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A novel preparation of highly active iron-doped titania photocatalysts with a p–n junction semiconductor structure

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ABSTRACT

Iron (III)-doped TiO_2 powder photocatalysts were prepared by modified uneven doping method using ammonium oleate in order to promote the formation of p–n junction composite structure, and were characterized by X-ray diffraction (XRD), TEM, BET, UV–vis and PL spectroscopy. The photocatalytic activities of TiO_2-based nanoparticles were evaluated by the photocatalytic rate of methyl orange oxidation. These iron (III)-doped TiO_2 photocatalysts are the composite powders having the p–n junction of n-type undoped TiO_2 with p-type TiO_2 doped by Fe evenly, were shown to have a much higher photocatalytic destruction rate than that of undoped TiO_2. The n–n junctions may be responsible for the high photocatalytic activity of P25 and other mix-phase crystalline titania.

1. Introduction

In recent years, titania photocatalyst have attracted much attention as an environmentally harmonious and clean catalyst. However, the efficiency of the photocatalytic degradation reaction is limited by the high recombination rate of photoinduced electrons and holes [1]. The fast recombination is in competition with the reactions decomposing the pollutants. Many scientists tried to solve these problems by changing the electronic structure of the photocatalyst via doping titania with transition metal ions [1]. Among many candidates, iron (III) ion seems to be the promising for this purpose [1–41]. Some investigators reported that doping of iron ion in TiO_2 increased its photocatalytic activity [1–30], though others have shown that Fe doping can reduce photocatalytic activity [31–40]. The photocatalytic activity of iron-doped titania strongly depends on the doping method and the concentration of iron in the photocatalysts. Iron-doped titania samples have been prepared by controlled hydrolysis [1,2,24,40], ultrasonic [3], sol–gel [4–9,20,26,29,30], mechanical alloying [10], co-precipitation [9,11,33,38], hydrothermal [12,25,29,34], microemulsion [13,39], reactive magnetron sputtering [14,15], metal organic chemical vapor deposition [16], combining sol–gel method with hydrothermal treatment [17,35], controlled hydrolysis followed by hydrothermal treatment [18], homogeneous precipitation-hydrothermal [19], hydro-alcohol thermal [21], impregnation [22,31,32], electrochemical anodic oxidation [23], high-pressure crystallization [27], solvothermal [28], plasma oxidative pyrolysis [36] and solution combustion method [37]. Recently, Li et al. prepared metal ions (Mo^{6+} and Ni^{2+}) doped TiO_2 thin films by two kinds of methods of doping, i.e., even doping and uneven doping processes [42–44]. They found uneven doping process was able to improve the photocatalytic activity significantly compared with the traditional process (even doping).

In previous paper [45], we prepared two kinds of iron (III)-doped TiO_2 powder photocatalysts by even doping and uneven doping methods, and found that TiO_2 photocatalysts doped by Fe unevenly with a p–n junction semiconductor structure were shown to have a much higher photocatalytic destruction rate than that of TiO_2 photocatalysts doped by Fe evenly and undoped TiO_2. There were some reports on photocatalyst being combined with p–n semiconductors to improve charge separation that minimizes the energy wasteful electron-hole recombination [46–62].

In the present paper, we prepared the iron-doped TiO_2 powder photocatalysts by a modified uneven doping method using ammonium oleate in order to promote the formation of p–n junction composite structure and found modified uneven doping could enhance the photocatalytic activity greatly. To the best of our knowledge such preparation method (modified uneven doping method) of iron (III)-doped TiO_2 powder has not been reported earlier.

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Table 1
Samples preparation condition and results.

Sample	Doping mode	Fe/at%[a]	Specific area ($m^2\ g^{-1}$)	Apparent rate constant (min^{-1})
P25	–	0		0.098
Pure TiO_2	–	0	79.7	0.0087
0.065%Fe–TiO_2	Even doping	0.065		0.0081
0.5%Fe–TiO_2	Even doping	0.50	76.4	0.0041
6.7TiO_2/0.5%Fe–TiO_2	Uneven doping	0.065	78.7	0.024
6.7TiO_2/0.5%Fe–TiO_2/M	Modified uneven doping	0.065	69.3	0.12

[a] Content of iron in total uneven and modified uneven doping samples.

2. Experimental

2.1. Preparation

Pure titania catalyst using tetrabutyl titanate as a titanium precursor was synthesized using the sol–gel method at room temperature. 40 mL of absolute ethyl alcohol, 10 mL of glacial acetic acid and 5 mL of double-distilled water were mixed as solution *a*, then it was added drop-wise under vigorous stirring into the solution *b* that contains 17 mL of tetrabutyl titanate and 40 mL of absolute ethyl alcohol. The resulting transparent colloidal dispersion (marked as TiO_2-sol) was stirred for 0.5 h and aged for 2 days till the formation of xerogel, then grounded into powder. The powder was calcined at 400 °C for 3 h, and then grounded in agate mortar to obtain fine titania powders finally.

Several TiO_2 powders doped by Fe evenly (abbreviated hereafter as FeTiE) were generated using the sol–gel method at room temperature by taking precursor $Fe(NO_3)_3{\cdot}9H_2O$ 40 mL of absolute ethyl alcohol, 10 mL of glacial acetic acid and 5 mL of the required concentration of $Fe(NO_3)_3$ solution were mixed as solution *c*, then it was added drop-wise under vigorous stirring into the solution *b*. The following procedures were carried according to the pure titania. The Fe^{3+}–TiO_2 catalysts had a nominal atomic ratio (Fe/Ti) of *x*%, so they are named as *x*%Fe–TiO_2 in this study.

One TiO_2 powder doped by Fe unevenly was generated using the sol–gel method at room temperature with the following procedure: 0.6 g of 0.5%Fe–TiO_2 powders was put into TiO_2-sol under stirring and the resulting suspension was stirred continuously for several days (during the several days, the solvent volatilized slowly). Then, the mixture was dried at 100 °C for 4 h, and fired at 400 °C for 3 h. The as-prepared photocatalysts are named hereafter as 6.7TiO_2/0.5%Fe–TiO_2, 6.7 is the nominal molar ratio of titania of TiO_2-sol to that of 0.5%Fe–TiO_2.

One doped TiO_2 powder was prepared by the modified uneven doping method. Firstly, 3 g 0.5%Fe–TiO_2 powders were sonicated in 30 mL of 0.01 M ammonium oleate aqueous solution (generated by mixing equal moles of ammonia with oleic acid) for 1 h and then stirred for 2 h. Secondly, the solids were separated by centrifugation and washed 3 times with ethanol. The purified powders were dried at 60 °C for 4 h and cooled at room temperature (The as-prepared powders are named hereafter 0.5%Fe–TiO_2–O). Thirdly, 0.6 g of 0.5%Fe–TiO_2–O powders was put into TiO_2-sol under stirring and the resulting suspension was stirred continuously for several days (during the several days, the solvent volatilized slowly). Finally, the mixture was dried at 100 °C for 4 h, and fired at 400 °C for 3 h. The as-prepared photocatalysts are named hereafter as 6.7TiO_2/0.5%Fe–TiO_2/M.

2.2. Characterization

Powder XRD patterns for samples were recorded using a Rigaku Dmax-IIIA diffractometer with Ni-filtered Cu-Kα radiation ($\lambda = 0.154056$ nm). The average crystal sizes were calculated from the X-ray diffractograms by the Scherrer formula. A transmission electron microscope (TEM), JEM-2010, was applied to observe the morphology of catalysts and estimate the particle size. The surface area of catalysts was determined using a standard Brunauer–Emmett–Teller (BET) apparatus (Micromeritics TristarII3020). The pore size distribution of the catalysts was determined by the Barrett–Joyner–Halenda (BJH) method. Diffuse reflectance UV/vis spectra were recorded on a Hitachi UV-3010 spectrometer equipped with an integrating sphere of 60 mm in diameter using $BaSO_4$ as a standard. Photoluminescence spectra were collected on a Fluorescence spectrometer (Hitachi F-4500) with a powder holder accessory under room temperature.

2.3. Photoreactivity measurements

Photo decolorization of methyl orange in an aqueous medium was used as a probe reaction to access the photocatalytic activity of all the powders. A Pyrex cylindrical photoreactor with an effective volume of 250 mL was used to conduct photocatalytic degradation experiments, which is surrounded by a Pyrex circulating water jacket. An 8-W UV lamp (Toshiba, Inc.) with a main emission at 365 nm is positioned at the center of the cylindrical vessel and used for photoreaction. For each experiment, 200 mg of photocatalyst was added to 250 mL of 5 mg/L methyl orange solution stirred with a magnetic stirrer. The aerated suspension was first stirred in the dark for 60 min, which was sufficient to reach adsorption equilibrium of methyl orange. The concentration of aqueous methyl orange was determined with a Hitachi UV-3010 spectrometer by measuring the absorbance at 464 nm.

3. Results

3.1. Characterization of photocatalysts

The XRD patterns of TiO_2-based nanoparticles are shown in Fig. 1. The TiO_2 in all the TiO_2-based nanoparticles exist mainly in anatase phase form. The mean crystallite size of pure TiO_2, 0.5%Fe–TiO_2, 6.7TiO_2/0.5%Fe–TiO_2 and 6.7TiO_2/0.5%Fe–TiO_2/M are 13.6, 13.0, 12.4 and 17.2 nm, respectively, indicating that iron modified uneven doping increased the size.

TEM images in Fig. 2 reveal that the prepared samples consisted of aggregates of primary particles of 7–20 nm in diameter. The averaged sizes of pure TiO_2 and 6.7TiO_2/0.5%Fe–TiO_2/M are estimated to be approximately 12 and 17 nm, respectively, which is in general agreement with the XRD determination.

The N_2 adsorption–desorption isotherms of catalysts in Fig. 3 are characteristic type-IV curves according to the BDDT classification with hysteresis loops [63]. The BET surface areas of the photocatalysts are summarized in Table 1. All samples exhibited fairly high surface area in the range of 69–80 $m^2\ g^{-1}$, which were little affected by doping. The BJH pore size distributions (Fig. 4) calculated on the basis of the desorption branches of the isotherms show peaks centered at 7.1, 6.9, 5.4 and 19.5 nm for pure TiO_2, 0.5%Fe–TiO_2, 6.7TiO_2/0.5%Fe–TiO_2 and 6.7TiO_2/0.5%Fe–TiO_2/M, respectively. The formation of mesoporous structure in the samples is attributed to the aggregation of TiO_2 crystallites [20]. There are two probable factors causing the great increase of average pore size for 6.7TiO_2/0.5%Fe–TiO_2/M compared with other samples. One is that larger crystallite aggregation forms larger pores. The other is that the decomposition of ammonium oleate during the process of drying and calcination resulted in a more abundant formation of mesoporous structure.

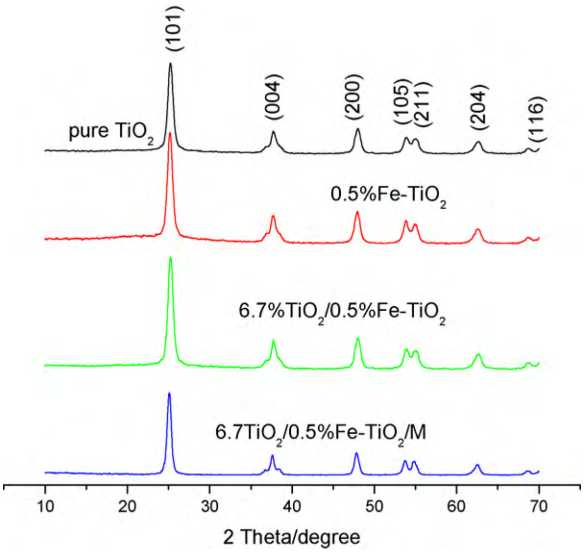

Fig. 1. XRD patterns of catalysts.