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Preparation and Catalytic Performance of Fe3+ Doped Nano-materials

Jianhui Chen,Yuxiu Liu,Zhiqin Ye

School of Materials Science and Engineering, Liaocheng University of Technology, Shandong, China

ABSTRACT

Fe3+-doped nano-TiO2 powders were prepared by sol-gel method. The photocatalytic activity of Fe3+-doped TiO2 nanoparticles was studied by using UV lamp as light source and methylene blue as degradation target. The photocatalytic activity of Fe3+-doped TiO2 was studied by degradation of 4L methylene blue solution with initial concentration of 10mg · L - 1. The results show that the photocatalytic activity of TiO2 can be improved by the addition of Fe3+. When the molar ratio of Fe3+ is 0.5-1%, the calcination temperature is 500 °C. The photocatalytic degradation of methylene blue is the best.

KEYWORDS: Sol - gel method; Doped iron nanometer; TiO2 methylene blue

1. Introduction

With the development of global industrialization process, energy crisis and environmental pollution is becoming increasingly serious, industrial waste gas, waste water, agricultural pesticides and other pollutants surge, how to solve the energy and environmental problems has become a hot topic of social concern. Due to the excellent photocatalytic performance, the semiconductor photocatalyst has a wide development and application prospect in sewage treatment, air purification, cleaning and sterilization. TiO2 photocatalyst has become the most promising photocatalytic material because of its stable chemical properties, strong oxidation and reducibility, non-toxic and low cost. It can convert many organic or inorganic pollutants Degradation into H2O, CO2 and salts and other substances, to achieve harmless purification of the environment [1].

The photocatalytic properties of nano-TiO2 are used to degrade toxic and harmful substances in the environment in order to optimize the environment. It is an important aspect of nano-TiO2 application. TiO2 as a photodegradation catalyst has the following advantages [2]: (1) The use of natural light without additional energy, energy conservation, to avoid the energy regeneration process caused by environmental problems; (2) TiO2 nano-catalyst purification efficiency, wide range of applications, from water treatment to air purification, are very applicable; (3) TiO2 itself stable nature can be long-term use, the human body non-toxic harmless

With the development of photocatalytic materials and properties of TiO2, the preparation of photocatalytic materials and the research of photocatalytic environmental protection devices have been paid more and more attention [3].

1.1. What is a Nanomaterial?

Nanometer (nm) is the length of the unit, 1 nanometer is 10-9 meters (one billionth of a meter), the macro substance, the nano is a small unit, as the diameter of the hair is generally 7000- 8000nm, the diameter of human erythrocytes is generally 3000-5000nm, the general diameter of the virus is also tens to hundreds of nanometer size, the metal grain size is generally in the order of microns; for microscopic substances such as atoms, molecules and other previously used to show , 1 angstrom corresponds to the diameter of one hydrogen atom, 1 nanometer is 10 angstroms [2].

It is generally believed that nanomaterials should include two basic conditions: one is the characteristic size of the material between 1-100nm and the other is that the material has some special physical and chemical properties that distinguish the conventional size material at this time.

1.2. Application of TiO2 in Wastewater Treatment

1.2.1 Treatment of organic wastewater

Nano-powder technology is the hotspot of materials science research, and has been widely used in industrial production and daily life. At present, the semiconductor used for photocatalytic oxidation of organic semiconductors are mostly semiconducting semiconductor materials, such as TiO2, ZnO2, WO3, SnO2 and so on. Because TiO2 itself has high photocatalytic activity, high chemical stability, low cost, safe to use. As a new generation of environmental purification materials, it has been widely used. TiO2 photocatalyst can degrade water, most of the organic matter in the air, inorganic, and has the ability to antibacterial, deodorant and clean air [1].

1.2.1.1 Organophosphorus pesticide wastewater treatment

The results of the degradation of organic phosphorus showed that the photocatalytic oxidation of phosphorus in the suspension of TiO2 could be completely inorganic and could produce PO quantitatively. Similarly, sulfur-containing organic matter is photocatalytic oxidation of TiO2; a similar result can be obtained in which sulfur is oxidized to SO2 quantitatively. Chen Shifu's research on dichlorvos and monocrotophos pesticides showed that the photolysis rate of TiO2 glass fiber was more than 90% for 50 min.

1.2.1.2 Chlorinated organic wastewater treatment

Japan's Tokyo University Noguchi real use of nano-TiO2 photocatalyst and ozone combined treatment of waste water in the 3-chlorophenol, with 3-chlorophenol completely removed; with the surface coated nano-TiO2 photocatalyst ceramic tube treatment of trichlorethylene aqueous solution, Trichlorethylene is also completely decomposed soon. British London and Ontario Nuclear Technology Environment Company developed a new room temperature photocatalytic technology using artificial lighting and nano-TiO2 to completely decompose PCBs from industrial waste and contaminated groundwater into CO, HO and HCI [2].

1.2.1.3 Oily wastewater treatment

Oily wastewater containing aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, organic acids and phenols., It is difficult to degradation. Using nano-TiO2 photocatalytic oxidation technology, can quickly degrade these organic matter. The effects of sunlight and nano-TiO2 powder on the aqueous solution of phenol and aqueous sodium dodecylbenzene sulfonate were tested by the Chinese Academy of Sciences. The results showed that the concentration of phenol was 0.5mmoL / L in the cloudy and cloudy days Has been completely degraded, the concentration of 1moL / L of sodium dodecyl benzene sulfonate is also basically completed degradation, high clarity and no secondary pollution, Zhao Wenkuan et al. prepared a TiO2 powder carrying a floating type photocatalyst. In the ultraviolet light irradiation, can effectively degrade the surface of the oil pollutants and inhibit the crude oil in the natural oxidation process of the formation of harmful copolymer [2].

1.2.1.4 Wastewater treatment with surfactant

Household or industrial surfactants are one of the main sources of pollution of water, which is prone to odor and foam. Surfactants mainly contain sodium dodecyl sulfonate, which are difficult to naturally or biodegradably, have a long residence time, and sometimes produce toxic or insoluble intermediates. The use of nano-TiO2 photocatalytic decomposition of surfactants has made some progress. The mechanism, reaction kinetics and influencing factors of photocatalytic degradation of sodium dodecyl sulfonate by TiO2 were studied [1-2].

1.2.1.5 Wool dyeing and finishing wastewater treatment

The glass filler filled with nano-TiO2 film is filled in the glass reactor. The waste water is circulated in the reactor for photocatalytic oxidation. The organic matter in the wastewater can decompose into H2O and CO2 quickly, and the catalyst can be used continuously without separation Recovery, with high efficiency, energy saving, no secondary pollution and other characteristics, to facilitate industrial applications [2].

1.2.2 Treatment of inorganic wastewater

The inorganic pollutants in water are mainly heavy metal ions, such as Hg, Cr, Pb and so on. The photocatalytic degradation of nano-TiO2 can also solve the pollution problem of metal ions such as mercury, chromium and lead. Mercury is the main heavy metal pollutants in the water body, great harm to the human brain system. Chromium is a serious carcinogen, can cause local sarcoma, the incidence of cancer increased. Lead is easy to cause poisoning, may also lead to respiratory cancer. Hydrogenation of nano-TiO2 in the presence of citrate ions, Hg2+ from the oxygen solution was e-reduced to Hg deposition on the surface of TiO2, this method also applies to lead.

Dai et al. investigated the effect of ZnOgI 'io2 ultrafine powder on the reduction of hexavalent chromium in aqueous solution under different reaction conditions, and discussed the feasibility of this method. Skubal modified the surface of TiO2 with arginine, and then adsorption and reduction efficiency of the photocatalytic reduction rig was increased to 99.9%. Serpone et al. reported the process of reducing Au from Au (CN) 4-1 by TiO2 photocatalysis while oxidizing CN to NH3 and CO2, and pointed out that treatment of electroplating industrial wastewater can not only restore the precious metal in the bath, but also eliminate the cyanide pollution in the bath. It is a practical method to deal with it. It can be seen that the application of TiO2 photocatalyst in the treatment of inorganic wastewater has a good effect and great application potential.

1.3. The use of nano-TiO2 can prevent the production of sewage

Light nano – TiO2, at its interface, macroscopically exhibits hydrophilic and lipophilic amphiphilic. Nano-TiO2 will be applied to the production of chemical fiber, so that the surface of the fiber contains a certain amount of TiO2, chemical fiber also has an amphipathic performance. The use of the chemical fiber production of military, agricultural tents can play a role in self-cleaning. Such as the chemical fiber made of people clothes, curtains and other daily necessities, due to amphipathic, self-cleaning degree is very large, the clothes are not easy to dirty, even dirty clothes, wash with water can be easy to wash, without chemical detergent, both reduced waste water discharge and the formation of pollution, but also save the water, electricity, detergents, reduce the burden on people's lives, but also reduce the people's manual labor.

1.4. Application of nanometer TiO2 in tap water treatment

Many tap water is taken from the surface water, the conventional purification can remove suspended solids and other toxic substances, but for some easy to dissolve impurities and bacteria and other commonly used fungicides Ag, Cu can make cells lose their activity, but the bacteria were killed After the resulting endotoxin cannot be eliminated. Endotoxin is a deadly substance that can cause typhoid fever, cholera and other diseases, so that water quality standards are not high, affecting people's health.

University of Tokyo, Japan, Department of Engineering, Professor Teng Daozhao and other experiments have proved that Nano-titanium dioxide on Pseudomonas, Escherichia coli, Staphylococcus aureus and other strong kill ability. Therefore, nano-titanium dioxide will be a good treatment of water treatment. In 1998, Tongji University Li Tian and others using fixed titanium dioxide on the glass fiber network to form a catalytic film, the depth of purification of drinking water, the results show: the total amount of organic matter in tap water removal rate of 60%, 19 kinds of priority pollutants, Completely removed, the other 21 kinds of harmful organic matter has 10 kinds of concentrations below the detection limit. At the same time, the total number of bacteria is also significantly reduced, a comprehensive increase in water quality, to achieve direct and safe drinking requirements [4].

1.5. Crystal structure of TiO2 and its relationship with photocatalytic activity

TiO2 is an important N-type semiconductor, according to its crystal form, can be divided into plate titanium, rutile and Anatase three phase. Figure 1 for the Anatase TiO2 two crystal structure. Anatase and rutile crystals can be represented by interconnected TiO6 octahedrons (Figure 1), the difference between the octahedral distortion and the octahedral connection is usually considered Anatase is the highest activity of a crystal form, Followed by rutile type, while the plate titanium and amorphous TiO2 did not have obvious photocatalytic activity. However, it is simple to think that Anatase is more stringent than rutile activity, and their activity is affected by some factors in its crystallization process. The results showed that the activity of TiO2 was related to the preparation method and the calcination temperature. The rutile TiO2 exhibited high photocatalytic activity under certain conditions [2]. The photocatalytic activity of TiO2 was better than that of rutile TiO2.

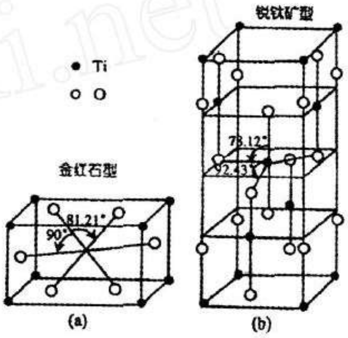

Fig.1 Two crystal structure of nano-TiO2 [2]

It can be seen that both Anatase and rutile TiO2, they may have a high activity, and the level of activity is mainly depends on the grain surface properties and size and other factors. Recent studies have shown that mixed crystals composed of Anatase and rutile in an appropriate proportion are generally higher than single crystal activity. The mixed crystals exhibit higher activity because the formation of thin rutile layers in the Anatase during the crystallization process can effectively improve the electron-hole separation efficiency (called the mixed crystal effect) in the Anatase crystal form through the rutile layer, 100% Anatase was not as high as 100% rutile activity, while that of the two mixtures showed higher activity than pure Anatase or rutile, especially 30% gold Redstone and 70% Anatase composed of the highest mixed crystal activity, we can see that the two crystal forms do have a certain synergistic effect [2].

2. Catalytic Principles of Fe3+ Doped TiO2

The photocatalytic technology utilizes the photocatalytic activity of the semiconductor material to excite the electrons and holes in the light to participate in the photochemical reaction to complete the degradation of the microbial organism of the organic gas. Anatase TiO2 semiconductor, for example, the band structure is filled with electronic low energy band (Valence BandVB) and empty high-energy conduction band (Conducti on Band, CB), between the price band and conduction band gap (Forbidden band, FB), conduction band and valence band gap between the 3.2eV, wavelength λ <385nm light can overcome the bandgap energy. As shown in Fig. 2, when the TiO2 semiconductor is irradiated with light at a wavelength of λ <385 nm, the electrons on the valence band are excited to transition to the conduction band, holes (h +) are generated on the valence band, and electrons are generated on the conduction band (E -), the photogenerated hole has a strong oxidizing property, can be adsorbed on the surface of the semiconductor particles of substances oxidized into high-priced substances, and electrons are reducible, can be absorbed on the semiconductor surface of the electronic receptor reduction. Photogenerated electrons and holes in addition to participate in the redox reaction, part of the composite directly in the semiconductor, and the release of energy, the size of the semiconductor photocatalytic activity and electron hole recombination probability is directly related. In general, the smaller the size of the semiconductor particles, the smaller the time of electrons and holes migrating to the surface, the smaller the probability of recombination. At the same time, the smaller the particle size, the larger the specific surface area, the more favorable the adsorption of the reactants. This is the use of nano-TiO2 material instead of bulk semiconductor materials for the reasons, the use of nano-particles as a catalyst for photocatalytic technology is often referred to as nano-photocatalytic technology.

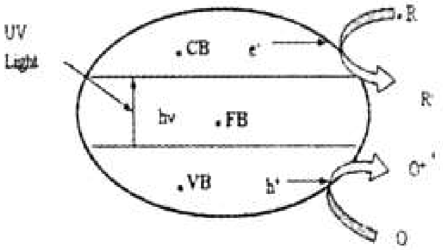

Figure 2 Schematic diagram of photocatalytic reaction

However, because TiO2 is a kind of wide band gap semiconductor, only the use of ultraviolet excitation, the utilization of sunlight is low, and the excited state of electrons and holes easy to complex, resulting in further reduction of photon quantum efficiency, seriously affected its application. The In order to promote the practical application of TiO2 photocatalytic materials, some means must be used to improve its catalytic activity.

Doping is one of the most commonly used methods to improve the catalytic performance of TiO2. Since the crystal is only perfect at an approximate absolute zero, so that each crystal has a different degree of lattice defects, when other substances into the crystal, the lattice defects may be replaced, the replacement of the defect can make electronic - cavities effectively separate and inhibit their recombination, resulting in improved catalyst performance. Fe3+ can be used as the acceptor of electrons. When the doping concentration is low, the capture electrons and holes cannot be effectively separated, and the number of capture centers for electrons or holes is not enough to improve the catalytic activity With the increase of the doping amount, the capture space also increases, the surface space charge layer becomes narrower, and the photo-generated electrons and holes can be effectively separated by the photoexcitation. The lifetime of the photogenerator is prolonged. When the doping concentration is high, the transition metal may become a composite center of holes and electrons, increasing the recombination probability of electrons and holes, resulting in an increase in the surface photogenerated recombination centers, thereby reducing the photocatalytic activity.

$TiO2 + hv \rightarrow h + + e-$ (1 - 1)

$O2 + e- \rightarrow O2-$ (1 - 2)

$H + + H2O \rightarrow H + + \cdot OH$ (1 - 3)

2e - + O2 + H + → OH (1 - 4)

O 2 + e - + 2H + → H2O2 (1 - 5)

The reason and method of preparing Fe3+ doped TiO2

However, because TiO2 is a kind of wide band gap semiconductor, only the use of ultraviolet excitation, the utilization of sunlight is low, and the excited state of electrons and holes easy to complex, resulting in further reduction of photon quantum efficiency, seriously affected its application. The In order to promote the practical application of TiO2 photocatalytic materials, some means must be used to improve its catalytic activity. Ion doping is undoubtedly an important means to improve its photocatalytic activity. The transition metal ions such as Fe3+, Cr6 +, V4 + and other research is more extensive. And there are many reports on the photocatalysis of Fe3+ doped in TiO2 phase. Therefore, Fe3+ ion doped TiO2 was used to improve the catalytic activity of TiO2.

At present, the preparation methods of TiO2 mainly include sol-gel method, coprecipitation, dipping method, ion implantation method and magnetron sputtering method. In this experiment, Fe3+ doped TiO2 powder was prepared by sol-gel method.

3. The purpose and content of this study

The purpose of this experiment is to prepare Fe3+ -doped TiO2 powder to explore the effect of different doping amount and different calcination time on the degradation rate of methylene blue on TiO2 powder. The optimum conditions for the preparation of TiO2 powder and the optimum conditions for degradation of methylene blue were studied.

The study includes the following aspects:

(1) Sol - gel synthesis of Fe3+-doped TiO2 photocatalyst

(2) Performance test of photocatalyst

4. Preparation of 4 Fe3+-doped TiO2 Photocatalyst

4.1. Experimental materials and methods

4.1.1 Experimental materials and instruments

Table 1 shows the main experimental equipment.

Table 1 Main experimental equipment

Instrument Name	Model	Manufacturer	Use
Constant temperature magnetic stirrer	85-2	Jintan medical equipment factory	Mixing
Electric thermostatic blast oven	101-3-s	Shanghai Yuejin Medical Equipment Factory	Dry and dry
Electronic balance			Weighing
EleBox-type resistance furnace		Shanghai Bairide Industrial Co., Ltd.	Roasting
K series temperature controller	Zhejiang Province 02810218	Yuyao Jin Point Instrument Co., Ltd.	Adjust the temperature
UV spectrophotometer			
UV Photocatalytic Reactor	KL-1	Wuhan Kelin Environmental Protection Technology Co., Ltd.	Photocatalytic Reactor
Centrifugal separator			Centrifugal separation

Table 2 shows the main reagents.

Table 2 Major reagents

Drug name	Chemical grade	Grade	Manufacturer
Anhydrous ethanol	CH3CH2OH	AR	Tianjin Tianchen Chemical Reagent Factory
Titanium tetrachlorate	Ti(OC4H9)4	BR	Tianjin Beilian Fine Chemicals Development Co., Ltd.
Iron nitrate	Fe(NO3).9H2O3	AR	Tianjin Beilian Fine Chemicals Development Co., Ltd
Nitrate	HNO3	AR	Tianjin North Union Fine Chemicals Development Co., Ltd
Glacial acetic acid	CH3COOH	AR	Tianjin Tianchen Chemical Reagent Factory
Methylene blue (MB)	C16H18ClN3S3H2O	AR	Tianjin Branch of the European chemical reagents development center

The preparation of different concentrations of Fe (NO3) 39H2O solution was prepared according to Table 3.

Table 3 Preparation of Fe (NO3) solution

Miscellaneous	0.5%	1%	5%	20%
Fe(NO3)39H2O(g)	0.4000	0.3000	15.6000	74.2000
Distilled water (ml)	100	100	100	100
Density (mg/L)	0.0080	0.0300	0.1560	0.7420

As long as the addition of 2ml of Table 3 of different Fe (NO3) 39H2O solution to get different Fe3+ doped TiO2 powder. The photocatalysts with different doping amounts and calcined at different temperatures are labeled as An (n is the mole percent of Fe3+ dopant, 0.5, 1, 5, 20) refers to the sample obtained by calcination, Bn, Cn, Dn, respectively, at 400,500 and 600 ℃ under the calcined sample.

4.1.2 Test methods

4.1.2.1 Synthesis of Fe3+ -doped TiO2 photocatalyst by sol-gel method [6]

Proceed as follows:

(1) 5 ml of tetrabutyl titanate was dissolved in 34 ml of absolute ethanol and stirred well.

(2) Adding 2 ml of glacial acetic acid to form a complex with Ti to inhibit the hydrolysis of tetrabutyl titanate.

(3) And then slowly add 2ml dissolved in a certain amount of iron nitrate deionized water, with 1ml / L nitric acid to adjust the pH value ≈ 2.0, stirring overnight can be Fe3+ doped TiO2 photocatalyst precursor.

(4) It was finally dried in an electric thermostatic blast oven at 70 ° C until it became a powder and calcined at a different temperature (300 ° C to 600 ° C) for 2 h with a box-type resistance furnace.

The following is a picture of the Cn roasting 500 ° C group:

Figure 3 Doping amount of 0.5% of the powder C1

Figure 4 doping content of 1% powder C2

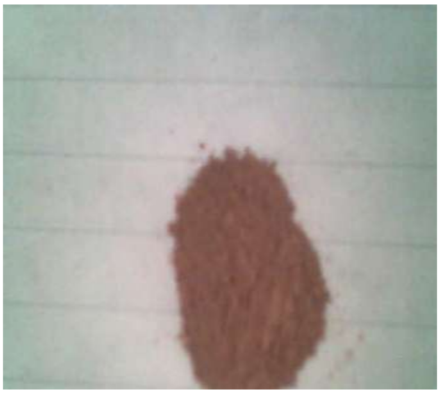

Figure 5 Doping amount of 5% powder C3

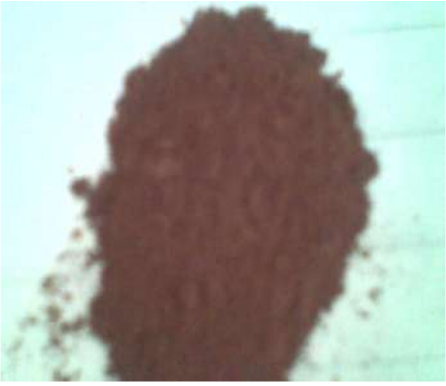

Figure 6 Doping amount of 20% powder C4

4.1.2.2 Performance test of photocatalyst

The photocatalytic activity of the catalyst is evaluated by photocatalytic degradation of methylene blue (MB), which is a kind of non-degradable colored compound. The azo and formula structure under acidic and alkaline conditions is the main structure of the dye compound. Therefore, it has a certain representation as a dye compound model. The photocatalytic activity of Fe3+ doped TiO2 powder was tested by KL-1 UV photocatalytic reactor with 10 mg / L MB solution as standard. The test procedure was as follows: 0.3 g of the catalyst powder was dispersed in an aqueous solution of 4 L MB (10 mg / l-1), and the solution was passed through a cylindrical photocatalytic reactor using a low pressure mercury lamp as a line light source. The reaction was allowed to proceed for 30 minutes and centrifuged at 15 min. The MB concentration in the middle of the night was measured at 690 nm using a UV-VIS spectrophotometer. The lighting time is 3 hours. Calculate the degradation rate (η%) with absorbance instead of concentration:

$$\eta\% = \frac{A_0 - A_t}{A_0} \times 100\% \qquad (2)$$

Where A0 is the initial absorbance value of the methylene blue solution; At is the absorbance value of the methylene blue solution after photocatalytic degradation.

Figure 7-1 KL-1 type UV photocatalytic reactor

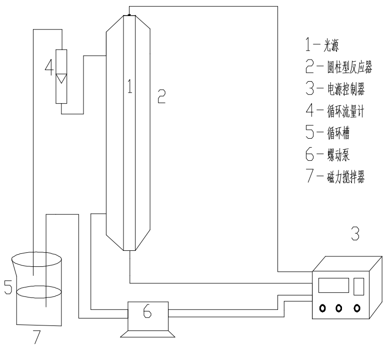

Figure 7-2 KL-1 type UV photocatalytic reactor diagram

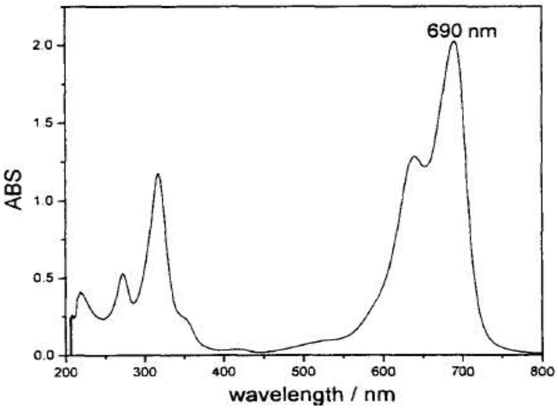

Figure 8 Ultraviolet-visible absorption spectra of methylene blue

5. Experimental results and discussion

5.1. Experimental results

5.1.1 XRD characterization analysis

The XD-3 X-ray diffractometer was used to analyze the crystal form of the powder by X-ray diffraction spectrometer. According to the half-width of the diffraction peak, the grain size was calculated by Scherrer equation (3).

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (3)$$

Fig. 9 shows the XRD patterns of Dn samples. It can be seen from the figure that the content of rutile increases with the increase of Fe3+ doping amount, which indicates that Fe3+ can promote the conversion of TiO2 from anatase phase to rutile phase. There is no obvious Fe2O3 crystal phase in the figure, and Fe2O3 may exist in small clusters. Or Fe3+ into the TiO2 lattice, the formation of Ti-O-Ti structure, from D0.5 to D20, A (101) surface diffraction angle gradually shifted to high angle, which is due to the formation of Ti-O-Ti structure of the lattice constant is less than the anatase caused by the lattice constant. The absorption intensity of Fe3+ modified TiO2 was higher than that of pure TiO2, and the pure TiO2 was only strongly absorbed in the ultraviolet region, and the spectrum of the Fe3+ modified TiO2 catalyst had a certain degree of red shift in the visible region. The results show that Fe3+ can improve the absorptive capacity of TiO2 on the visible light. Fe3+ modified anatase TiO2 crystal, the TiO2 valence band position to move up, while the conduction band position unchanged, the forbidden band becomes smaller, TiO2 forbidden band formed in the impurity level, so that the absorption wavelength range extended to the visible area [13]. With the increase of the amount of Fe(NO3)3, the amount of Fe3+ added to the surface of TiO2 was increased, and the absorption of visible light was enhanced by the catalyst [6].

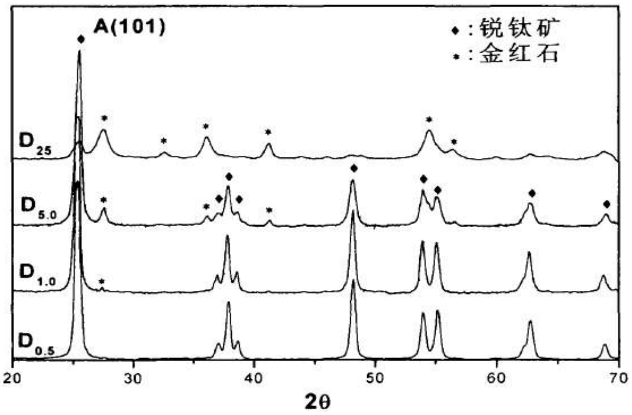

Figure 9 X-ray diffraction patterns of group D samples

Using the XRD pattern, four groups of different doping amounts of rutile content can be calculated according to the commonly used formula (4):

$$W_R = \frac{I_R}{0.886 I_A + I_R} \qquad (4)$$

The IA and IR are the diffraction intensities of the diffraction peaks of the (101) plane of the Anatase phase and the diffraction peaks of the (110) plane of the rutile. The rutile content and grain size of all samples are listed in Table 4. It can be seen from the data in the table that the amount of Fe3+ (0.5-5.0at%) doping can inhibit the growth of TiO2 grains, with the doping amount continues to increase, rutile content increased rapidly, and at the same temperature The growth rate of rutile is greater than that of Anatase. The temperature of the immersion of the pure TiO2 from the Anatase phase (A) to the rutile crystal phase (R) is generally 600-700 °C, while the transition temperature of the rutile in Fe3+ doped TiO2 is about 400 °C The Fe3+ doping reduces the transition temperature of TiO2 from A-R. There may be two reasons: on the one hand, the melting point of ferric nitrate is only 47 °C, 100 °C can begin to break down, molten iron salt can play similar to the alumina system observed in the role of liquid sintering additives, liquid phase sintering is favorable for the decrease of AR phase transition temperature. On the other hand, part of the decomposed Fe2O3 exists in the form of small clusters, which is distributed in TiO2 and is likely to be the center of R phase nucleation.

Table 4 Rutile content and grain size of different samples

Sample	IA	IR	Rutile content /%	Grain size /nm	
				dA	dR
A0.5	908.4	-	0	1.23	-
A1	808.4	-	0	1.22	-
A5	536.58	-	-	0.92	-
A20	234.3	-	-	0.86	-
B0.5	1196	-	0	1.48	-
B1	1249	-	0	1.50	-
B5	813.9	-	-	1.17	-
B20	270.9	91.0	0.27	1.03	0.61
C0.5	1639	-	0	2.01	-
C1	1806	-	0	2.47	-
C5	1023	69.23	7.10	1.23	0.58
C20	402.8	112.43	23.96	1.06	1.95
D0.5	2830	42.25	1.66	3.52	0.47
D1	3100	64.3	2.29	3.70	1.02
D5	2000	234.2	11.67	2.47	2.83
D20	226.3	361.2	64.30	1.51	3.44

5.1.2 Fe3+ doping amount on the catalytic activity of nano-TiO2

The catalytic activity of photodegradation of MB after calcination at different temperatures is shown in Fig. 10-13. It can be seen from the test results that the appropriate amount of Fe3+ (0.5-5.0at %) greatly improved the photocatalytic activity of TiO2, MB degradation rate increased from 68.124% to 95.008% but excessive Fe3+ but negative for photocatalytic reaction. Because Fe3+ over doping will make a large number of Fe2O3 clusters on the surface of TiO2, reducing the contact area of TiO2 with the degradation of the substrate, thereby reducing the activity of the catalyst [6].

Table 5 Degradation rates of TiO2 at different roasting temperatures with different doping values η%

Component	light time / min							
	15	30	45	60	75	90	105	120
A1	13.078	18.309	29.547	40.527	55.318	63.187	63.876	68.124
A2	11.309	18.902	31.257	48.314	59.867	66.758	70.248	71.025
A3	9.098	12.307	32.047	41.067	54.78	69.317	71.254	72.314
A4	8.965	11.305	23.619	40.357	52.39	58.342	60.327	61.058
B1	10.547	17.354	26.958	48.389	61.524	68.024	74.03	76.024
B2	14.503	20.354	35.68	54.025	74.324	80.657	84.125	85.694
B3	15.367	25.068	41.302	61.038	80.124	82.036	84.219	85.312
B4	8.157	15.034	24.961	44.324	56.368	61.328	63.589	69.315
C1	15.361	34.258	58.764	70.124	80.367	82.567	83.104	83.547
C2	19.023	40.124	70.214	84.025	92.316	92.415	92.963	93.064
C3	20.461	47.314	76.325	90.001	94.123	94.861	95.036	95.008
C4	9.258	14.201	26.058	45.012	57.146	60.159	63.14	67.124
D1	16.06	22.397	33.257	55.681	68.741	79.04	83.047	86.015
D2	14.367	20.751	30.569	52.605	65.3	74.398	83.128	85.347
D3	12.036	18.069	30.285	51.304	60.247	67.524	73.025	75.21
D4	10.067	14.364	20.478	30.154	48.387	64.014	68.159	73.058

6. Conclusions

The photocatalyst precursor was prepared by sol - gel method using tetrabutyl titanate and Fe (NO3) 3 · 9H2O as raw materials. Fe-doped nano-TiO2 with different disperse particle size and anatase phase was prepared at different doping amount and different calcination temperature. The composite doping of Fe3+ reduced the transition temperature of anatase crystal to rutile phase. The photocatalytic performance of nano - TiO2 with Fe3+-doped calcination temperature of 500 ℃ has excellent photocatalytic performance. Under the acidic condition, the degradation rate of the degradation of methine blue by Fe3+ -doped nano-TiO2 was close to 92% after 120 min irradiation with low pressure mercury lamp.

Main Problems and Application Prospects of 7 Nanometer Materials

TiO2 photocatalytic oxidation is a promising water treatment technology, has been a large number of studies have shown that it has low energy consumption, easy operation, no secondary pollution and other advantages, and the ozone is difficult to oxidize some organic matter such as trichloride Methane, carbon tetrachloride, hexachlorobenzene and hexachlorobenzene can effectively degrade and become a frontier and research hotspot in environmental management, but it is still in the experimental research stage and has not yet matured in the actual wastewater treatment project Available processes. In this paper, the modification method of TiO2 photocatalyst is discussed. With the rapid development of TiO2 photocatalytic oxidation method, the catalyst is prepared by high efficiency and the proper carrier is used to realize solidification and practical photocatalytic reactor. In the industrial, agricultural, environmental protection and other fields play an increasingly important role [15].

The current use of TiO2 catalyst because of its bandgap width of 3.2 eV, can only use the wavelength of less than 388 × 10-9 range of ultraviolet light, so the absorption spectrum of solar spectrum accounted for a small part of the solar energy cannot take full advantage of only Artificial energy mercury lamp and UV lamp, so not only energy consumption, but also limits the further development of photocatalytic technology and practical application. In foreign countries, has developed a GPG method, it can well absorb the sun spectrum, is an economical and effective way to degrade organic pollutants in sewage. In addition, the photon flux of TiO2 also needs to be improved [16].

In the aspect of nano functional and structural materials, high-tech new products such as abnormal optical properties, electrical properties, magnetic properties, mechanical properties, sensitive properties, catalysis and chemical properties of nanomaterials, and the modification of traditional materials Focusing on breakthroughs in various types of nano-functional and structural materials, the industrialization of key technologies, detection technology and characterization technology. Multi-functional nano-composite materials, high-performance nano-carbide for chemical, and building materials, light industry, metallurgical and other industries by leaps and bounds to provide a wide range of opportunities. It is expected that during the 15th period, the industrialization of various kinds of nanomaterials may form a large number of large enterprises or enterprise groups, which will have an important impact on the national economy. The application of nanotechnology will gradually penetrate into all areas involving the people's livelihood and will generate new economic growth [22].

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