Synthesis and Photocatalytic Activity of Fe-doped TiO$_2$ Supported on Hollow Glass Microbeads

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Abstract: In this paper, Fe-doped TiO$_2$ photocatalyst supported on hollow glass microbeads (Fe-TiO$_2$/beads) is prepared by dip-coating method, which uses hollow glass microbeads as the carriers and tetrabutylorthotitanate [Ti(OC$_4$H$_9$)$_4$] as the raw material. The phase structure, ingredient, morphologies, particle size and shell thickness of the products are characterized by X-ray powder diffraction (XRD), energy-dispersive spectroscopy (EDS) and field emission scanning electron microscope (FESEM). The feasibility of photocatylic degradation of Rhodamine B (RhB) under illumination of UV-vis light is studied. The results show that the core-shell structure catalyst is composed of Fe-doped anatase TiO$_2$ and hollow glass microbeads, and the catalytic activity of the TiO$_2$ is markedly enhanced by Fe ion doping. The optimum concentration of Fe ion is 0.1% (molecular fraction) in the precursor and the photocatalytic activity can be increased to 98% compared with that of the undoped one. The presence of ferrum elements neither influences the transformation of anatase to rutile, nor creates new crystal phases. The possible mechanism of photocatalytic oxidation is also discussed.

Keywords: TiO$_2$; Sol-gel method; Semiconductor; Photocatalytic activity; Hollow glass microbeads

Introduction

In recent years, the public has become more concerned about environmental pollution and decontamination of polluted water and air by photocatalysis. Using a semiconductor as the photocatalyst to degrade various organic and inorganic pollutants in wastewater has become a kind of water treatment technology with the best prospect of utilization [1-3]. Among various oxide semiconductor photocatalysts, TiO$_2$ has proven to be one of the most suitable materials for widespread environmental applications due to its biological and chemical inertness, strong oxidizing power, low cost, and long-term stability against photocorrosion and chemical corrosion [4,5]. Furthermore, the organic pollutants could be completely degraded into CO$_2$, H$_2$O and other mineral acids by TiO$_2$ photocatalysis method under normal temperature and air pressure [6-8]. Some scholars predict that in the near future the photocatalysis method will become one of the most effective means in dealing with various kinds of industrial wastewater. However, two important scientific and technological problems still remain to be solved in the application of photocatalytic technology of TiO$_2$ semiconductor for

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the treatment of industrial wastewater [9]. One problem is that photocatalytic efficiency is not high since TiO_2 is active only under ultraviolet (UV) light and recombination of photogenerated electron-hole pairs, resulting in low photo quantum efficiency. Another problem is that it is difficult to reuse the TiO_2 semiconductor powder and make it possible to treat industrial wastewater on a large scale since the powder is very fine and therefore difficult to be separated from water. In order to improve TiO_2 photocatalytic activity and utilize sunlight fully and efficiently, various types of TiO_2-based photocatalysts are created [10-14]. The results show that metal ion doping and using the carrier to form compound photocatalyst is a reasonable approach [15-17].

Therefore, in order to improve TiO_2 photocatalytic activity and effectively utilizing the sunlight we have developed two methods. One approach is to dope transition metals into TiO_2, and another is to form coupled photocatalysts with hollow glass microsbeads. In this paper, we will describe the preparation process of synthesizing compound photocatalyst Fe-TiO_2/beads. The compound photocatalyst is characterized by X-ray powder diffraction (XRD), energy dispersive X-ray spectroscopy (EDS) and field emission scanning electron microscope (FESEM). The photocatalytic activity of compound photocatalyst is also investigated by degradation of Rhodamine B (RhB) under the illumination of UV-vis light. The results, compared with pure TiO_2, were satisfactory.

The possible mechanisms of the photocatalytic oxidation are also discussed. Because the density of the coupled photocatalyst is lower than 1.0 g/cm^3, they can float on the surface of water and use broader sunlight directly. At the same time, the photocatalyst is easily separated from water.

Experiment

The synthesis procedure for the photocatalyst Fe-TiO_2/beads composite is illustrated in Fig. 1 and detailed as follows.
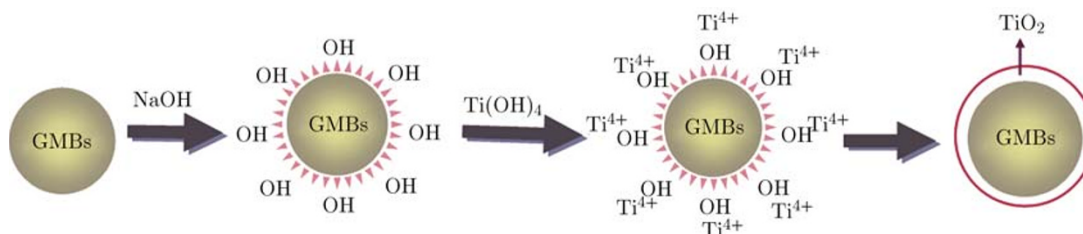

Fig. 1   The scheme of the procedure used to synthesize Fe-TiO_2/beads composites.

In order to make the coating formed on hollow glass microsbeads to precipitate, the surfaces of beads were processed. First, the beads were washed several times with distilled water, and then dipped in CH_2Cl_2 to remove the residual organic matter. Later, they were treated with NaOH solution (0.5 mol/L) by ultrasonic treatment to create OH functional groups at the surfaces of the beads, acting as the nucleation sites of TiO_2 nanoparticles, followed by filtration from the solution. Subsequently, the beads were dried at 80°C for about 2 h.

The colloid dispersion solution was prepared according to the following procedure. A solution of tetrabutylorthotitanate (TBOT) (13.6 ml) in ethanol (15 ml) was gradually added into the reaction vessel containing ethanol (27 ml), CH_3COOH (6.9 ml), distilled water (8.1 ml), appropriate amount of $Fe(NO_3)_3 \cdot 9H_2O$ and a small amount of acetyl acetone ($C_5H_8O_2$) under magnetic stirring at room temperature. The hydrolysis reaction was allowed to proceed. A highly stable colloid dispersion was obtained after stirring vigorously for about 6 h. The final colloid dispersion was aged for 10 h before being deposited on the hollow glass microsbeads. All materials and chemicals used in this study were purchased from Beijing Chemical Reagent Company.

The processed hollow glass microbeads were coated with the colloid dispersion using the following procedure. The hollow glass microbeads were dipped into the colloid dispersion for approximately 10 min and continuously stirred, and then the beads were withdrawn from the colloid dispersion and dried at 80°C for 2 h in a dust-free environment. The above operations were repeated for three times. Finally, the colloid /beads were heated in the muffle at 600°C for 3 h to form different TiO_2/beads samples. After calcinations, the Fe-TiO_2/beads samples were slowly cooled to room temperature.

The crystal phase purity of the products was characterized by X-ray powder diffraction (XRD) using an X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å) on a Rigaku D/max-2500. Field emission scanning electron microscope (FESEM, JEOL JSM-6700F) equipped with an energy dispersion X-ray spectrometer (EDS) was employed to examine the morphology, particle size and analyze the composition of the particles. The photocatalytic activities of the as-synthesized samples were evaluated via the degradation of photodegradable Rhodamine B (RhB).

Results and discussion

XRD results and EDS analysis

When the samples were calcinated in muffle at 600℃ for 3 h, XRD patterns of the samples shown in Fig. 2 exhibit only anatase crystal phase of TiO_2 (No. 84-1286). There was no diffraction peak of rutile, no ferrum compound was found. Figure 2(b) reveals all peaks correspond to the characteristic peaks of TiO_2 and beads. This indicates that a layer of TiO_2 nanoparticles is coated on the surfaces of beads. Compared with Fig. 2(a) and 2(b), we can conclude that the presence of transition metals Fe neither influences on the transformation of anatase to rutile, nor creates new crystal phases and the composite photocatalysts are not present the color of it's oxide. Comparing the two illustrations in Fig. 3, we can conclude that the element Fe is also included in the samples (see Fig. 3(b)). This testifies that Fe is indeed doped in the products.
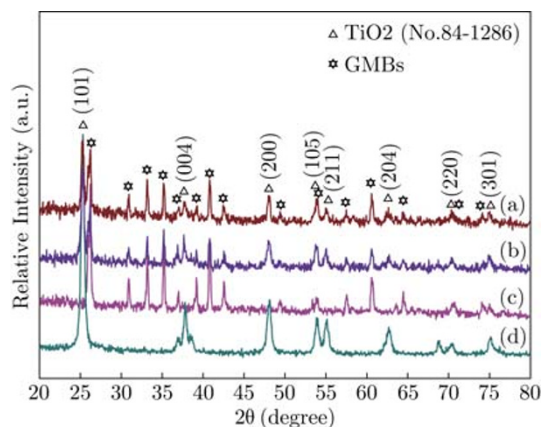

Fig. 3 EDS images: (a) TiO_2/beads; (b) Fe-TiO_2/beads.

Fig. 2 XRD patterns: (a) Fe-TiO_2/beads; (b) TiO_2/ beads; (c) bare beads; (d) TiO_2.

FESEM micrographs of Fe-TiO2/beads nanoparticles

The morphology of the products is examined by FESEM (Fig. 4). It is shown that the surface of beads is smooth (Fig. 4(a)) before coated. The hollow structure can be clearly observed from the image of the broken microsphere (Fig. 4(b)). Compared with Fig. 4(a), it is clearly observed that the beads' surface is coated with TiO_2 (Fig. 4(b-f)). The corresponding magnified surfaces micrographs is show in Fig. 4(e). The thickness of the coating is about 2 μm as shown in the transverse section (Fig. 4(f)). Thus, FESEM analyses suggest the uniform and continuous Fe-TiO_2 coating on the surfaces of beads, which agrees well with the previous results obtained from XRD and EDS observation.
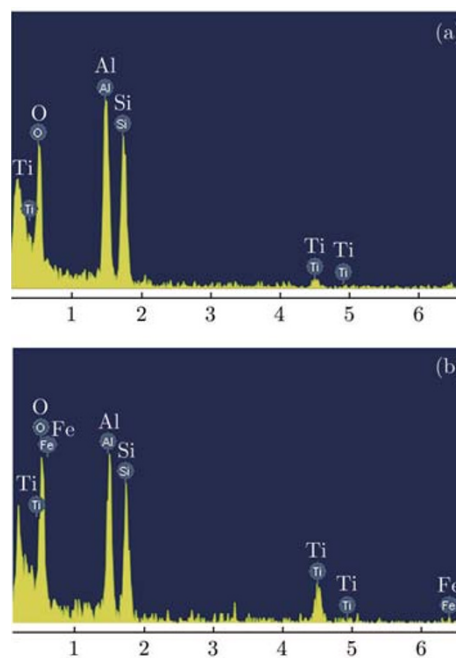
The characterization of photocatalytic activity

The photocatalytic activities of the as-prepared samples for the decomposition of RhB as a function of TiO_2 content under UV illumination are presented in Fig. 5. All samples were prepared in muffle at 600℃ for 3 h. The photocatalytic performance of commercial photocatalyst, Degussa P25 is also given in the Fig. 5 for comparison. Figure 5(a) is undoped TiO_2 coated on the surface of beads, which indicate that the RhB is the least degraded under UV irradiation in all the samples. Curves (b), (c), (d) and (e) are Fe-TiO_2/beads with the different molecular fraction (0.01%, 0.05%, 1%, and 0.1%) in precursors, respectively. Comparing the curves in Fig. 5, it can be concluded that (1) the photocatalytic activities is increased with the augment of Fe proportion and then to be downtrend, (2) when the molar ratio of Fe is 0.1% in precursors, the photocatalytic activity can be increased to 98% (Fig. 5(e)), (3) all the samples have lower photocatalytic activities than Degussa P25, which is known as the best photocatalyst commercially available, (4) the photocatalytic activity of the Fe-TiO_2/beads is higher than the undoped TiO_2/beads. Therefore, we can adjust the photocatalytic activity of TiO_2 by controlling the molecular fraction of the Fe ion in precursors.

The process for the TiO_2 photocatalyzed oxidation based on the basic principles and studies reported in the literature can be summarized as follows [18,19]: Under the illumination of UV light, electron-hole pairs (e^-/h^+) may be created. The e^- and h^+ might migrate to the surface of the TiO_2 nanoparticle and react with adsorbed RhB resulting in the desired process, or they may undergo undesired recombination [20].
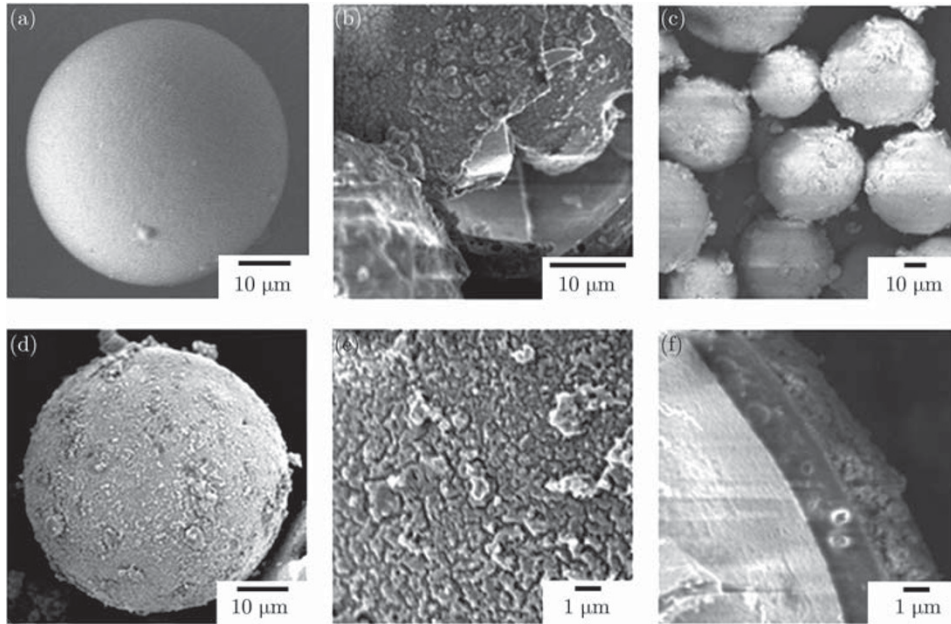
Fig. 4　FESEM images of: (a) bare beads; (b) broken TiO$_2$/beads; (c-d) TiO$_2$/beads; (e) the magnified surfaces of Fig. 4(d); (f) the transverse section of the broken Fe-TiO$_2$/beads.
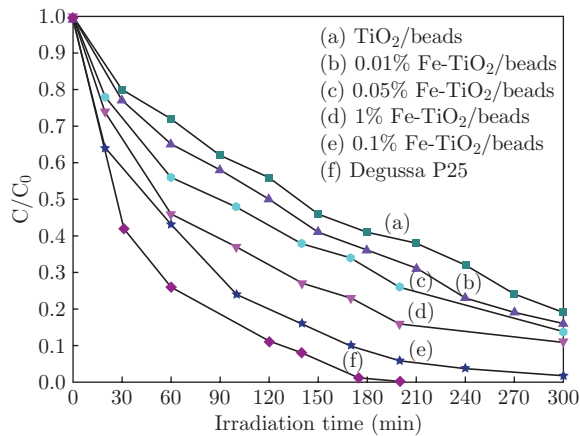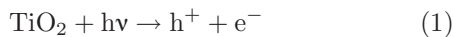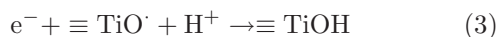

Fig. 5　Relationship between the photooxidation efficiency and illumination time with different photocatalysts: (a) TiO$_2$/beads; (b-e) Fe-TiO$_2$/beads with different doping ratio (0.01%, 0.05%, 1%, 0.1%, respectively); (f) Degussa P25.

(i) Charge carrier generation

$$TiO_2 + h\nu \rightarrow h^+ + e^- \tag{1}$$

(ii) Recombination reaction

$$h^+ + e^- \rightarrow TiO_2 + heat \tag{2}$$

$$e^- + \equiv TiO^. + H^+ \rightarrow \equiv TiOH \tag{3}$$

Oxygen adsorbed on the TiO$_2$ surface prevents the recombination of electron-hole pairs by trapping conduction band electrons;

(iii) Surface trapping

$$e^- + O_2 \rightarrow O_2^{.-} \tag{4}$$

$$h^+ + \equiv TiOH \rightarrow \equiv TiO^. + H^+ \tag{5}$$

Hydroxy radicals (OH$^.$) are produced from holes reacting with either H$_2$O or OH$^-$ adsorbed on the TiO$_2$ surface and also formed from O$_2^{.-}$;

(iv) Production of hydroxyl radicals

$$H_2O + h^+ \rightarrow OH^. + H^+ \tag{6}$$

$$OH^- + h^+ \rightarrow OH^. \tag{7}$$

$$O_2^{.-} + 2H^+ \rightarrow 2OH^. \tag{8}$$
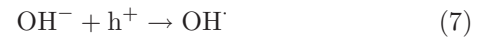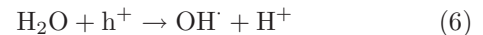
The hydroxyl radical (OH$^.$) are widely accepted as a primary oxidant in the heterogeneous photocatalysis R- (Herein, R represents RhB);
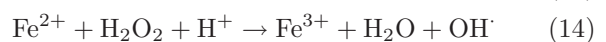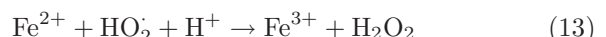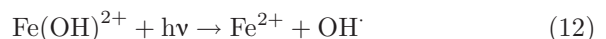
(v) Oxidation of the organic compound R-

$$OH^. + R - H \rightarrow R + H_2O \tag{9}$$

or

$$OH^. + R \rightarrow R^. - OH \tag{10}$$
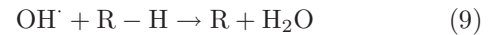
When TiO$_2$ are present, adding a small amount of Fe^{3+} (up to 0.1%), the photodissolution efficiency of the RhB increased rapidly; with continuously increasing the Fe^{3+} concentration (up to 1%), the degradation ratio of RhB decreased gradually (Fig. 5). This is because when a suitable amount of Fe^{3+} is present, Fe^{3+} behaves as an electron scavenger and preventing the combination of electron-hole pairs, which increases the amount of OH$^.$ and enhances the photocatalytic efficiency of TiO$_2$ [21].

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{11}$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^. \tag{12}$$

$$Fe^{2+} + HO_2^. + H^+ \rightarrow Fe^{3+} + H_2O_2 \tag{13}$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + OH^. \tag{14}$$

While Fe^{3+} dopant content exceeds 1%, Fe_2O_3 becomes the recombination centers of the photoinduced electrons and holes because of that the interaction of Fe_2O_3 with TiO_2 leads to that the photoinduced electrons and holes of TiO_2 transfer to Fe_2O_3 and recombine quickly, which is unfavorable to the photocatalytic reaction [22]. In this study, the photocatalytic efficiency of 1% Fe doping is lower than that of 0.1% and the best Fe^{3+} dopant content is 0.1%. Therefore, the concentration of dopant is a key factor for synthesizing the compound photocatalyst.

Conclusion

The present studies show that floating photocatalysts $Fe-TiO_2$/beads can be successfully synthesized by the method of dip-coating from the colloid solution of tetrabutylorthotitanate. The photocatalytic activities were measured by the photodegradation of RhB under UV illumination. The results indicate that (1) The photocatalytic efficiency of TiO_2 can be greatly improved via chemical and electronic modifications; (2) Fe-doping broadens the absorption profile, improves photo utilization of TiO_2; (3) The optimum concentration of Fe ion is 0.1% (molecular fraction) in the precursor and the photocatalytic activity can be increased to 98% compared with that of the undoped one. It is that the TiO_2 compound photocatalysts will become one of the most effective photocatalysts in dealing with industrial wastewater with the best prospect of utilization.

Acknowledgment

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