Chemical Engineering Journal 244 (2014) 327–334

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

High performance, recoverable Fe_3O_4—ZnO nanoparticles for enhanced photocatalytic degradation of phenol

Xiaohui Feng [a], Haijuan Guo [b], Kunal Patel [a], Hong Zhou [c], Xia Lou [a,*]

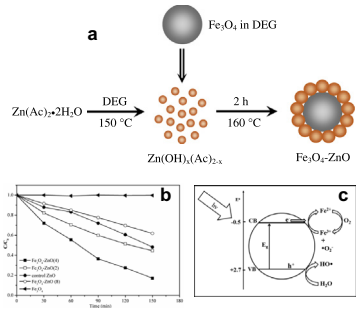
[a] Department of Chemical Engineering, Curtin University, Bentley, WA 6102, Australia
[b] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China
[c] Key Laboratory for Green Chemical Process of Education Ministry, Wuhan Institute of Technology, Wuhan 430073, China

HIGHLIGHTS

- Fe_3O_4—ZnO hybrid nanoparticles were synthesized.
- Increased phenol degradation efficiency by Fe_3O_4—ZnO (82.3%) was observed in comparison with ZnO (52%).
- The improved photocatalytic activity was well maintained after repetitive usage.
- An 89% recovering yield was achieved.

GRAPHICAL ABSTRACT

A schematic illustration of (a) the synthesis of the Fe_3O_4—ZnO hybrid nanoparticles, (b) the phenol degradation efficiency, and (c) the hypothesized photocatalytic reaction mechanism of the hybrid nanoparticles.



ARTICLE INFO

Article history:
Received 5 September 2013
Received in revised form 23 January 2014
Accepted 25 January 2014
Available online 2 February 2014

Keywords:
Photocatalysis
Magnetic photocatalysts
ZnO
Fe_3O_4—ZnO nanoparticles
Phenol degradation

ABSTRACT

In this paper, a novel type of magnetic photocatalyst, made of Fe_3O_4—ZnO hybrid nanoparticles, was prepared and characterized using various analytical instruments. Upon the degradation of phenol in water, the hybrid nanoparticles demonstrated significantly enhanced photocatalytic activity, achieving a phenol degradation efficiency of 82.3%, in comparison with that of 52% by the pure ZnO nanoparticles. A reduced photoluminescence in the hybrid nanoparticles revealed the suppressing effect of the hybrid nanoparticles on the recombination of photoinduced electron–hole pairs. A hypothesized reaction mechanism was presented, showing the possible presence of free iron ions that can act as an electron-trapping site to prevent the fast recombination of photogenerated charge carriers, therefore improving the photocatalytic properties. The stability and the recoverability of the hybrid nanoparticles were also investigated. A recovering yield of 89% was achieved. The strong photocatalytic activity was well maintained after three cyclic treatments, indicating both good recoverability and high performance of the novel photocatalyst. Photocorrosion caused loss of ZnO and Fe_3O_4 in the recycled hybrid nanoparticles was noticeable. Whilst the loss of ZnO might have led to the reduced photoreactivity of the recycled nanoparticles, the dissolution of iron ions could be critical for the enhanced overall photocatalytic properties of Fe_3O_4—ZnO.

1. Introduction

Heterogeneous photocatalysis in the presence of semiconductors has been investigated increasingly in the past two decades

* Corresponding author. Tel.: +61 892661682; fax: +61 892662681.
E-mail address: X.Lou@curtin.edu.au (X. Lou).

http://dx.doi.org/10.1016/j.cej.2014.01.075
1385-8947/

due to a wide variety of applications, particularly in the degradation of organic pollutants discharged into water [1]. Among those semiconductors, zinc oxide (ZnO) is widely recognized as an excellent material for photocatalytic processes, owing to its high photosensitivity, environmentally friendly nature and relatively low cost [2,3]. Zinc oxide is an n-type semiconductor with a wide band-gap of 3.2 eV. Upon exposure to ultraviolet (UV) radiation, ZnO can be photoexcited to generate negative electrons (e^-_{CB}) in the conduction band and positive holes (h^+_{VB}) in the valence band. The photoinduced electron–hole pairs are able to either recombine or be captured by other molecules, such as water or oxygen, forming reactive oxygen species (ROS) such as hydroxyl radical (·OH) and superoxide radical anion ($\cdot O_2^-$). The mechanism of formation of the electrons and holes, and their further chemical reactions with water and oxygen, is schematically illustrated in Fig. 1, in which the h^+_{VB} reacts with water to produce hydroxyl radicals (·OH), whilst the e^-_{CB} reacts with O_2 to form superoxide radical anions ($\cdot O_2^-$) and hydrogen peroxide (H_2O_2). The latter also can generate hydroxyl radicals (·OH). These ROS can destroy the structure of various organic pollutants, leading to the formation of non-toxic carbon dioxide and water [4,5].

Since the catalytic activities of ROS take place on the surface of the catalysts, nanoparticulate ZnO is generally more active than conventional bulk material [3]. However, the photocatalytic effectiveness of ZnO nanoparticles often is compromised by the fast recombination of the photoinduced electron–hole pairs, which has led to increasing developmental research on novel materials that can suppress the charge recombination [6]. Another concern in the industrial applications of ZnO nanoparticles is the difficulties encountered in re-collection of ultrafine nanoparticles from the treated waters. Often, a separation step, such as filtration or centrifugation, is required to prevent the possible large scale loss and the potential secondary pollution caused by the lost ZnO nanoparticles [7]. This gives rise to higher operation costs. A solution to these problems is the utilization of magnetic photocatalysts.

Nanostructured magnetic photocatalysts possess the property not only of high surface area-to-volume ratio but also of magnetism, making the nanoparticles more easily recovered and recycled via magnetic separation processes [8–10]. To date, most magnetic photocatalysts have dual components: a magnetic component (magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) or ferrite) with the separation function via an external magnetic field; and a photocatalytic component with a photocatalytic function, such as TiO_2 nanoparticles [11–13]. These materials have been proved to be effective in both separation and reuse [14]. For instance, the core–shell structured $Fe_3O_4/SiO_2/TiO_2$ particles can be recovered using an external magnetic field and their photocatalytic activity is maintained, even after eighteen cycles of use [15]. Enhanced photocatalytic activity also has been seen in Fe_3O_4/TiO_2 nanocomposites, reportedly due to the decelerated electron–hole recombination in the presence of iron ions [16]. It is desirable to develop magnetic photocatalysts with efficient separation ability and effective photocatalytic properties.

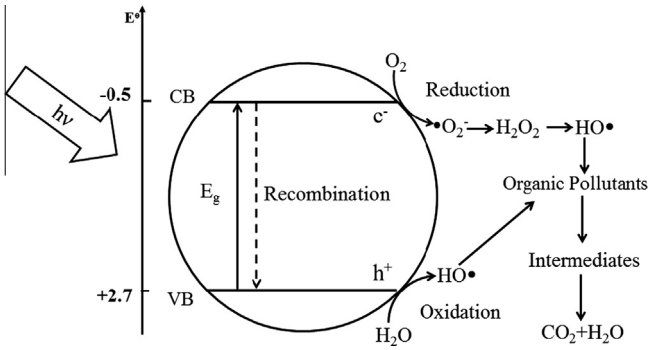


Fig. 1. A schematic illustration of the ZnO photocatalytic reaction mechanism.

In this work, novel magnetic Fe_3O_4—ZnO hybrid nanoparticles were synthesized via a seed-mediated growth process using Fe_3O_4 nanoparticles as seeds and $Zn(Ac)_2$ as a reactant. The size and morphology of the obtained hybrid nanoparticles were examined using a field emission scanning electron microscope (FESEM) and a transmission electron microscope (TEM) equipped with an energy dispersive spectrometer (EDS). The chemical compositions of the derived samples were characterized using Fourier transform infrared (FTIR) spectroscopy, atomic absorption spectrometry (AAS) and X-ray diffraction (XRD) methods. The optical properties were analysed using an ultraviolet–visible diffuse reflectance spectroscope (UV–Vis DRS). The photocatalytic property of the Fe_3O_4—ZnO hybrid nanoparticles was investigated based on the photodegradation reaction of phenol, a target organic pollutant that commonly has been used as a model chemical for the evaluation of photocatalysts [17,18]. The photocatalytic properties in relation to the particle size, the chemical composition (the ratio of Fe_3O_4 to ZnO), and the possible interfacial electron transfer between the Fe_3O_4 and ZnO will be discussed.

2. Experimental

2.1. Materials and chemicals

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 99.99%), ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, 99.99%), zinc acetate dihydrate ($Zn(Ac)_2{\cdot}2H_2O$, Ac = CH_3COO, ⩾98%), hydrochloric acid solution (HCl, 7.3%), diethylene glycol (DEG, 99%) and ethanol anhydrous (⩾99.5%) were obtained from Sigma–Aldrich. Ammonia solution ($NH_3{\cdot}H_2O$, 25%) and tetramethylammonium hydroxide (TMAH, 25%) were obtained from Fluka. Deionized water was used in all experiments.

2.2. Synthesis of Fe_3O_4 nanoparticles

Magnetite (Fe_3O_4) nanoparticles were synthesized using the chemical co-precipitation method reported by Massart [19]. The chemical reaction is illustrated as follows:

$$2Fe^{3+} + Fe^{2+} + 8OH^- \Longleftrightarrow Fe(OH)_2 + 2Fe(OH)_3 \rightarrow Fe_3O_4 + 4H_2O \quad (1)$$

In brief, a 2 M $FeCl_2$ solution and a 1 M $FeCl_3$ solution were prepared by dissolving iron salts in 2 M HCl solution. One ml of $FeCl_2$ solution was mixed with 4 ml of $FeCl_3$ solution under nitrogen atmosphere with vigorous stirring, and then 50 ml of ammonia solution was added, dropwise, to the Fe^{2+}/Fe^{3+} mixture. After allowing the reaction to proceed for 15 min, the black precipitate was washed with deionized water (3 × 15 ml) to remove any excess reactants. The obtained Fe_3O_4 nanoparticles were dispersed in TMAH solution to prevent aggregation. In general, 0.4 g of Fe_3O_4 was dispersed in 0.5 ml TMAH solution and then further diluted with deionized water to a total volume of 4.0 ml.

2.3. Synthesis of Fe_3O_4—ZnO hybrid nanoparticles

Fe_3O_4—ZnO hybrid nanoparticles were prepared by dehydrating $Zn(Ac)_2{\cdot}2H_2O$ in the presence of various amounts of Fe_3O_4 nanoparticles in DEG. In a typical procedure, 2.24 g (0.01 mol) $Zn(Ac)_2{\cdot}2H_2O$ was added to 100 ml DEG and the reaction mixture was heated to 150 °C under nitrogen protection. Thirty ml of DEG, containing 0.1 g (0.43 mmol) of Fe_3O_4 nanoparticles, was added, dropwise, to the reaction mixture. The temperature of the reaction mixture then was heated up to 160 °C and maintained for 2 h. The reaction