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Effect of Fe-doped TiO_2 nanoparticle derived from modified hydrothermal process on the photocatalytic degradation performance on methylene blue

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Abstract

Anatase Fe-doped TiO_2 nanoparticles with 10–15 nm particles sizes were directly prepared with amorphous TiO_2 nanoparticles and $Fe(NO_3)_3{\cdot}9H_2O$ by hydrothermal method. The TiO_2 crystallite grain sizes decreased with the increase of Fe contents. When Fe contents increased, the diffuse reflectance spectra of Fe-doped TiO_2 nanoparticles displayed a red shift in the band gap transition. And the absorbing band edge moved to visible range when the Fe contents were more than 2 mol%. XPS analysis showed that Fe^{3+} was not on the surface of TiO_2 nanoparticles, but inserting into the matrix interior. As a result, the photoactivity degradation of MB on Fe-doped TiO_2 nanoparticles decreased.

Keywords: Titania; Nanoparticles; Hydrothermal; Methylene blue; Photocatalyst

1. Introduction

Nano-sized titania has attracted increasing attention because of its wide application in many fields, such as photocatalysts, anti-UV agent, ceramics, inorganic membranes, sensors, solar energy conversion and so on [1,2]. In particular, recently numerous works have been carried out to display its photocatalytic activity due to its promising performance in degrading various organic and inorganic environmental pollutants [3,4]. It has been reported that the addition of Pt [5], Cr^{3+} [6], Cu^{2+} [7], Fe^{3+} [8–14] or other cation into anatase titania can improve its photoactivity. Among them, Fe-doped TiO_2 system is considered as a potential candidate for photocatalyst, and it has reported that the photocatalyst improved with optimal Fe content [8,9,11].

Various methods have used to synthesize Fe-doped TiO_2 nanoparticles, such as sol–gel method [9,11], impregnation [10] and hydrothermal method [8,13,14]. Among these, hydrothermal method is an important method to synthesize titania nanoparticles. Janes et al. [14] prepared Fe-doped TiO_2 powders by hydrolysis of titanium alkoxide in an aqueous solution of iron (II) following hydrothermal processing. Zhu et al. [8] also prepared it with titanium tetra-*tert*-butoxide and $FeCl_3$ by hydrothermal process. In the hydrothermal treatment, grain size, particle morphology, crystalline phase, and surface chemistry can be controlled via processing variables. The process of preparing Fe-doped TiO_2 nanoparticles determines its physico-chemical and photocatalytic properties and the effect mechanisms of Fe are not yet fully elucidated. So changing the hydrothermal conditions to investigate the effected of Fe^{3+} on TiO_2 is necessary.

In the present work, Fe-doped TiO_2 nanoparticles were directly prepared with amorphous TiO_2 nanoparticles and $Fe(NO_3)_3{\cdot}9H_2O$ by hydrothermal method. It was founded that photoactivity degradation of MB decreased with the content of Fe decreased, which was different with the former reports [8,9,11]. This was due to that Fe^{3+} was not on the surface of TiO_2 nanoparticles, but inserting into the matrix interior of TiO_2 nanoparticles.

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2. Experimental

2.1. Synthesis of samples

2.1.1. Preparation of amorphous TiO_2

At 25 °C, with magnetic stirring, the solution of 2.5 ml titanium *n*-butoxide and 25 ml C_2H_5OH was dropped to the solution of 13 ml H_2O and 13 ml C_2H_5OH in 30 min to form a white suspension. After stirred for 30 min, it was filtered and washed by C_2H_5OH. Finally, the product was dried at 110 °C and was grinded. Then the amorphous TiO_2 nanoparticles were obtained.

2.1.2. Preparation of Fe-doped anatase TiO_2

0.0946 g $Fe(NO_3)_3{\cdot}9H_2O$, 2 g amorphous TiO_2 and 50 ml H_2O were added into a Teflon-lined autoclave to hydrothermal react at 200 °C for 24 h. The resulted product was filtered and dried at 110 °C. Then 1 mol% Fe-doped TiO_2 was obtained. Samples with different Fe contents (0%, 0.1%, 0.5%, 1.0%, 2.0%, 5.0% and 10.0% (M/M)) were also prepared by the same process through varying the content of added $Fe(NO_3)_3{\cdot}9H_2O$.

2.2. Characterization of samples

The crystalline phase particles were determined using X-ray diffraction (XRD) performed on a D/max2500 diffractometer (40 kV, 30 mA, Cu Kα radiation). The morphology of particles was observed by transmission electron microscope (TEM, Hitachi-600-2). The BET surface area was calculated by nitrogen adsorption at 77 K on Tristar3000 (Micromeritics, Co.). The concentration of Fe was measured by inductively coupled plasma optical emission spectrometer (ICP, AtomScan 16). The element composition and the chemical state of particle surface were determined by X-ray photoelectron spectroscopy (XPS, PHI5300X, PerkinElmer Physics Electronics, Mg Kα as radiation source). UV–vis diffuse reflectance spectra (DRS) were measured on Shimadzu UV-2101 apparatus, equipped with an integrating sphere, using $BaSO_4$ as reference.

2.3. Photodecomposition of methylene blue (MB)

The photochemical reactor was consisted of a cylindrical jacketed quartz tube with 5.0 cm in diameter and 27 cm in length. A 300 W highly pressure mercury vapor lamp with a wavelength at 365 nm was placed inside the reactor. The light source assembly was placed concentrically inside the 300 ml Pyrex glass container of 6.0 cm in diameter and 28.5 cm height filled with 250 ml MB solution. The distance between the source and bottom of the vessel was 1.5 cm to aid for better stirring using a magnetic stirrer. To keep the temperature of the solution during the reaction, water was circulated through the annulus of the jacket quartz tube. The MB concentration was 100 ppm with a catalyst loading of 0.5 kg/m^3. Before irradiation, the suspension aqueous solution was stirred continuously in dark for 30 min to ensure adsorption/desorption equilibrium. The adsorption equilibrium concentration was used as the initial value for the further kinetic treatment of the photodecomposition processes. Samples were collected from the mixture solution at regular intervals and centrifuged to analyze by Shimadzu UV-2101 apparatus to determine the concentration of MB.

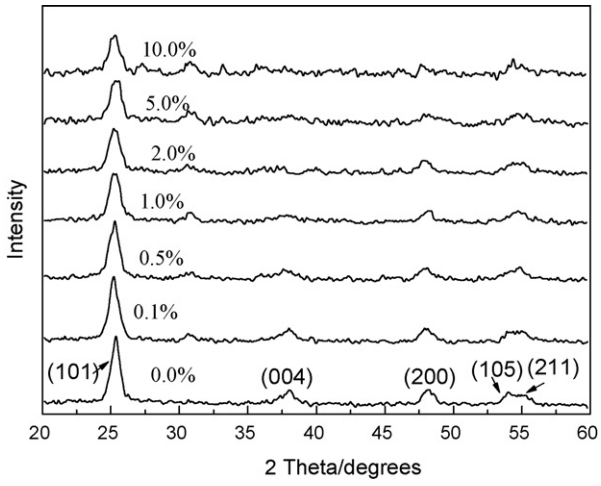

Fig. 1. XRD patterns of Fe-doped TiO_2 nanoparticles with different Fe content.

3. Results and discussion

3.1. The crystalline phase of particles

The XRD patterns of Fe-doped TiO_2 nanoparticles are shown in Fig. 1. It could be seen that all samples were anatase phase. In addition, no characters peaks of iron oxides phases appeared for all samples, which meant that iron oxide existed as amorphous phase. This suggested that iron distribution was possibly continuous in the particles. At the same time, Fig. 1 suggested a decrease of crystallinity of the Fe-doped TiO_2 nanoparticles in comparison with the undoped TiO_2, indicated by the decrease in the intensity of TiO_2 peaks. It suggested that the addition of Fe^{3+} could occupy regular lattice site of TiO_2 and distorted crystal structure of the host compound. The crystalline grain sizes of TiO_2 calculated by Scherrer formula decreased from 15.2 to 10.7 nm when the Fe content increased from 0.0% to 10.0%.

3.2. The morphologies of nanoparticles

The TEM images of undoped TiO_2 and 5.0% Fe-doped TiO_2 nanoparticles are showed in Fig. 2. The nanoparticles were spherical with narrow size distribution. The average particles sizes were about 15 and 12 nm for undoped TiO_2 and 5.0% Fe-doped TiO_2 nanoparticles, respectively. The Fe-doped TiO_2 nanoparticles owned smaller sizes and were more dispersed and uniformed than undoped TiO_2. Both narrow size distribution of nanoparticles and excellent dispersibility were in favor of photoactivity and anti-UV agent. The specific surface area of samples decreased when Fe content increased. It was 113 m^2 g^{-1} for undoped TiO_2, but it was 111 and 108 m^2 g^{-1} for 1% and 5% Fe-doped TiO_2 nanoparticles, respectively. It was inconsistent with the fact that the particle sizes decreased when Fe contents