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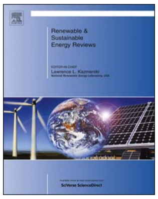

A review of ZnO nanoparticles as solar photocatalysts: Synthesis, mechanisms and applications

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ABSTRACT

Persistent organic pollutants (POPs) are carbon-based chemical substances that are resistant to environmental degradation and may not be completely removed through treatment processes. Their persistence can contribute to adverse health impacts on wild-life and human beings. Thus, the solar photocatalysis process has received increasing attention due to its great potential as a green and eco-friendly process for the elimination of POPs to increase the security of clean water. In this context, ZnO nanostructures have been shown to be prominent photocatalyst candidates to be used in photodegradation owing to the facts that they are low-cost, non-toxic and more efficient in the absorption across a large fraction of the solar spectrum compared to TiO_2. There are several aspects, however, need to be taken into consideration for further development. The purpose of this paper is to review the photo-degradation mechanisms of POPs and the recent progress in ZnO nanostructured fabrication methods including doping, heterojunction and modification techniques as well as improvements of ZnO as a photocatalyst. The second objective of this review is to evaluate the immobilization of photocatalyst and suspension systems while looking into their future challenges and prospects.

1. Introduction

In recent years, implementation of water reclamation and reuse is gaining attention rapidly world-wide due to the water scarcity occurred as a result of climate change and poor water resource management (i.e. limited access to clean water resources and water demands exceed the available resources). Access to clean water is becoming an ever increasing problem in an expanding global economy and population countries [1]. One of the attractive solutions in response to water issues is implementation of wastewater reclamation and reuse projects to ensure a sustainable water development and management. However, concerns still arise from the fact that persistent organic pollutants (POPs) could still be present in treated water.

POPs are carbon-based chemical substances that are resistant to environment degradation and have been continuously released into the environment. POPs can cause severe harm to human beings and wildlife because of their poor biodegradability and carcinogenic characteristics in nature. Advanced treatment technologies are crucial to ensure that the reclaimed water is free of POPs. Various water treatment techniques have been employed to remove POPs from water streams including adsorption, membrane separation and coagulation [2]; however these processes only concentrate or change the recalcitrant organic pollutants from the water to solid phase. Additional cost and treatments are thus needed to treat the secondary pollutants and regenerate the adsorbents [3]. For this reason, advanced oxidation processes (AOPs) have been proposed for the elimination of recalcitrant organic pollutants, especially for those with low biodegradability. According to Capelo et al. [4], AOP is a process that involves in situ generation of highly potent chemical oxidants with the assistance of ozone (O_3), hydrogen peroxide (H_2O_2), Fenton's reagent, UV light or a catalyst. The generated hydroxyl radicals (·OH) are strong oxidants that are able to oxidize recalcitrant organic compounds. AOPs offer several advantages such as: (i) rapid degradation rate, (ii) mineralization of organic compounds to green products, (iii) ability to operate under ambient temperature and pressure, and (iv) reduction of the toxicity of organic compounds.

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AOP mechanisms can be classified as homogeneous or heterogeneous photocatalysis. Homogeneous photocatalysis employs Fenton's reagent, which is a mixture of hydrogen peroxide and an Fe^{2+} salt to produce hydroxyl radicals under UV irradiation at wavelengths above 300 nm [5]. In contrast, heterogeneous photocatalysis employs semiconductor oxides as a photocatalyst [6]. Among semiconductors, titanium dioxide (TiO_2) has been the most studied compound in past decades. Owing to its low production cost and good chemical stability, it has been widely employed in photo-degradation of organic compounds, such as those with a high loading of nitrogen-containing organic compounds [7], saturated hydrocarbons (alkanes) [8], aromatic hydrocarbons [9] , non-biodegradable azo dyes [10], volatile organic compounds [11] and pesticides [12] with a UV light source. As reported by Wang et al. [13], the application of TiO_2 using solar energy is highly restricted by its large band gap (3.2 eV) and low quantum efficiency. Considerable attempts such as doping [14], formation of nanocomposites [15], surface modification, dye sensitization [16], noble metal [17] and non-noble metal deposition [18] have been made toward extending photoresponse and photoactivity of TiO_2 in visible light region. Comparable to TiO_2, ZnO is an n-type semiconductor oxide but has not been well investigated in previous studies. ZnO has been proposed as an alternative photocatalyst to TiO_2 as it possess same band gap energy but exhibits higher absorption efficiency across a large fraction of the solar spectrum when compared to TiO_2 [19,20]. In order to evaluate the photosensitization of ZnO and TiO_2, Fenoll et al. [21] compared the photo-degradation of fungicides in leaching water using the ZnO and TiO_2 under solar irradiation and found non-stoichiometric of ZnO rendering it a better photocatalyst compared to TiO_2 under solar irradiation.

Although AOPs have been shown to be effective in batement of recalcitrant organic matter, there is still much room for improvement. Firstly, the cost related to AOPs is a notable criterium in determining the applicability of the process in water treatment plants. Expensive chemicals and electricity consumption may lead to high operational costs and limit the applicability of AOPs in water treatment plants. Secondly, the rate of the degradation/oxidation reaction is dependent on the production of hydroxyl radicals and regeneration of ions [22]. Without sufficient formation of hydroxyl radicals, the effectiveness of AOPs in batement of recalcitrant organic pollutants is diminished. Many attempts have been made in the past decade to enhance the generation rate of hydroxyl radicals to improve AOP treatments [23]. Thirdly, there is a great need for understanding the toxicity of the intermediates and mineralization products generated from AOP. In a work by Rodriguez et al. [24], nicotine removal by employing Fenton's Reagent was used to study the mineralization and toxicity of intermediates generated in AOPs. They found that there was incomplete mineralization even though 100% of the nicotine was removed and the toxicity of the intermediates generated (especially those at initial stage of the oxidation process) was 15 times more greater than the initial solution.

Due to the advances in using photocatalysis in the degradation of recalcitrant organic pollutants, this technique has been developed for photocatalytic membrane reactors in large scale applications. Semiconductor oxides to be used in heterogenous photocatalysis are typically either – suspended in the effluent to be treated or immobilized on a support. The inconvenience of slurry-type reactors, in which the semiconductor oxides are suspended in the effluent, is the requirement of an additional step to recover the photocatalyst; such a process is not required using an immobilized-type reactor. Integration of photocatalysis into a membrane process is an approach that promises a continuous operation in addition to a good photocatalyst recovery [25].

The merits of photocatalysts suspended in the aqueous solutions are: low pressure drop across the reactor, good mass transfer of pollutants from the bulk liquid phase onto active surface sites of photocatalysts, and provision of a better platform for pollutants adsorption and desorption process throughout the reaction [26]. To compensate for the cost limitation of recovering the photocatalyst, heterogeneous photocatalysis which utilizes solar irradiation has been proposed as a more cost-effective process that can be conducted without the need for an artificial, and often costly, irradiation source.

Recently, more and more papers on fabrication and implementation of photocatalyst have been published due to the advantages of photocatalysis process. Hence, a review about the selection of appropriate photocatalyst fabrication methods to obtain desired dimension of ZnO nanostructures based on specific application and suitability of solar photocatalytic system should be carried out to ease the implementation of this technology in a bigger scale. The main objectives of the current review is to evaluate the employment of ZnO nanoparticles as solar photocatalysts, application of ZnO nanoparticles in water treatment, solar-photodegradation mechanisms of zinc oxide photocatalysis, synthesis methods of ZnO nanoparticles, comparisons between photocatalytic membrane reactor and the suspended system, as well as future challenges and prospects of using ZnO nanoparticles in these processes. Advantages through understanding the properties and characteristics of the ZnO photocatalyst in this paper, produced under various fabrication and modification methods, can provide researchers with different perceptions towards photocatalysis results that can possibly be obtained when the ZnO photocatalysts are integrated into different treatment systems.

2. Fundamental and mechanism of zinc oxide photocatalysis

ZnO is a type of semiconductor having a broad direct band gap width (3.37 eV), large excitation binding energy (60 meV) and deep violet/borderline ultraviolet (UV) absorption at room temperature [27]. It is an excellent semiconductor oxide that possesses favorable excellent electrical, mechanical and optical properties [28], similar to TiO_2. In addition, ZnO not only has antifouling and antibacterial properties, but also good photocatalytic activity [29]. Furthermore, as reported by Liang et al. [30], the production cost of ZnO is up to 75% lower than that of TiO_2 and Al_2O_3 nanoparticles. Due to the advantages of ZnO over TiO_2, ZnO has been suggested to be used in heterogeneous photocatalysis. According to Herrmann et al. [31], the heterogeneous photocatalytic oxidation steps can be explained as shown in Fig. 1.

1. Organic pollutants diffuse from the liquid phase to the surface of ZnO.
2. Adsorption of the organic pollutants on the surface of ZnO.
3. Oxidation and reduction reactions in the adsorbed phase.
4. Desorption of the products.
5. Removal of the products from the interface region.

When ZnO is photo-induced by solar light with photonic energy ($h\nu$) equal to or greater than the excitation energy (E_g), e^- from the filled valence band (VB) are promoted to an empty conduction band (CB). This photo-induced process produces electron-hole (e^-/h^+) pairs as shown in (Eq. (1)). The electron-hole pairs can migrate to the ZnO surface and be involved in redox reactions as shown in (Eqs. (2)–(4)), wherein the H^+ reacts with water and hydroxide ions to produce hydroxyl radicals while e^- reacts with oxygen to produce superoxide

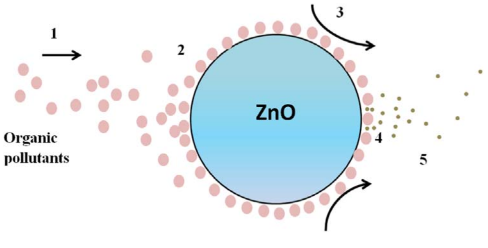

Fig. 1. Heterogeneous photocatalytic oxidation steps.
Adapted with permission from [31].