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Hierarchical magnetic petal-like Fe_3O_4-ZnO@g-C_3N_4 for removal of sulfamethoxazole, suppression of photocorrosion, by-products identification and toxicity assessment

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HIGHLIGHTS

- *In situ* growth of g-C_3N_4 on ZnO enhanced both efficiency and stability.
- Toxicity of solutions and generated by-products were assessed.
- The FZG particles were easily separated from water by magnetic force.
- SMX removal rate constant was increased by 2.6 times by using FZG1 compared to ZnO.
- Release of Zn^{2+} was decreased ~50% by using g-C_3N_4 as a protective layer.

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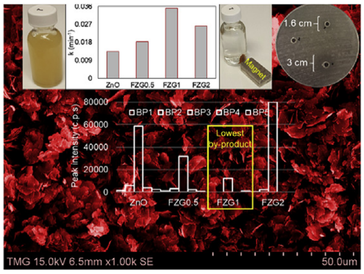
GRAPHICAL ABSTRACT



ABSTRACT

Herein, a petal-like photocatalyst, Fe_3O_4-ZnO@g-C_3N_4 (FZG) with different g-C_3N_4 to ZnO ratios was synthesized with hierarchical structure. The FZG1 photocatalyst, having the weight ratio of 1:1 for the initial urea and Fe_3O_4-ZnO (Fe-ZnO), presented the highest sulfamethoxazole (SMX) degradation rate of 0.0351 (min^{-1}), which was 2.6 times higher than that of pristine ZnO. Besides the facile separation, the performance of photocatalyst was improved due to the function of iron oxide as an electron acceptor that reduced the electron/hole recombination rate. The coating of g-C_3N_4 on the Fe-ZnO surface not only acted as a protective layer for ZnO against photocorrosion, but it also enhanced the photocatalytic activity of the catalyst for SMX degradation through the heterojunction mechanism. By using the FZG1 photocatalyst, 95% SMX removal was obtained after 90 min reaction, while 47% COD and 30% TOC removal were achieved after 60 min treatment under a low energy-consuming UV lamp (10 W). Moreover, a substantial reduction in the solution toxicity was shown after the treatment, as compared with the SMX solution before treatment. The LC-HR-MS/MS analysis results showed that the concentration of most detected by-products produced after 90 min reaction by FZG1 was considerably lower than those obtained using other synthesized photocatalysts. By performing radical scavenging experiments, OH° radical was found to be the major reactive species. The FZG1 photocatalyst also displayed excellent reusability in five cycles and the leaching of zinc and iron ions was reduced by 54% and ~100%, respectively, after coating Fe-ZnO with g-C_3N_4.

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1. Introduction

The presence of antibiotics in water bodies has a high potential to impose adverse effects on ecosystem and human health and they may induce antibiotic resistance even at trace concentrations (Gong and Chu, 2018; Mirzaei et al., 2018). A significant portion of prescribed antibiotics are excreted in feces and urine and they increase the number of antibiotic resistant bacteria which is an important public health concern (Gao et al., 2018; Su et al., 2016). Particularly, the occurrence of sulfonamide antibiotics such as sulfamethoxazole (SMX) in the environment has showed adverse effects in promoting antibiotic resistance genes (Tzeng et al., 2016). Because of its high consumption and frequent detection in surface waters and drinking water in the range of 60–150 ng/L and 10–12 ng/L, respectively, (Kumar et al., 2018), SMX is usually considered as an indicator of antibiotic pollution (Jiang et al., 2014). Conventional biological treatment processes are inadequate to eliminate SMX in the water and wastewater treatment plants due to the recalcitrant properties (Kumar et al., 2018; Mirzaei et al., 2017b). In different countries, high concentrations of SMX, varying from 0.01 to 2.0 μg/L have been reported in the effluent (Trovó et al., 2009), and between 1 and 178 μg/kg in the sludge of municipal sewage treatment plants (Geng et al., 2018). Physical treatment techniques such as adsorption, membrane separation and coagulation-flocculation are non-destructive and merely transfer such contaminants to another phase (Gao et al., 2018; Mirzaei et al., 2017a). Photocatalytic degradation has emerged as a green, sludge-free and highly efficient alternative to biological techniques for the removal of emerging contaminants such as antibiotics (Wang et al., 2017c). Zinc oxide (ZnO) is one the most widely used photocatalysts in environmental remediation processes due to its unique characteristics such as nontoxicity, high oxidation capacity, high electron mobility and low cost (Mirzaei et al. 2016, 2018; Xue et al., 2015). However, the low surface area, fast recombination of photo-induced charge carriers, low visible light absorbance and photocorrosion are the main limitations of ZnO photocatalyst (Jo and Selvam, 2015; Lee et al., 2016). Graphitic carbon nitride (g-C_3N_4) is an organic metal-free semiconductor with a medium bang gap (~2.7 eV) which has recently attracted the attention of researchers in various fields including CO_2 reduction, photocatalytic degradation of contaminants and hydrogen production, owing to the attractive characteristics such as excitement under visible light, high physicochemical stability, facile synthesis, environmental friendliness and cheap precursors (Kumar et al., 2018; Liu et al., 2017). Nevertheless, the inherent limitations of g-C_3N_4 such as low redox potential, fast recombination charge carriers and aggregation, hinder its application as a self-sufficient semiconductor for the photodegradation of contaminates (Kumar et al., 2017b). It has been reported that the conjugation of g-C_3N_4 with other semiconductors could enhance the photocatalytic activity of produced composite (Liu et al. 2012, 2016a). Several studies have concluded that the coupling of g-C_3N_4 with ZnO enhances the photocatalytic activity of ZnO by improving charge separation through the heterojunction (Guo et al., 2017; Jo and Selvam, 2015; Wang et al., 2017a) or by the Z-scheme mechanism (Nie et al., 2018). Li et al. (2015) concluded that the conjugation of ZnO with g-C_3N_4 not only improved the photocatalytic activity for tetracycline degradation, but it also improved ZnO stability against photocorrosion by acting as a protective layer.

Hierarchical micro/nanostructure semiconductors with multidimensional domains at different levels possess interconnected and readily accessible porous networks with high specific surface areas, which not only enhance the adsorption of reactants and improve quantum efficiency, but also facilitate the transport of reagents, intermediates and products to the active sites (Li et al., 2016). In addition, the inevitable aggregation of nanoparticles which leads to an unwanted reduction in the availability of active sites could be substantially reduced by hierarchical micro/nanostructure configuration (Wang et al., 2010). Nie et al. (2018) reported high photocatalytic CO_2 reduction ability by using hierarchical g-C_3N_4/ZnO microspheres. Despite the beneficial effects of hybrid photocatalysts, the poor attachment of the produced composites restricts the charge carriers transfer between heterojunction interfaces and reduces the stability of the resultant photocatalysts (Chen et al., 2016; Pan et al., 2012). Therefore, the design of an efficient conjugated composite of semiconductors and g-C_3N_4 remains a challenge (Chalasani and Vasudevan, 2013; Qin et al., 2016). In general, most catalysts with high specific surface area and high activity exist as nano-powders which make them difficult to collect from the effluent for reuse (Qin et al., 2016). To address the above problem, magnetic nanoparticles have been given considerable attention since they can easily be separated from the treated solutions by applying an external magnetic field (Chalasani and Vasudevan, 2013; Zhao et al., 2008). The magnetic separation method is very attractive from practical point of view since it is quick, simple, energy-efficient and inexpensive (Zhao et al., 2008).

Inspired by the abovementioned studies, a magnetic hierarchical Fe_3O_4-ZnO@g-C_3N_4 photocatalyst was synthesized by *in situ* growth of g-C_3N_4 on Fe_3O_4-ZnO. It is concluded by the authors that the photocatalytic performance, separability and stability of ZnO are considerably improved by synthesizing a magnetic hierarchical shape conjugated with g-C_3N_4 and by enhancing the interfacial connection by *in situ* growth of g-C_3N_4 on ZnO, instead of the conventional ultrasonic dispersion method. The performance of synthesized photocatalyst was examined in terms of the photocatalytic degradation of SMX from water, mineralization and formation of by-products and the associated changes in the toxicity of solution after the treatment. In addition, the stability and reusability of photocatalyst were evaluated in consecutive experiments and also by measuring the concentrations of zinc and iron ions in the solution as indicators of photocorrosion. By combining the benefits of magnetization, hierarchical micro/nanostructure and heterojunction, a unique method has been developed for the preparation of highly active, low-cost, highly stable and readily separable photocatalysts for use in water treatment processes.

2. Experimental section

2.1. Materials

All chemicals were analytical-grade and were used as received without further purification. Zinc acetate, urea, ethylene glycol (EG), anhydrous ethanol, *tert*-butyl alcohol, potassium iodide and disodium EDTA were supplied by Fisher Scientific (ON, Canada). Sulfamethoxazole and iron oxide nanoparticles (Fe_3O_4) were purchased from Sigma-Aldrich Inc., USA.

2.2. Preparation of photocatalysts

The ZnO photocatalyst was synthesized via a facile one-step hydrothermal method. Hydrothermal technique is generally used for the growth of high quality crystals (Sharma et al., 2017a). In a typical experiment, zinc acetate (3.96 g) and urea (3.28 g) were dissolved in 150 mL of EG and deionized water (DIW) with a volume ratio of 1:1. Afterwards, 39.6 mg Fe_3O_4 nanoparticles (Fe_3O_4: zinc acetate = 1 wt%) was added to the solution and it was mixed by sonication for 15 min. The obtained solution was transferred into a 200 mL Teflon-lined autoclave and was maintained for 12 h at 160 °C before cooling down naturally to room temperature. The