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One-pot approach for synthesis of N-doped $TiO_2/ZnFe_2O_4$ hybrid as an efficient photocatalyst for degradation of aqueous organic pollutants

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HIGHLIGHTS

- N-doped $TiO_2/ZnFe_2O_4$ catalysts were prepared by a one-pot vapor-thermal method.
- The UV–vis-light-driven photocatalytic activities of the hybrids were evaluated.
- Influence factor, degradation kinetics, and mechanism, have been analyzed.
- Active species in the degradation process were detected by using the scavengers.
- N-doped $TiO_2/ZnFe_2O_4$ showed to be a promising catalyst and simple separation.

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ABSTRACT

N-doped $TiO_2/ZnFe_2O_4$ catalysts were successfully prepared by coupling nitrogen modified TiO_2 with $ZnFe_2O_4$ via a one-pot vapor-thermal method. The physicochemical properties of the as-prepared catalysts have been characterized using various spectroscopic and microscopic techniques. The UV–vis-light-driven photocatalytic activities of the hybrids were evaluated and the effects of the amount of photocatalyst, different types of dyes, catalyst stability on photodegradation of organic dyes were investigated. Moreover, degradation kinetics and mechanism as well as the roles of N doping, $ZnFe_2O_4$ and TiO_2 have been analyzed. It was revealed that N-doped $TiO_2/ZnFe_2O_4$ exhibited an improved performance compared with $TiO_2/ZnFe_2O_4$ or $ZnFe_2O_4$ because of the formation of a heterostructure at the interface as well as the introduction of N species. Active species such as holes, electrons, hydroxyl radicals, and superoxide radicals involved in the photodegradation process were detected by using different types of scavengers. Because of $ZnFe_2O_4$ in the hybrid, the catalyst shows ferromagnetism, and thus, the hybrid catalyst is easily isolated from the reaction mixture after the photocatalytic experiments. This work not only offers a simple method for the fabrication of N doped $TiO_2/ZnFe_2O_4$ hybrids, but also provides an effective and conveniently recyclable photocatalyst for the purification of water.

1. Introduction

In the past few years, there has been tremendous research and development in searching for a safe, abundant and inexpensive photocatalyst to solve the current environmental issues, especially wastewater treatment and water purification [1]. Compared to other materials, titanium dioxide (TiO_2) as an excellent photocatalyst has drawn the most attention due to its unique characteristics in band position and surface structure, as well as its biological and chemical inertness, non-toxicity, resource abundance, and

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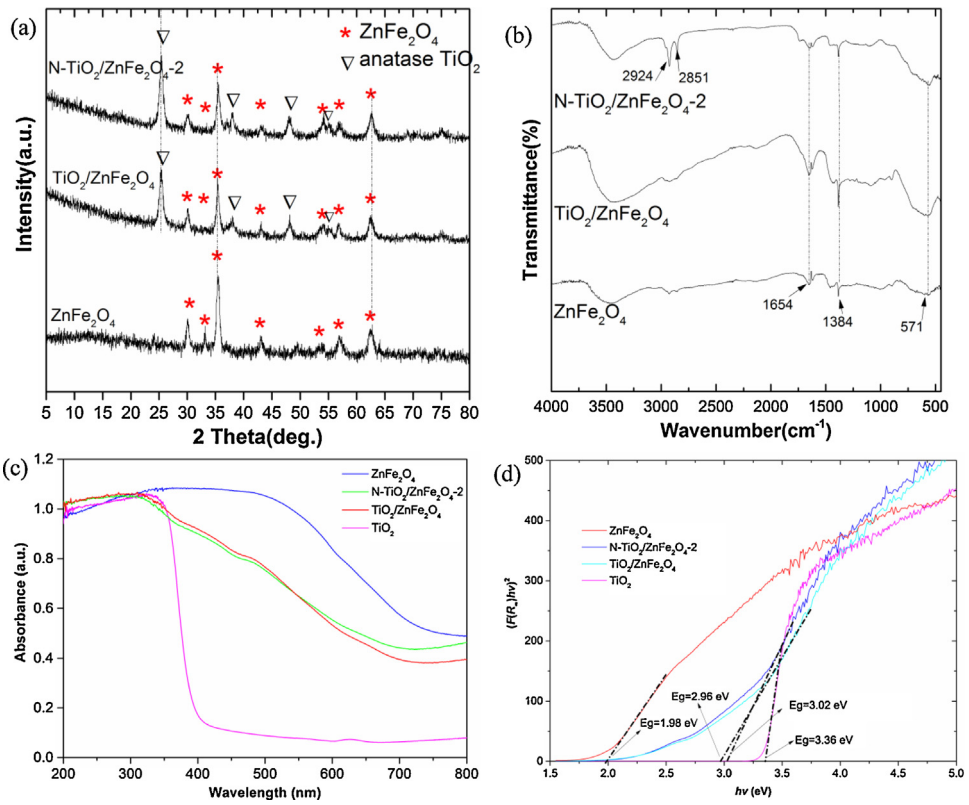

Fig. 1. (a) XRD and (b) FT-IR of pure $ZnFe_2O_4$, $TiO_2/ZnFe_2O_4$ and N–$TiO_2/ZnFe_2O_4$-2. (c) Diffuse reflectance spectra (DRS) and (d) plot of transferred Kubelka–Munk vs energy of the light absorbed of the samples.

resistance to photocorrosion [2]. However, the implementation of pure TiO_2 in a large scale is still limited due to its disadvantages of wide bandgap (E_g = 3.2 eV for anatase TiO_2) and rapid recombination of photogenerated charge carriers [1,3]. To tackle the problem and enhance the efficiency, the development of novel TiO_2-based photocatalysts is requisite.

To date, much efforts have been made to develop highly efficient photocatalytic TiO_2 by doping metals such as Ag [4], Ce [5], Fe [6] or Pd [7] to Ti sites and nonmetals such as N [7,8], S [9], F [8] or B [10], to O sites, or by coupling with narrow band semiconductors such as RuO_2 [11], $Zn_xCd_{1-x}S$ [12], $InBO_3$ [13], Nb_2O_5 [14], $BiVO_4$ [15]. Among these strategies, doping TiO_2 with nitrogen has attracted considerable interest because nitrogen has a similar size to oxygen as well as low ionization energy [16]. Conventional methods used for the synthesis of N-doped TiO_2 include sputtering, thermal nitridation of TiO_2, direct amination, and pulsed laser deposition [7,8,17,18]. All these N-doping procedures were carried out at high temperatures or required the complicated and expensive equipment, which make them difficult to be widely used in industry. Nevertheless, further investigations addressing the shortcomings of TiO_2-based materials would be of great interest.

Although photocatalysis is efficient, the separation of TiO_2 powder is a major bottleneck that limits the application. The powder catalysts were difficult to recover for reuse in aqueous solution because of their good dispersive properties. To allow for the easy removal of catalysts from reaction mixtures, a strategy to integrate TiO_2 nanocrystals with magnetic nanoparticles such as Fe_3O_4 [19–21], $NiFe_2O_4$ [22], $ZnFe_2O_4$ [23–27], $BiFeO_3$ [28] and $CoFe_2O_4$ [29,30], was proposed, which can remove and recycle the magnetic particles by applying an external magnetic field. Magnetic separation can effectively prevent the loss of the catalysts during recovery, and the process has been used for removing organic pollutants from water [31].

A particular interest in photocatalysts are the development of zinc ferrite ($ZnFe_2O_4$) with a spinel crystallographic structure and a narrow band-gap (1.9 eV), which exhibits a wide range of functional properties for practical applications, such as magnetic behavior, visible light response, and good photochemical stability [32]. Previous studies showed that $ZnFe_2O_4/TiO_2$ hybrids exhibited excellent activities in degradation of organic contaminants, more effective than TiO_2-based materials [23–27]. In our previous reports [33,34], $ZnFe_2O_4$-based materials showed high performance for degrading aqueous dyes and could be separated easily using an external magnet. Nevertheless, some drawbacks still existed in these magnetic composite materials, such as relatively harsh synthetic conditions, complicated synthesis routes, high cost, and low energy conversion efficiency. Thus, the development of a facile and green method for constructing highly efficient photocatalysts that can be recycled completely from the treated solution is vitally important and highly desirable.

It is of great interest to prepare and develop multifunctionalized TiO_2-based photocatalysts by the combination of doping and heterostructure, which can provide an approach to achieve more efficient charge separation, leading to an enhanced photocatalytic activity. In the present investigation, we provide a facile and feasible route to synthesize N-doped $TiO_2/ZnFe_2O_4$ hybrids with some advantageous properties, such as higher adsorption capacities, photocatalytic activities, easy separation, and excellent recyclability. Herein, the physical and chemical characterizations of catalysts were conducted, and the photocatalytic activity was evaluated in the photocatalytic degradation of organic dyes. Subsequently, the effects of amount of photocatalyst, different types of dyes, and catalyst stability were investigated. The reaction kinetics, dye degradation mechanism, as well as the roles of N doping, $ZnFe_2O_4$ and TiO_2 have also been analyzed to provide insights to the material properties and reaction process.