Chemical Engineering Journal 298 (2016) 300–308

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Fabrication of $FeVO_4/Fe_2TiO_5$ composite catalyst and photocatalytic removal of norfloxacin

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HIGHLIGHTS

- $FeVO_4/Fe_2TiO_5$ heterojunction composite was firstly designed and successfully prepared via one pot hydrothermal method.
- $FeVO_4/Fe_2TiO_5$ photocatalytic removal norfloxacin was first reported.
- $FeVO_4/Fe_2TiO_5$ exhibited high photocatalytic activity and excellent stability.

ARTICLE INFO

Article history:
Received 18 December 2015
Received in revised form 26 February 2016
Accepted 21 March 2016
Available online 28 March 2016

Keywords:
$FeVO_4$
Fe_2TiO_5
Composite heterojunction
Photocatalytic
Norfloxacin

ABSTRACT

A new type of $FeVO_4/Fe_2TiO_5$ composite heterogeneous catalysts was firstly designed and successfully synthesized via a one pot hydrothermal method. The new as-prepared $FeVO_4/Fe_2TiO_5$ exhibited high photocatalytic activity and excellent stability while being used for norfloxacin (NFX) removal from aqueous solution under visible light irradiation. The high photocatalytic activity may attribute to synergistic effect photogenerated electron–hole with $^{\cdot}OH$ and h^+. In the complex photocatalytic degradation process, the piperazine ring within norfloxacin was firstly attacked and ruptured. As the properties of abundant raw material and facile prepared method, $FeVO_4/Fe_2TiO_5$ composite could be met with a great practical application prospect. Meanwhile, this study could offer a new insight into the design and synthesis of other new and high activity composite structure photocatalysts.

1. Introduction

Norfloxacin [1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-carboxylic acid], one kind of fluoroquinolone antibiotics which are probably the most important class of synthetic antibiotics, is widely used both in human and veterinary medicine. Antibiotics are largely unchanged in the body, causing many residues were excreted into environment and increasingly accumulated. The increasing accumulation may lead to a series of latent harms such as toxicity to microorganism, aquatic organisms and possible risks to human health through drinking water or food chain. Extensive concerns have been paid on how to treat these accumulations. Many studies have been carried on degradation of these accumulations. However, existing treatments of environment accumulating FQs are considered complex, expensive, incomplete and inefficient and so on. The environmentally benign and inexpensive approaches of photocatalytic removal for organic pollutions were caused increasing research interests [9–14].

However, the catalytic efficiencies of current photocatalysis systems are often poor. Usually, photocatalytic efficiency is limited by the recombination of photogenerated charge carriers. The short charge-separation may result in low quantum capabilities and limit the photocatalytic potential of photocatalysts. For the purpose of overcoming the obstacles, more and more attentions have been paid on finding new approaches within the characteristics of efficient, environmental benign, and low cost for reducing pollution [1–5], and many methods have been studied to improve the catalytic efficiency of photocatalysts, such as the formation of junctions and the shape controlling, etc. It showed that the photogenerated electrons and holes tend to separate into two different regions of the catalyst by building junctions. Meanwhile, building proper composite junctions can efficiently accelerate charge separation and enlarge surface active area. Hence, the composite heterostructural photocatalysts could show superior photocatalytic efficiency [6].

As the characteristics of easy-prepared, inexpensive, environmentally friendly and narrow band gap, $FeVO_4$ has been studied for potential applications in catalysis and electrochemistry [7]. The relative studies revealed that the band gap of $FeVO_4$ is about

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http://dx.doi.org/10.1016/j.cej.2016.03.107
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2.1 eV, showing that $FeVO_4$ has a visible light responsed catalytic activity. However, similar to others single catalyst, the visible light responsed catalytic efficiency of $FeVO_4$ is low. This disadvantage could be surmounted by designing and building of $FeVO_4/Fe_2TiO_5$ heterojunction structured composites. Meanwhile, Fe_2TiO_5 is also a narrow band gap semiconductor of 2.2 eV with the valence band (VB) surpassing the VB level of $FeVO_4$, the conduct band (CB) of Fe_2TiO_5 lies above the energy level as that of $FeVO_4$. According to the theory of band matching, the energy level of Fe_2TiO_5 matches well with $FeVO_4$. The closely contacting between $FeVO_4$ and Fe_2TiO_5 would allow a fast separation of the photogenerated hole–electron interface. Thus, the photocatalytic efficiency for removing organic pollutants would be improved [8].

Consequently, in this present work, a novel heterojunction structured photocatalyst $FeVO_4/Fe_2TiO_5$ composite was successfully constructed by one-step hydrothermal route. The photocatalytic activity of the $FeVO_4/Fe_2TiO_5$ heterostructure composite was investigated by a representative model of norfloxacin degradation in the aqueous solution under xenon lamp light irradiation. The $FeVO_4/Fe_2TiO_5$ heterostructure composite has high catalytic efficiency and stability. Detailed the conceivable degradation pathways were proposed by detecting (using LC–TOF-MS) the major transformation photoproducts generated in the reaction processes.

2. Experimental

2.1. Chemicals

Ferric nitrate [$Fe(NO_3)_3{\cdot}9H_2O$, 98.5%], partial ammonium vanadate (NH_4VO_3, 99.0%), tetrabutyl titanate ($C_{16}H_{36}O_4Ti$, 99.0%), norfloxacin ($C_{16}H_{18}FN_3O_3$, 98%) and the other chemicals used in the experiments were of analytical reagent, and all chemicals were used as received without further purification. MilliQ water was employed for preparation of all aqueous solutions.

2.2. Catalyst synthesis

In a typical synthesis process, 3 mmol $Fe(NO_3)_3{\cdot}9H_2O$ was dissolved in 40 mL H_2O under magnetic stirring at room temperature, 1 mmol NH_4VO_3 was added. After stirring for 10 min, 1 mmol $C_{16}H_{36}O_4Ti$ was added. After stirring for another 10 min, the pH value was adjusted to 12 using NaOH solution, stirring for 0.5 h. The mixture was transferred into a 50 mL Teflon-lined autoclave and heated at 180 °C for 24 h under autogenous pressure. The product was collected when the autoclave was cooled down to room temperature, washed three times with water and anhydrous ethanol, respectively, and dried at 60 °C in oven for 3 h [15,16].

To study the effect on catalytic efficiency of $FeVO_4/Fe_2TiO_5$ composites as different ratios of $FeVO_4$ and Fe_2TiO_5, a series of different moral ratios (4:1, 2:1, 1:1) of $FeVO_4/Fe_2TiO_5$ composite catalysts were prepared by a similar procedure but for different mole ratios of starting materials. Meanwhile, pure $FeVO_4$ and Fe_2TiO_5 were also prepared as comparison via the same conditions, but the starting materials were 1 mmol $Fe(NO_3)_3{\cdot}9H_2O$ and 1 mmol NH_4VO_3 or 2 mmol $Fe(NO_3)_3{\cdot}9H_2O$ and 1 mmol $C_{16}H_{36}O_4Ti$.

2.3. Catalyst characterization

To study the phase structure and morphology of as-prepared samples, following relevant devices were employed to characterize these properties. X-ray diffraction patterns were obtained with a XRD-6000 X-ray powder diffractometer (Shimadzu) with monochromatic Cu-Kα radiation at a setting of 40 kV and 30 mA. The scanning rate was 6° (2θ) min^{-1} and the scanning range was 10–90°. X-ray photoelectron spectroscopic (XPS) analysis was performed with a PHI 5000 Versa Probe spectrometer (ULVAC-PHI, Japan) with monochromatized Al Ka radiation. The binding energy positions were calibrated against the C1s at 284.6 eV. Scanning electron microscopy (SEM) images and energy-dispersive spectroscopy (EDS) of the as-prepared samples were taken on QUANTA FEG 250. Transmission electron microscopy (TEM) observations were performed on a JEM-200CX instrument. UV–vis diffuse reflectance spectra (DRS) were recorded using a UV-3600 spectrophotometer equipped with an integrating sphere attachment at room temperature. The scan range was from 200 nm to 800 nm, and reflectance standard was $BaSO_4$. Photoluminescence spectra (PL) were recorded at room temperature over a wavelength range of 300–450 nm on a Horiba HJY FM-4P-TCSPC type fluorescence spectrophotometer with excitation wavelength of 280 nm. The specific surface area was estimated based on nitrogen adsorption–desorption isotherm according to the Brunauer–Emmett–Teller model (BET ASAP 2020 Micrometrics, USA).

2.4. Photocatalytic testing

The photocatalytic activities of as-prepared composite catalysts were evaluated by the decomposition of norfloxacin aqueous solution under visible light irradiation in a photoreaction apparatus. The photocatalytic reaction experiments were performed in a photochemical reactor (XPA-V, Xujiang, Nanjing, China), and the reactor system was cooled down by a circulating water bath to keep the reaction temperature at ambient temperature.

The reaction was conducted in a cylindrical quartz reactor by using a 500 W Xe lamp irradiation as the simulated light source and in each experiment as-prepared catalyst (0.05 g) was added to a norfloxacin aqueous solution (50 mL 10 mg L^{-1}). Before irradiation, the suspensions were magnetically stirred in the dark for 0.5 h to establish an adsorption–desorption balance between catalyst and norfloxacin. After initiation of light irradiation at given time intervals, 3 mL of the sample solution were taken and immediately centrifuged, then filtered through a 0.22 μm pore size filter to remove the catalyst particles for using subsequent analysis. To investigate the stability and reusability of the photocatalyst, cyclic degradation tests were carried out. After each cycle of degradation, the catalyst was separated by centrifugation and used for the next cycle of degradation without any pre-treatment.

The active species of photocatalytic reactivity were detected by the trapping experiments with similar the process used of the photodegradation experiment. The scavengers of benzoquinone (BQ), ammonium oxalate (AO) and isopropanol (IPA) were added into norfloxacin aqueous solution before the initiation of light irradiation, to scavenge the reactivity of $O_2^{\cdot-}$, h^+ and $^{\cdot}OH$, respectively [17–20].

2.5. Analytical investigation

The concentration of norfloxacin in the supernatant was preliminarily determined by UV–vis spectroscopy (UV–vis 750, PerkinElmer), then was accurately determined by high performance liquid chromatography (HPLC 1200, Agilent) with a diode array detector and a C18 column (Zorbax Eclipse XDB-C18 4.6 mm × 250 mm, 5 μm, Agilent). The measurement was performed in a water/acetonitrile (=85:15, v/v 0.1% formic acid containing in water) as mobile phase with a flow rate of 1 mL min^{-1} and the maximum absorbance wavelength at 278 nm.

The photocatalytic degradation removal rate (η) of norfloxacin over various catalysts was calculated using the equation $\eta = (C_0 - C)/C_0 \times 100\%$, where C_0 represents to the initial concentration of norfloxacin and C represents to the concentration of norfloxacin measured after light irradiation at given time intervals.