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Review Paper

Research progress on iron oxide-based magnetic materials: Synthesis techniques and photocatalytic applications

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Abstract

Heterogeneous photocatalysis is a promising strategy for advanced oxidation environmental remediation. Herein, this review aims to highlight recent development in the preparation of iron oxide-based magnetic nanoparticles and their applications for photocatalytic removal of organic pollutants in aqueous solution. The usage of iron oxide-based magnetic photocatalysts has received considerable attention in recent years due to their unique properties such as excellent magnetic properties, high stability against corrosion, large surface area and high surface modification flexibility. The synthesis routes for iron oxide nanomaterials such as co-precipitation, thermal decomposition, solvothermal, hydrothermal and microelmulsion processes had been summarized. Recent advances on the surface modification of iron oxide incorporating impurity doping, metal-loading, composite semiconductors and encapsulation of iron oxide are reviewed. In addition, the effect of surface modified iron oxide-based materials on the photocatalytic degradation performance and photocatalytic reaction mechanism are discussed in detail. Lastly, the toxicological effects owing to the iron oxide-based magnetic nanoparticles and potential challenges on their application in a sustainable way are also discussed.

Keywords: Photocatalysis; Iron oxide; Magnetic; Modification; Mechanism

Contents

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1. Introduction

Photocatalysts utilize light energy to carry out oxidation and reduction reactions. During photocatalytic oxidation, photocatalyst absorbs light energy and excites electron from the valence band to the conduction band. The resulting electron and hole can then further react with oxygen (O_2) and water (H_2O) to form superoxide anion (O_2^-) and hydroxyl radical ($\cdot OH$), respectively [1]. These two species possess strong oxidizing capability to oxidize organic pollutants. Until now, the most commonly used semiconductors as photocatalyst for degradation of organic pollutants are titanium dioxide (TiO_2) and zinc oxide (ZnO). The major drawback for these photocatalysts is related to its relatively wide band gap energy, i.e. 3.2 eV for anatase TiO_2 [2], 3.02 eV for rutile TiO_2 [3] and 3.2 eV for ZnO [1]. These semiconductors can only be excited by photons which are close to the UV region and utilize only 4–6% of solar light, which limits their practical applications [4].

In order to promote more efficient utilization of solar light, the development of visible light active or narrow band gap semiconductors as photocatalyts has attracted extensive attention. In this context, iron oxide with appropriate valence state and chemical composition can be considered as a high promising photocatalyst owing to its narrow band gap energy [5], high chemical stability [6], superior stability against corrosion [5] and low toxicity. It has been reported that iron oxide could absorb and utilize about 40% of the incident solar spectra [2]. However, its photocatalytic efficiency still depends on other factors such as particle size, aggregate size in suspension, crystalline phase, crystallinity and other structural parameters [7].

The separation of photocatalysts from treated water by using centrifugation or filtration is a time consuming and expensive process. This factor restricted the application of suspended photocatalysts in industrial scale. In order to overcome this deficiency, immobilizing photocatalysts on a suitable support has been developed. However, an obvious disadvantage of the immobilization system is the limitation of mass transfer rate [8]. Consequently, suspended system has generally received more attention in the literature. It should be noted that the catalyst surface is only active if the catalyst particle is illuminated. The particles in both suspended and immobilized systems which are further away from the light source may be shielded from the radiation by those near the light source [9,10]. This will decrease their photocatalytic efficiency.

Magnetic separation technology is a convenient approach for separation and recycle of catalyst. The technology utilizing superconducting high gradient magnetic field has been successfully applied in various industries field such as steel mill industry and water purification plant [11,12]. Hence, magnetic particles which possess both magnetic and photocatalytic properties have been attracting increasing attention in recent years. The key factor for preparation of magnetic photocatalysts is that they must be stable during the reaction under light irradiation. Photoreactor with photocatalysts in suspension might suffer limited depth of light incident penetration due to the light blockage (shading effect [13]) or scattering by the catalyst particles. Yet, most of the research works in wastewater tend to coincide that fine particles exhibit higher catalytic activity compared to immobilized catalyst [8]. Efforts on combining other treatment technologies such as acoustic cavitation will help in minimizing shading effect encountered during photocatalysis [13]. However, this is not the focus in this review.

Various methods to synthesize magnetic iron oxide nanoparticles such as co-precipitation of Fe ions in alkaline solutions [14,15], thermal decomposition of iron precursor in organic solution [16], hydrothermal [17], solvothermal [18] and microemulsion [19] have been reported in the literature. All the methods have been investigated to synthesize particles with small size distribution and homogeneous composition. The methods differ in terms of underlying principle, practicality and cost of the necessary equipment. Iron oxide can be obtained in several phases such as hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and magnetite (Fe_3O_4, $Fe(II)Fe(III)_2O_4$), depending upon the synthesis method and conditions. This review is focussed on these three forms of iron oxides since they are the most commonly obtained phases through synthesis procedures.

Hydrophobic surface of iron oxide particles will result in hydrophobic interactions between particles which in turn will cause the agglomeration of particles to form large clusters and reduce the effective surface area [20]. In order to prevent these limitations, magnetic particles are usually coated with the shell of an organic material such as surfactant and polymer [21] to enhance the particles dispersion. Meanwhile, the coating with inorganic material such as silica (SiO_2), carbon and polymer