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Preparation and characterization of Fe^{3+}-doped TiO_2 on fly ash cenospheres for photocatalytic application

Bing Wang, Qin Li, Wei Wang, Ying Li, Jianping Zhai*

State Key Laboratory of Pollution Control and Resource Reuse, and School of the Environment, Nanjing University, Nanjing 210093, PR China

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ABSTRACT

Fe^{3+}-doped TiO_2 film deposited on fly ash cenosphere (Fe–TiO_2/FAC) was successfully synthesized by the sol–gel method. These fresh photocatalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetric analyses (TGA). The XRD results showed that Fe element can maintain metastable anatase phase of TiO_2, and effect of temperature showed rutile phase appears in 650 °C for 0.01% Fe–TiO_2/FAC. The SEM analysis revealed the Fe–TiO_2 films on the surface of a fly ash cenosphere with a thickness of 2 μm. The absorption threshold of Fe–TiO_2/FACs shifted to a longer wavelength compared to the photocatalyst without Fe^{3+}-doping in the UV–vis absorption spectra. The photocatalytic activity and kinetics of Fe–TiO_2/FAC with varying the iron content and the calcination temperatures were investigated by measuring the photodegradation of methyl blue (MB) during visible light irradiation. Compared with TiO_2/FAC and Fe^{3+}-doped TiO_2 powder (Fe–TiO_2), the degradation ratio using Fe–TiO_2/FAC increased by 33% and 30%, respectively, and the best calcined temperature was 450 °C and the optimum doping of Fe/Ti molar ratio was 0.01%. The Fe–TiO_2/FAC particles can float in water due to the low density of FAC in favor of phase separation to recover these photocatalyst after the reaction, and the recovery test shows that calcination contributes to regaining photocatalytic activity of Fe–TiO_2/FAC photocatalyst.

1. Introduction

Recently, modification of TiO_2 has been extensively studied to overcome the limitation of pure TiO_2 which has wide energy band gap and low quantum yields. Many groups have been involved in depositing transition metal ions, such as Fe, Au, Ag, V, Cr and Ni, onto the surface of titania to improve the separation of electrons and holes [1–5]. Among these elements, Fe is very cost-effective and can contribute to shifting the absorption edge of TiO_2 into visible light range. Nevertheless, these modified photocatalysts cannot be easily retrieved after the reaction on account of their nanometer scales, which restricts their industrial application. These problems have motivated the development of supported photocatalysts, wherein TiO_2 is immobilized on the materials that facilitate phase separation. Some of the recent studies have reported the use of MCM-41 [6,7], silica [8], clays [9], steel webnet [10], and activated carbon [11,12] as an effort to increase the efficiency and immobility of the catalysts. The present investigation attempts to support TiO_2 over fly ash cenospheres (FACs), aluminosilicate-rich by-products generated in coal-firing powder plants which bring great challenge to our environment because of their considerable amount. Due to their advantageous properties, such as nontoxicity, low cost, chemical/physical stability, and low density, FACs have been reported as substrates in many studies [13,14]. In this study, FACs were employed as supports for the preparation of buoyant and efficiently combinative Fe^{3+}-doped TiO_2/FAC composites (Fe–TiO_2/FAC).

The doping of Fe^{3+} in the titania matrix and coating of catalyst onto surface of a support have been prepared by impregnation [15,16], metal organic chemical vapor deposition (MOCVD) [17–19], and sol–gel techniques [20,21]. However, the coating of catalyst by impregnation is not homogeneous and is easily detached from substrates. On the contrary, CVD and sol–gel techniques can generate a relative homogeneous coating. Nevertheless, high temperature CVD required usually induces the grain growth and lowing of the surface area, hampering the enhancement of photocatalytic activity [22]. Therefore, due to its low-cost, low-temperature processing, and good shaping ability [23,24], the sol–gel method is chosen in this present paper for the preparation of Fe–TiO_2/FAC composites. This study aims at characterizing the properties of this novel catalyst and exploring the best experimental conditions for photocatalysis.

2. Experimental

2.1. Materials and chemicals

FACs are collected from Nanjing Yangzi Petrochemical Company. The received particles are sieved, and those passed through

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* Corresponding author.
E-mail address: jpzhai@nju.edu.cn (J. Zhai).

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120 mesh and retained on 150 mesh (100–125 μm) are chosen for preparation of Fe–TiO_2/FAC. All the major chemicals, including acetylacetone ($C_5H_8O_2$, >99%), ethanol (C_2H_6O, >99.7%), iron (III) sulfate ($Fe_2(SO_4)_3$) and Ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, >98.5%) are analytical reagent, while tetrabutyl titanate (TBOT, $C_{16}H_{36}O_4Ti$, >98%) and nitric acid (HNO_3) are chemical pure and guaranteed reagent, respectively. Deionized water was used for all the experiments.

2.2. Pretreatment of FACs

The sieved FACs were treated in 10% dilute nitric acid for 12 h to cleanse the surface in favor of improving the adhesion between Fe-doped TiO_2 film and FAC. The substrates were then washed three times with deionized water followed by drying in an oven at 120 °C for 3 h [25].

2.3. Photocatalysts preparation

In the preparation process of Fe–Ti–precursor sol, 34 ml TBOT was mixed with the solution of 90 ml absolute ethnol and 10 ml acetylacetone. Then the mixture was slowly added into 50 ml water–ethanol solution (deionized water:absolute ethanol = 9:250, v/v), and the predetermined amounts of iron nitrate were added to the precursor titanium sol followed by adjusting PH of mixed solution to 5 with 67% HNO_3 under the stirring for 1 h at room temperature. 2 g PEG was added into the sol intermittingly as the surfactant with continuous stirring for 1 h in constant water bath at 50 °C [26], and then the FACs were added under further stirring for 1 h at room temperature. The compounds were aged at room temperature for 24 h to form the Fe–Ti–precursor sol, followed by filtering and drying the particles at 120 °C for 2 h. Finally, calcination for 2 h resulted in the Fe–TiO_2/FAC particles. In order to obtain homogenous films, the obtained particles were again put into the filtered sol under the stirring for 1 h followed by the same subsequent processes. The molar ratios of Fe to Ti were 0, 0.005%, 0.01%, 0.05%, 0.1%, and 0.5%.

In the preparation of Fe–TiO_2 photocatalysts, the primary processes were the same as the method described above before adding FACs. Then the resultant mixed solution was stirred for 1 h at room temperature and aged for 24 h, followed by dehydrating the aged wet sols and removing the alcohol in an 80 °C water bath. The xerogel were dried at 120 °C for 2 h and calcined for 2 h to remove organic substance.

2.4. Characterization

Phase structure is obtained from an X'TRA x-ray diffractometer ((XRD) ARL, Switzerland) using Cu Kα radiation. Surface morphology is investigated by S-3400 N II (Hitachi, Japan) scanning electron spectroscope (SEM). Thermogravimetric analyses (TGA) were conducted by a STA 449C-Thermal Star 300 (Netzsch, Germany) apparatus under nitrogen gas atmospheres with a flow rate of 25 ml/min and a heating rate of 10 °C min^{-1}. UV–vis spectra were recorded on an UV-2450PC spectrometer (Shimadzu, Japan).

2.5. Batch reactor and photodegradation of Methylene blue (MB)

Photoreactions are carried out in a home-made reactor equipped with halide lamp (175 W, 300 nm–1000 nm), quartz reaction tube (54 cm diameter), aerating apparatus (7/8.5 W), and cooling water circulation device in which 0.1 mol/l $Fe_2(SO_4)_3$ solution flow circularly to filter ultraviolet light and maintain a constant temperature. All the ultraviolet light can be absorbed and only the wavelength ranged from 400 nm to 1000 nm can penetrate the circulating liquid to be received by the photocatalysts, which has been proved by Qi et al. [27]. In all experiments, a volume of 600 ml of the aqueous solution of MB (C_0 = 20 mg/l) is introduced in reactor with 1.8 g of photocatalysts, and then the reaction mixture is stirred in the dark for half an hour before starting the illumination to reach the dissolved oxygen saturation and absorption equilibrium whereafter the first sample is picked up as original data [28–30]. The halide lamp is turned on to decompose methylthionine and process of photochemical decomposition is monitored by measuring the irradiated solution (5 ml) withdrawn from the reactor after certain intervals. UV–visible spectroscopy is performed to measure the absorbency A of samples at 660 nm spectrum .According to Lamber–Beer law:

$$A_t = lg\left(\frac{I_0}{I}\right) = abc \tag{1}$$

where A_t is absorbance at time t, I_0 is the intensity of emitted light and I is the intensity of transmitted light, a is constant of absorption, b is the thickness of cuvette, a and b are determinants, and A_t and c are linear relationships. Based on the formula of accounting decomposition ratio:

$$R = \left(1 - \frac{C_0}{C}\right) \times 100\%, \tag{2}$$

This can be converted to the following form:

$$R = \left(1 - \frac{A_0}{A}\right) \times 100\%, \tag{3}$$

where A_0 is the absorbance of original solution at zero time, R is the decomposition ratio of MB, C_0 is the initial concentration of MB, and C is the revised concentration considering MB adsorption on catalysts at time t.

3. Results and discussion

3.1. XRD patterns of composite photocatalysts

3.1.1. Effect of Fe^{3+} doping amount on microstructure of films

The phase structure and crystal form of different samples are performed by X-ray diffraction after annealing process at 450 °C for 2 h under air atmosphere. Fig. 1 shows the XRD patterns of TiO_2/FACs and Fe–TiO_2/FACs samples. The peak value of anatase in Fe–TiO_2/FACs increases compared with TiO_2/FACs and no characteristic peak of rutile phase or brookite phase is revealed, which means Fe element can maintain metastable anatase phase of TiO_2

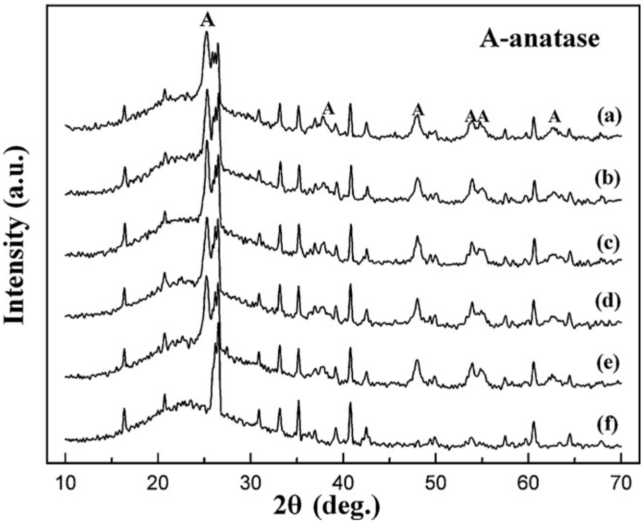

Fig. 1. XRD patterns of Fe–TiO_2/FAC with Fe/Ti molar ratio (a) 1%, (b) 0.5%, (c) 0.1%, (d) 0.05%, (e) 0.01%, and (f) 0%.