Chemical Engineering Journal 308 (2017) 377–385

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Precisely controlled fabrication of magnetic 3D γ-Fe_2O_3@ZnO core-shell photocatalyst with enhanced activity: Ciprofloxacin degradation and mechanism insight

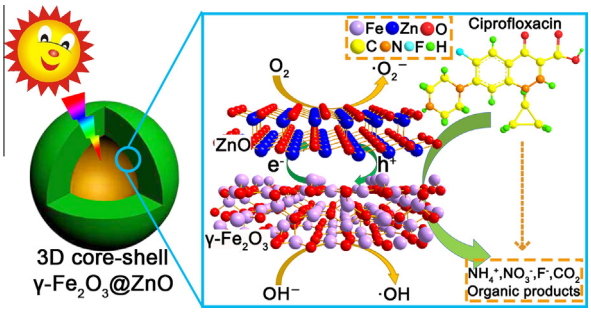
Ning Li, Jun Zhang *, Yu Tian *, Jianhui Zhao, Jian Zhang, Wei Zuo

State Key Laboratory of Urban Water Resource and Environment (SKLUWRE), School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin, 150090, China

HIGHLIGHTS

- The 3D ZnO shell was well-distributed on γ-Fe_2O_3 core in a controlled manner.
- The magnetic γ-Fe_2O_3@ZnO can be easily separated from solution.
- The photocatalyst exhibited enhanced activity under simulated sunlight irradiation.
- The separation of carriers was effectively accelerated by a type II heterostructure.
- The holes and hydroxyl radicals played major roles in ciprofloxacin degradation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 August 2016
Received in revised form 16 September 2016
Accepted 17 September 2016
Available online 19 September 2016

Keywords:
γ-Fe_2O_3@ZnO
Magnetism
Atomic layer deposition
Core-shell heterojunction
Ciprofloxacin degradation

ABSTRACT

A novel magnetically separable three-dimensional (3D) γ-Fe_2O_3@ZnO core-shell photocatalyst was successfully fabricated by hydrothermal-sintering and a subsequent atomic layer deposition (ALD) method. The uniform and conformal ZnO shell layer was precisely deposited on γ-Fe_2O_3, improving the specific surface area and surface potential. The photocatalytic capacity of γ-Fe_2O_3@ZnO composite was investigated by ciprofloxacin degradation. Results showed that the γ-Fe_2O_3@ZnO exhibited excellent degradation efficiency under simulated sunlight irradiation. The first-order kinetic rate constant of γ-Fe_2O_3@ZnO was demonstrated to be almost 4 and 20 times higher that of pure ZnO and γ-Fe_2O_3. Moreover, the recycling degradation experiments revealed that the γ-Fe_2O_3@ZnO core-shell photocatalyst was stable and reusable, which could be easily separated under an additional magnetic field. The mechanism of the remarkably enhanced photocatalysis was further explored by analyzing its heterostructure and determining the role of active radicals. The newly-designed type II heterostructure facilitated the separation of photo-induced carriers. Radical-trapping tests indicated that the holes and hydroxyl radicals played major roles in ciprofloxacin degradation. In prospect, the magnetic 3D γ-Fe_2O_3@ZnO core-shell photocatalyst has great potential for degradation of other refractory contaminants in water with solar light irradiation.

1. Introduction

Antibiotics have been widely used for humans and animals to treat diseases as well as prevent bacterial infection [1]. Most

* Corresponding authors at: No.73, Huanghe Road, Nangang District, Harbin City, Heilongjiang Province, China.
E-mail addresses: hitsunyboy@126.com (J. Zhang), hit_tianyu@163.com (Y. Tian).

http://dx.doi.org/10.1016/j.cej.2016.09.093
1385-8947/

antibiotics could not be decomposed thoroughly in a living body, leaving the residuals being excreted into the environment [2]. Among them, fluoroquinolones have attracted considerable attention due to the superior antimicrobial activity and extensive applications, which have been detected in the wastewater and surface water around the world [3]. The antibiotics even at low concentrations in water may promote the bacterial drug resistance, which could bring a great threat to human health and the safety of the entire ecosystem [3]. Thus, it is an urgent issue to select effective technologies for fluoroquinolones removal from water.

A large number of studies have focused on fluoroquinolones removal concerning physical, chemical and biological treatments [4]. Unfortunately, the physical method could only realize pharmaceuticals transfer from wastewater to absorbents. The pharmaceuticals are not degraded fundamentally and the contaminated absorbents need further security processing [5]. Moreover, the biological method exhibits major drawbacks with low removal rate and uncomplete degradation of pharmaceuticals attributed to the inhibited microorganism activity [5]. Alternatively, the advanced oxidation processes provide an effective approach for pharmaceuticals degradation [4]. The active oxygen radicals could be responsible for degradation of multiple contaminants owing to their excellent oxidizing power. Among the advanced oxidation processes, photocatalysis as an environmental-friendly technique is believed to have a promising prospect in the water purification field, which has aroused great concerns in recent years [4]. It is obvious that photons have a tendency to convert into reactive oxygen species in the presence of semiconductor photocatalyst, bringing better results for efficient pharmaceuticals degradation. Therefore, to design a high-performance photocatalyst would play an overwhelming role in the enhancement of pharmaceuticals degradation.

In order to widen the light-response range of photocatalysts and accelerate the separation of electron-holes, multi-component catalysts have been extensively fabricated instead of single-component ones in the field of photocatalysis [6]. To date, intensive efforts have been invested in composite photocatalysts fabrication including coprecipitation, sol-gel, impregnation and solution combustion methods [7]. However, there still exist some shortcomings such as uncontrollable composition distribution and irregular morphology. The doping components are more likely to serve as trapping centers of photo-induced carriers if the doping process is inappropriate, posing a key obstacle to the improvement of photocatalytic efficiency [8]. Atomic layer deposition (ALD) could achieve target materials to be deposited on substrate surface layer by layer. The ALD technology integrates the advantages of uniform deposition, three-dimensional (3D) conformality as well as precise control of deposition layer at nano-scale [9]. Recently, concerns have been raised regarding the ALD technology in the fields of material preparation and modification [10].

Taking the advantage of conformality, the 3D photocatalysts could be fabricated by ALD with enhanced surface area, facilitating the absorption and transfer of photon energy [11]. Furthermore, the thickness of deposition layer could be exactly controlled only by setting the number of ALD cycles, which could effectively prevent recombination of photo-generated electron-holes and thus improve the photocatalytic efficiency [11]. Magnetic catalysts have a distinct advantage of easy separation from the reaction system, bringing benefit to be recycled without consuming much energy. To our best knowledge, ALD technology has been utilized to deposit TiO_2 photocatalyst on mixed cellulose, carbon nanotube, silicon substrate and glass substrate successfully [12]. Nevertheless, the research about ALD technology combined with magnetic semiconductor catalysts was seldom reported.

The zinc oxide (ZnO), as an *n*-type semiconductor, exhibits high quantum efficiency and better photocatalysis. What's more, ZnO has the low price and non-toxic nature, presenting one of the most classic and commonly used catalysts [13]. The magnetic γ-Fe_2O_3 was found to have strong photo-response characteristic in wide wave length [14]. When these two components are combined together by ALD, the composite photocatalyst would be magnetically separable. Besides, the 3D ZnO layer formed on γ-Fe_2O_3 surface would bring benefits to the photocatalytic efficiency by enlarging specific surface area, extending the range of spectral response and promoting the separation of electron-holes. Ciprofloxacin, as a representative of fluoroquinolones, has been detected in drinking water and found inhibiting effects to photosynthesis of plants. Thus, ciprofloxacin was chosen for degradation in this study. Currently, the mechanism of interactions between ciprofloxacin-type antibiotics and the innovative magnetic photocatalyst was not elucidated during the process of photocatalytic decomposition. To explore the photocatalytic mechanism would provide theoretical foundation for the practical application of the novel photocatalyst.

Herein, the magnetic γ-Fe_2O_3@ZnO core-shell photocatalyst was first fabricated by hydrothermal and ALD method. The aim of this study was to investigate the photo-degradation efficiency of ciprofloxacin-type antibiotics under simulated sunlight. This study was mainly focused on: (1) fabrication and characterization of the magnetic γ-Fe_2O_3@ZnO core-shell photocatalyst; (2) photocatalytic capacity and recyclability of the novel γ-Fe_2O_3@ZnO heterojunction for ciprofloxacin degradation; (3) mechanism exploration of the enhanced photocatalysis of γ-Fe_2O_3@ZnO core-shell catalyst. The 3D magnetic γ-Fe_2O_3@ZnO core-shell photocatalyst prepared in this study has potential to remove other refractory contaminants from water.

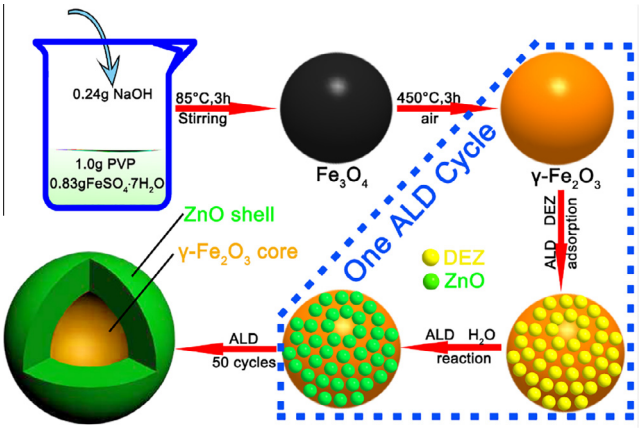
2. Experimental section

2.1. Materials

Ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), polyvinyl pyrrolidone (PVP, K30), sodium hydroxide (NaOH) and ethanol (75%, vol) were obtained from Xilong Chemical Co., Ltd. while diethylzinc (DEZ) and ciprofloxacin were purchased from Sigma-Aldrich Inc. Nitrogen (N_2) with the purity of 99.9% was obtained from LiMing Gas. All chemicals applied for photocatalyst preparation were analytic grade.

2.2. Fabrication of γ-Fe_2O_3@ZnO core-shell photocatalyst

Scheme 1 illustrated the fabrication process of the γ-Fe_2O_3@ZnO core-shell photocatalyst. The proposed fabrication



Scheme 1. Schematic diagram for fabrication process of the γ-Fe_2O_3@ZnO core-shell photocatalyst.