A Facile Synthesis of TiO₂ with Enhanced Photocatalytic Performance for Removal of Methylene Blue

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Abstract. Titanium dioxide (TiO₂) is the most representative and widely used photocatalyst. To further enhance the photocatalytic efficiency of titanium oxide, in this study, we developed a facile hydrothermal method to synthesize iron-doped TiO₂. Iron-doped TiO₂ was synthesized by hydrothermal method with titanium monoxide as raw material and iron sulfate as the dopant. The color of the TiO₂ powder was light yellow and the powders were characterized using scanning electron microscope, X-ray diffraction, and We demonstrated enhanced absorption of TiO₂ towards visible-light and enhanced photocatalytic efficiency through iron-doping method.

1. Introduction

With the improvement of people's living standards, people are increasingly concerned about environmental issues. Due to the year-by-year increasement of industrial wasted gas, wasted water, wasted residue and other industrial "three wastes", the environmental problems are getting worse[1], especially the water pollution and water shortages problem. So it is essential to repair and protect water. Among numerous treatments for removing the pollutants from wastewaters, photocatalytic technology is known as a promising case due to its ability to mineralize most of the organic pollutants by using only luminous energy. A large number of studies of the semiconductor photocatalysis which can remove the harmful substances in the water and degrade the organic pollution into inorganic small molecules have already been reported [2]. Considering about the advantages of fast oxidation speed, complete degradation and low energy consumption, semiconductor photocatalysis has attracted the attention of many researchers. Titanium dioxide catalyst which has the advantages of low toxicity, low cost, good stability and no secondary pollution, has attracted the attention of environmental workers in various countries[3]. However, TiO₂ has a wide energy band-gap(Eg=3.2eV, λ=387nm), so the valence band electrons can jump to the conduction band to form the e⁻_h⁺ pairs only under the excitation of ultraviolet light with wavelength less than 387nm. On the surface of TiO₂, the electrons(e⁻) have the reduction effect, and the hole(h⁺) has oxidation effect, so it can degrade some organic compounds. However, it can only be activated under the condition of UV light, which greatly limits its practical usage[4]. In theory, if a substance can absorb 100% of the light in the entire visible range, then it is certainly a complete black material. Otherwise, if there is no light absorption in the entire visible area, then this substance definitely shows a white color. In other words, if the light is unequally absorbed throughout the visible area, the substance will show a particular color (such as yellow, brownor green). Therefore, in order to absorb as much visible light as possible, the researchers made TiO₂ showing other colors to improve the photocatalytic performance.
Therefore, it is of great significance to improve the photocatalytic activity of TiO₂ under visible light[5]. In order to increase the limited optical absorption of TiO₂ under sunlight, intensive researches have been recently devoted to the preparation of lower band-gap or black titanium dioxide. Doping has been proven to be an effective strategy to modulate the optical band-gap or other physical properties. Many researchers have doped titanium dioxide to improve the catalytic efficiency of titanium dioxide[6]. In this paper, a simple and facile method for preparation of iron-doped titanium dioxide was introduced and an enhanced catalytic efficiency has been demonstrated.

2. Experimental Details

2.1. Preparation of Titanium Dioxide
Titanium dioxide was prepared by the hydrothermal method. Titanium monoxide, hydrochloric acid, ferric sulfate were purchased from the Sinopharm Chemical Reagent Co., Ltd. The water used in the experiment was deionized water. Titanium dioxide and iron-doped titanium dioxide were fabricated according to the related literature reports with little modification. The typical synthesis method is as follows: titanium monoxide(1.214g) and HCl(60ml 12mol/L) were firstly added to a reaction autoclave and stirred well for form a homogeneous solution. Then the autoclave was placed in an oven for hydrothermal reaction and the temperature of the autoclave was maintained at 150°C for 24 hours. After it cooled down to room temperature (RT) naturally, the product was centrifuged and washed with ethanol and DI water for several times. Finally, the powder was dried in an oven. For iron-doping of titanium dioxide, Fe₂(SO₄)₃ (0.9978g) and deionized water (60ml) were added to the mixtures. NaOH (0.01g) was then added to the solution to adjust the pH to make it weak alkaline. The solution was stirred at a speed of 2000 rpm for 24 hours on a magnetic stirrer. Then the mixture was filtered, centrifuged and washed with ethanol and DI water for several times. The obtained product was finally sintered at 550°C for 2.5 h in an oven to form a light yellow powder.

2.2. Characterization of Iron-Doped Titanium Dioxide Powders
The phase composition was analyzed by X-ray powder diffraction. (D8 ADVANCE) The morphologies of the powder was observed by scanning electron microscopy (SEM). The absorption spectra of the powder were measured by UV-Vis (Lambda 650 spectrophotometer).

3. Results and Discussions

![SEM images of Fe-TiO₂ powders: (a-d) morphologies of powders with different scale bars varying from 500 nm to 10 μm](image)

**Figure 1.** SEM images of Fe-TiO₂ powders: (a-d) morphologies of powders with different scale bars varying from 500 nm to 10 μm
We first studied the morphologies of the light yellow powders by SEM microscopy. Fig.1 (a)-(d) show the morphologies of powders with different scale bars varying from 500 nm to 10 μm. We can see from Fig.1 that the titanium dioxide powder presents a regular rectangular shape and is in a state of aggregation or stack, which forms a flower-like morphology.

To understand the crystal structure of the powder, we studied the typical X-ray diffraction (XRD) pattern of iron-doped TiO₂. Conventional XRD has been performed by Bruker D8 Advance diffract meter using Cu Kα radiation at 40 kV and 40 mA. Line traces were collected over 2θ values ranging from 10° to 80°. The results were shown in Fig.2. The diffraction peaks at 27.45, 36.10, 41.23 and 54.32° are assigned to the (1 1 0), (1 0 1), (1 1 1) and (2 1 1) planes of the rutile TiO₂ materials, respectively, which indicates that the synthesized TiO₂ is in the tetragonal phase, from the JCPDS card (21-1276).

![XRD pattern of Fe-doped TiO₂ powers.](image)

**Figure 2.** XRD pattern of Fe-doped TiO₂ powers. (h k l) (Y-axis counts)

Fig. 3 depicts the UV-vis absorption spectra of P25 and Fe-doped TiO₂ powders. We can conclude that P25 has strong absorption intensities at wavelengths in the range of 250-350 nm and it shows very low absorption in the visible range of 400-800 nm. While for iron-doped titanium dioxide, an obvious absorption redshift has been observed, suggesting that more visible light can be absorbed by doped titanium dioxide. As discussed above, the relatively wide band gap (~3.2 eV) of TiO₂ has hindered its large-scale applications for photocatalysis since most part of the visible light can not be used by the photocatalyst. Through doping strategy, the maximum absorption peak shifted from 300-350 nm to about 400 nm and the absorption edge shifted towards deep visible-light region, demonstrating a decreased optical band-gap and an enhanced visible light utilization. Therefore, the results are very promising for enhancing the photocatalysis performance of TiO₂.
We now verify the photocatalysis performance of the Fe-doped TiO$_2$. A solution of methylene blue with a concentration of 5 mg/L was prepared first and then 100 mg of Fe-doped TiO$_2$ powder was added. The solution was kept with constant stirring to make sure that the photocatalyst had full contact with methylene blue solution. The solution was then placed under a 300W xenon lamp and the distance between the lamp and the beaker is 10 cm. Finally, we monitored the absorption of the solution by taking 5 ml of the solution every half an hour. The results was presented in Fig.4. It can be seen from the figure that the Fe-doped TiO$_2$ shows good catalytic effect for removing methylene blue and the degradation rate could reach 81.2% in 3 hours.

\[ \frac{(A_0 - A)}{A_0} \]

\( t/\text{min} \)

**Figure 3.** UV-vis absorbance spectar of P25 and Fe-doped TiO$_2$ powders

**Figure 4.** Photodegradation of methylene blue.

\((A_0\) is the initial absorbance of the methyl orange solution and\(A\) is the absorbance of methyl orange solution when the degradation time is \(t\))
4. Conclusions
In summary, we introduced a very simple and facile method of preparing iron-doped titanium dioxide in this paper. According to the XRD result, we found that the powder was pure rutile phase. Through UV-vis study, we found that the Fe-doped TiO$_2$ shows a red-shift of absorption, suggesting a decreased optical band-gap and an enhanced absorption range. Therefore, the Fe-doped TiO$_2$ has demonstrated a good photocatalyst effect for degradation of methylene blue. For practical applications, we believe that our work is a great improvement. Our team will further apply this catalyst to the environment and energy areas.

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6. References
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