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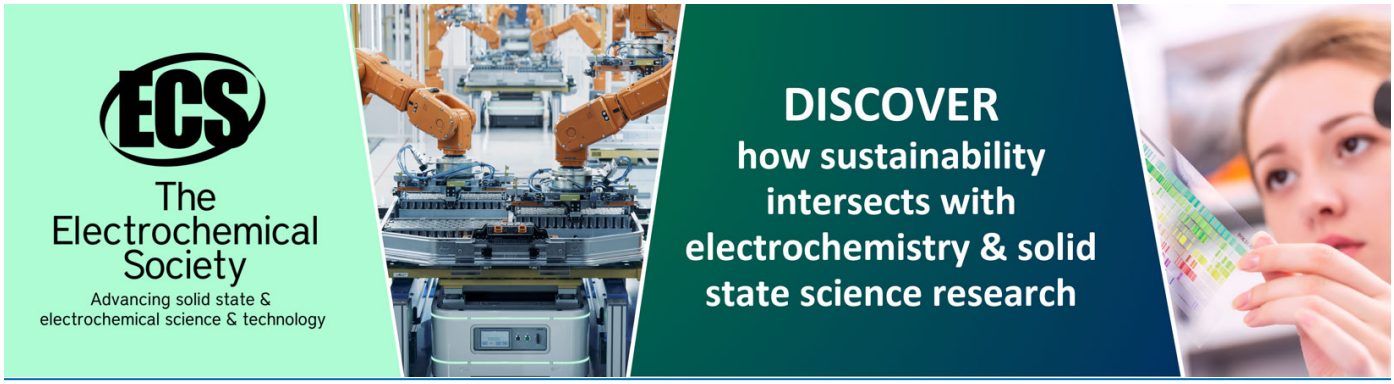

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Preparation And Photocatalytic Performance Of F-TiO_2 Photocatalyst

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Abstract. The environmental problems in today's society are becoming increasingly serious. It is imminent to seek an economic and efficient environmental governance method. Titanium dioxide has become one of the most suitable semiconductor for environmental purification due to its characteristic, such as excellent photocatalysis, stability, low cost and non-toxic, etc. Nevertheless, TiO_2 is limited by several undesirable characteristics, such as its wide band gap (3.2 eV) that can only be excited by ultraviolet light, which occupies only7 % of the entire solar spectrum. In addition, TiO_2 exhibits rapid recombination of photo-induced electrons and holes (e–/h+), which significantly decreases quantum efficiency.This thesis focused on increasing the photocatalytic activity of TiO_2 under simulated sunlight irradiation. F-TiO_2 composite was synthesized via a simple sol-gel method by using NaF as the fluorine source followed by heat treatment at aerobic or anaerobic calcination, and their photocatalytic ability has been evaluated. The research results are as followed: F-modification can generate more oxygen vacancies because of the replacement of surface -OH groups by the F species, which can inhibit the recombination of photoelectrons with holes by the captured photoelectrons, promote the generation of Ti^{3+} and narrow the band gap 2.75 eV, thereby enhancing the quantum efficiency of photocatalysis.

1. Introduction

1.1. Foreword

With the rapid development of social economy,the energy has been over-exploited and utilized,which has caused serious environmental pollution.It's imminent to seek an approach that is both economical and efficient in harnessing the environment.Semiconductor photocatalytic technology is a simple,environmentally friendly,economical,and attractive method.It not only can degradation of organic pollutants in the atmosphere and water using sunlight at normal temperature and pressure,but also do not cause secondary pollution[1].It has become a research hotspot for domestic and foreign scholars.

From a large amount of literature,Fluoride modified TiO_2 has an important role in the composition,grain size and morphology of the crystalline structure of titanium dioxide[2], these will directly and indirectly affect its photocatalytic activity. Le uses a single crystal phase of TiO_2 dispersed in potassium F solution for thermal shoch to prepare a fluorinedoped titania nanocatalyst with high catalytia activity.Analysis shows, the doping of F ion transforms Ti^{4+} in the crystal lattice into Ti^{3+} by charge compensation and the surface activity of TiO^{3+} traps photo-generated electons, reducing the recombination probability of electrons and hole pairs can improve photocatalytic activity. It's

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generally believed that the F atoms, which are almost the same size as the O atoms, can enter the titanium dioxide crystal lattice, and can improve the acidity of the TiO_2 surface, generate oxygen vacancies and new cativation points[3]. All of these will help increase the photocatalytic activity of TiO_2 under visible light.

2. Content

2.1. Objective

For low TiO_2 light energy utilization, the absorption band is limited to the ultraviolet region and the electron-hole recombination rate is high. F-TiO_2 was prepared by different calcination methods. In order to improve the separation efficiency of TiO_2 electron-hole pairs and enhance their photocatalytic effect under visible light., catalytic degradation of methylene blue under simulated sunlight[4-7].

2.2. Research Content

Photocatalytic properties

Degradation of methylene blue and study its photocatalytic properties

2.3. Study on Photocatalytic Performance of Samples

2.3.1. Selection of target degradants

In our country, printing and dyeing wastewater has become the main source of pollution. The large amount of emissions and difficult to deal with have become the research hotspots and difficulties. At the same time, the shortage of water resources has severely restricted the development of the printing and dyeing industry in China. Due to the characteristics of large chromaticity, high organic content, and poor biodegradability of dyeing and printing wastewater, many treatment methods fail to achieve the desired results. However, semiconductor photocatalytic technology can solve this problem. In this study, under simulated sunlight irradiation, methylene blue (MB) was selected as the target degradant for testing the catalytic effect of photocatalysts.

2.3.2. Performance Test

（1）Test Methods

Photocatalytic performance measurement

A 50 mg sample was subjected to photocatalytic degradation of 20 mL of methylene blue (20 mg/L) under simulated sunlight, and aerated and agitated. the photocatalytic time is 10 min, take 1.5ml of solution centrifuge every 2min. (8000 rpm, 10 min), and 1 ml of supernatant is taken up to 10 ml. The absorbance was measured with a spectrophotometer and the decolorization rate of methylene blue by the complex was calculated from the methylene blue concentration-absorbance standard curve. The decolorization rate of methylene blue was compared with TiO_2[8].

（2）Standard curve of methylene blue solution

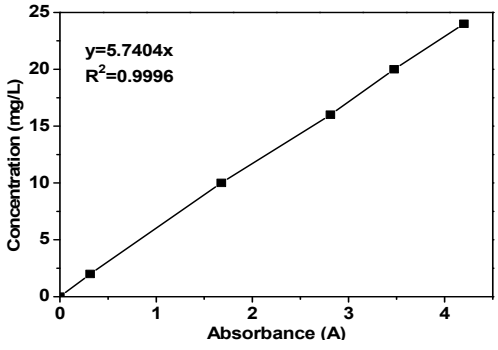


Fig. 1 Absorbance for MB solution as a function of concentration

Preparation of 20 mg/L methylene blue solution，and reference to deionized water，then full band scan of MB with UV-3000 UV-Vis Spectrophotometer. It was found to have a maximum absorption peak at 664 nm, determine the maximum absorption wavelength of 664 nm.

Measured different concentrations of standard solutions at the maximum absorption wavelength (λmax = 664 nm), with deionized wate as reference. According to absorbance and concentration, drawing standard graph 1. Linear regression analysis of the resulting curve, The resulting standard curve equation：y=5.7404x， Correlation coefficientR2=0.9996[9].

2.3.3. Photocatalytic performance evaluation

According to the measured absorbance values, the concentration of the solution was calculated in combination with the standard curve equation, and the MB degradation rate of the sample was then calculated[10].

$$\text{Degradation rate} = \frac{C_0 - C_t}{C_0} * 100\ \% \quad (1)$$

(1) In the formula：C_0, Initial MB solution concentration（mg/L）；C_t, Photocatalytic degradation of MB solution after t time（mg/L）.

3. Preparation and Photocatalytic Performance of F-TiO_2

In order to make TiO_2 have photocatalytic activity under visible light, non-metal doping modification is a good method. At the same time in many non-metallic ions， The atomic diameters of the fluoride ions with a radius of 0.133 nm and the oxygen ions with a radius of 0.132 nm in TiO_2 are the closest, and this creates a favorable prerequisite for the incorporation of fluoride into the TiO_2 lattice. And the performance of fluorine-modified TiO_2 is stable, because the single electron oxidation potential of fluoride ions is +3.6 V, it will not be oxidized by TiO_2 photogenerated holes (+2.7 V). Therefore, F-doped TiO_2 attracts the attention of scholars.

This experiment uses NaF as a fluorine source, Preparation of F-TiO_2 by Sol-Gel Method. The introduction of fluorine narrows the band gap of titanium dioxide, Enhances catalyst absorption in the visible region, so that it has superior photocatalytic activity.

3.1. Preparation of F-TiO_2

A certain amount of NaF was dissolved in a mixed solution consisting of 6 mL of deionized water, 8 mL of anhydrous acetic acid, and 30 mL of absolute ethanol, Stir magnetically for 50 min, label it as liquid A after mixing, and adjust the pH of solution A with 1 mol/L HCl. 20 mL of tetrabutyl titanate, 30 mL of anhydrous ethanol, and 4 mL of anhydrous acetic acid were stirred for 30 min to obtain a solution B. Under vigorous agitation, liquid A was added dropwise to liquid B at a rate of 5 ml/min. After completion, stirring was continued for 4 h. Finally, a wet gel was obtained. Putting the gel at room temperature for 2 days, then placed in an oven at 60°C for 24 hours, then milled to a micron level with a ball mill and calcined in a muffle furnace to obtain a fluorine-modified TiO_2 labeled F-TiO_2.

The above procedure was repeated without addition of NaF. The rest of the steps were the same, and TiO_2 nanoparticles were prepared and labeled as TiO_2.

3.2. Optical absorption properties

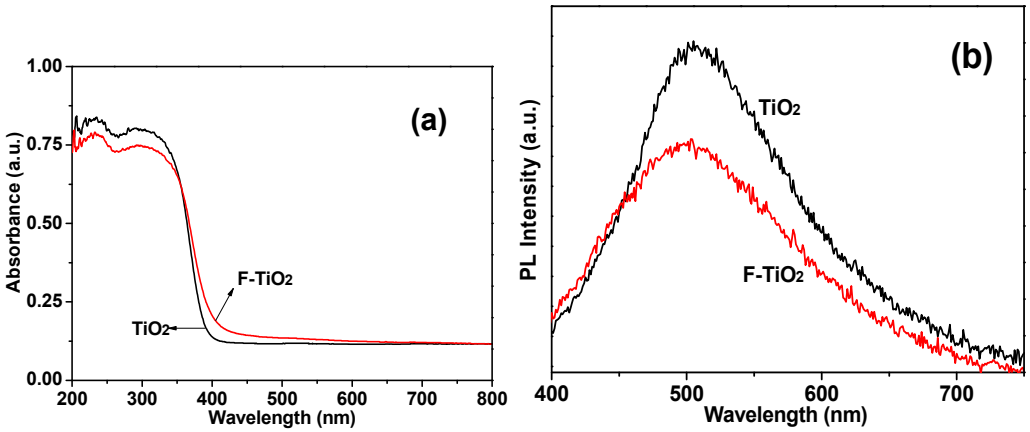
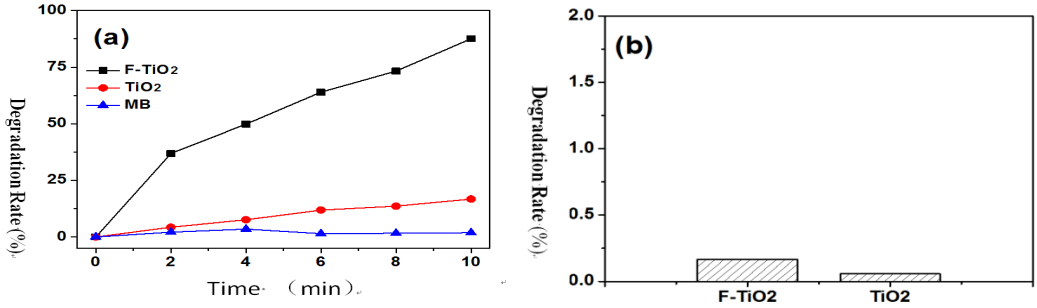


Fig. 2 (a) UV–vis absorption spectra and (b) PL emission spectra of F-TiO_2 and TiO_2

The UV-vis diffuse reflectance spectrum of F-TiO_2 and TiO_2 is shown in Fig. 2a. Compared with TiO_2, the diffuse reflection spectrum of F-TiO_2 has obvious red shift. According to the Kubelka Munk function graph, the tangent line shows that the forbidden band of F-TiO_2 and TiO_2 is 2.75 eV and 2.92 eV respectively. The narrowing of the band gap of F-TiO_2 is caused by the introduction of F ions , At the same time, in the photo-emission spectra of F-TiO_2 and TiO_2 (2b), the emission peak intensity of F-TiO_2 is also significantly lower than that of pure TiO_2. In general, when the luminescence spectrum corresponds to the bandgap energy, the stronger the luminescence peak, the stronger the composite effect of energy loss and the lower the photocatalytic activity. The lower luminescence peak indicates the low recombination rate of photoelectron-hole pairs in TiO_2. In addition, the luminescence peak is located at 500 nm. It has been reported in the literature that this is caused by oxygen vacancies on the surface of TiO_2 nanoparticles. Fluoride modification, it can replace the surface of OH to generate more oxygen vacancies. Studies have shown that fluorine doping does not broaden the absorption of light by TiO_2., Because the impurity level F 2p formed by F doping is below the valence band of TiO_2, Cannot have any direct overlap with the banned TiO_2, as a result, the band gap of TiO_2 cannot be narrowed. However, the presence of oxygen vacancies in F-TiO_2 can narrow the bandgap of TiO_2. The particle size of nanoparticles is very small, The average free moving distance of electrons is shorter, Makes oxygen vacancies on the surface of particles very easy to combine electrons to form excitons, And form an exciton energy level near the bottom of the conduction band (Ti 3d orbital), that is, the oxygen vacancy energy level. The oxygen vacancy energy level can shorten the distance between the conduction band and the valence band, and enhance the absorption of visible light by F-TiO_2.

3.3. Photocatalytic properties



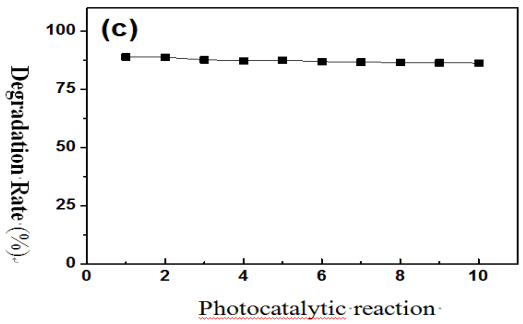


Fig. 3 (a) Comparison of photocatalytic activity between the F-TiO_2,TiO_2 and MB (no catalyst) in degrading MB. (b) adsorbability. (c)Photocatalytic stability of F-TiO_2 within 10 cycles

Figure 3a compares the photocatalytic activity of F-TiO_2 and TiO_2 samples under simulated sunlight. As can be seen from the figure, the MB degradation rate in the F-TiO_2 catalytic system can reach 87.54% after simulated sunlight irradiation for 10 min., However, the degradation rate of MB in pure TiO_2 catalyst system is only 16.75%. The photocatalytic activity of the former is much higher than that of the latter. It shows that the introduction of fluoride ions greatly promotes the degradation of MB by TiO_2. In order to eliminate the interference of MB self-degradation under ultraviolet light, the blank experimental group of MB self-degradation was set up. The results show that the degradation of MB in simulated sunlight is very weak and negligible. It is proved that F-TiO_2 has strong photocatalytic activity. Fig. 3b is a comparison of the dark adsorption capacity of F-TiO_2 and TiO_2 samples. The adsorption capacity of MB is very small, and F-TiO2 is only few higher than pure TiO_2. In order to determine the stability of F-TiO_2, the photocatalytic reaction was repeated 10 times, and the photocatalytic degradation rate of MB for each catalyst was shown in figure 3c. As the picture shows, 1. No significant decrease in degradation rate was observed in the 10 photocatalytic reactions, indicating that the performance of F-TiO_2 is stable.

4. Conclusion

This article aims to improve the response and photocatalytic activity of TiO_2 to the visible light region, First use NaF as doping source, Sol-gel method, .F-TiO_2 prepared by aerobic calcination (muffle furnace calcination) The adsorption and photocatalytic properties of F-TiO_2 were studied, Reached the following main conclusions：

F-TiO_2 complex, Uniform dispersion of TiO_2 nanoparticles, Is a typical anatase structure, Grain size 16.89 nm. F-Atom Replacement of TiO_2 Surface-OH Chemical Adsorption on TiO_2 Surface, Promotes the production of Ti^{3+}. Oxygen vacancies generated by fluorine-modified TiO_2 form oxygen vacancy energy levels below the conduction band, Narrow the band gap to 2.75 eV, which promotes its absorption of visible light, And the introduction of fluoride ions reduces the recombination rate of TiO_2 photogenerated electron-hole pair. Compared with pure TiO_2, F-TiO_2 exhibits excellent photocatalytic performance under simulated sunlight.

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