocatalysis

The term photocatalysis refers to a process in which the rate of the chemical transformation is enhanced by a substance, i.e. photocatalyst, under the illumination of light without its ultimate alteration [29]. In this process, the incidence of light generates e^-/h^+ pairs in the conduction (CB) and valance bands (VB) of the semiconductor that take part in the redox reactions to produce the final products [30]. The photocatalytic reactions can be processed in a homogeneous and/or heterogeneous systems. The homogeneous photocatalysis involves the application of soluble photosensitive molecules such as photoactive dyes, whereas the photoreaction is accelerated in the presence of semiconductor photocatalyst in the heterogeneous systems [31,32]. In contrast to homogeneous catalysts, the heterogeneous photocatalysts are simply separated from the reaction medium, thus providing a greener route for application of this system at industrial scale [33,34]. The heterogeneous photocatalysis has a great potential to be applied in various disciplines, including removal of organic pollutants from air and water [35–37], disinfection of different microorganisms [38,39], CO_2 reduction [40], hydrogen generation via water splitting [41], nitrogen photofixation [42], synthesis of organic compounds [43], and anti-tumor activity [44].

Generally, four major steps take place during photocatalytic reactions after the absorption of light by a photocatalyst (Fig. 2): (i) formation of the charge carriers over the VB and CB, (ii) recombination of the photogenerated e^-/h^+ pairs, (iii) trapping of the e^-/h^+ pairs in redox reactions and finally (iv) the main photocatalytic reactions such as degradation of the pollutant [45,46]. In the first step, the incidence of light with the same or higher energy than the energy gap (E_g) of the employed



Fig. 1. The major advantages of photocatalysis systems for wastewater treatment.

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