Preparation of Photocatalyst, Reaction Mechanism and Its Application in Environmental Control

Ruiting Zhou

College of Chemical Engineering, Qinghai University, Xining, Qinghai Province, China 810016

19892931230@163.com

Abstract. At present, due to the overuse of resources in the process of human development and the neglect of the concept of green development, environmental pollution has become increasingly serious, which has become a major problem to be solved all over the world. Common environmental pollution, such as wastewater pollution, air pollution and bacterial pollution, pose a great threat to the ecological environment and human health. As a material emerged in the 1930 s, photocatalyst has been proved to be able to effectively degrade a variety of inorganic and organic pollutants, and most of the reactions are green and environmentally friendly. It will not produce more pollutants, can effectively alleviate the environmental crisis, and is widely used in antibacterial, resource development and other fields. This paper mainly introduces the preparation methods of three common photocatalysts, the mechanism of TiO2 photocatalyst, and the application of photocatalyst in environmental governance.

Keywords: Photocatalyst, environmental pollution, environmental protection.

1. Introduction

As an important material that can improve the rate of chemical reaction, catalyst is widely used in various chemical reactions. As an important component, photocatalyst is often used to decompose organic compounds, some inorganic compounds, bacteria and viruses. Photocatalyst is a kind of material that can promote the chemical reaction process under the irradiation of light, and does not change itself before and after the reaction. The most basic conditions as a photocatalyst are small size, large specific surface area and good photocatalytic activity [1]. At present, N-type semiconductor materials are widely used in the field of photocatalysis, such as ZrO_2, ZnO, CdS, WO_3, Fe_2O_3, PbS, SnO_2, $SrTiO_2$, SiO_2, etc [2]. TiO_2 is favored by researchers because of its high activity, good heat resistance, good ductility, low cost, and harmless to human body. It has become the most widely used photocatalyst semiconductor material. Tracing back to the development history of photocatalyst, as early as the 1930s, scientists had discovered the photocatalyst material based on ZnO. Up to now, photocatalyst has been developed for nearly a hundred years. Experiments have proved that photocatalyst has a good development prospect in environmental treatment, such as wastewater purification and air treatment. In the process of human's constant pursuit of survival and development, the environmental pollution and destruction caused by human activities are becoming more and more serious. The entire ecological environment is now facing various problems such as ecological degradation and resource depletion. In this context, exploring the field of photocatalysts, constantly developing more excellent photocatalysts, and applying more efficient photocatalysts to environmental governance have been a hot topic for researchers.

In this paper we will introduce the preparation process of three common types of photocatalysts, namely, nano metal oxides and nano metal sulfides represented by TiO_2, surface coupled nano semiconductor photocatalysts represented by CdS-ZnO, and Nanophotocatalysts supported on precise metals, graphene and carbon nanotubes, aiming to provide reference for researchers to study the preparation methods of different photocatalysts. The basic mechanism of photocatalyst action is also introduced with TiO_2 as the matrix. Finally, three kinds of applications for photocatalyst in environmental treatment are smmarized including wastewater treatment, air treatment and antibacterial application. The review is to enable scientific researchers to provide ideas for solving pollution problems by using more appropriate photocatalysts according to different environmental problems.

2. Main types of photocatalysts and their preparation methods

2.1. Nanometer metal oxides and nano metal sulfides

TiO_2 is a kind of photocatalyst with the highest research value because of its good heat resistance, high catalytic activity, good ductility and harmless to human body [3]. There are also many composite photocatalysts with better performance developed based on this material. The photocatalysis of nano TiO_2 has been widely used in wastewater treatment, harmful gas purification, sterilization and disinfection of building coatings, etc [4].

There are many methods for preparation of it. Generally, it can be divided into gas phase and liquid phase method.title.

2.1.1. Gas phase method

The primary processes of preparing nano TiO_2 by gas phase method includes gas phase chemical reaction, surface reaction, homogeneous nucleation, multiphase compression, condensation, and coalescence or melting [2].

The main methods for preparing nano TiO_2 by chemical vapor phase method are $TiCl_4$ gas phase hydrogen flame hydrolysis, $TiCl_4$ gas phase oxidation, titanium alkoxide gas phase hydrolysis and laser method.

(1) $TiCl_4$ gas phase hydrogen flame hydrolysis

Take $TiCl_4$ as raw material, introduce $TiCl_4$ gas into a high-temperature hydrogen oxygen flame (about 800°C) for high-temperature hydrolysis to prepare nano TiO_2. The chemical equation is $TiCl_4(g)+2H_2+O_2 \rightarrow TiO_2+4HCl$

(2) $TiCl_4$ gas phase oxidation method

With $TiCl_4$ as the raw material, oxygen as the oxygen source, and nitrogen as the carrier gas, a homogeneous chemical reaction takes place between $TiCl_4$ and O_2 under high temperature (about 1200°C) to generate a precursor of titanium dioxide and grow into titanium dioxide particles through nucleation. The chemical equation is $TiCl_4(g)+O_2(g) \rightarrow TiO_2+2Cl_2$ $nTiO_2(g) \rightarrow (TiO_2)_n(s)$

(3) Titanium alkoxide vapor phase hydrolysis

With high-purity nitrogen as carrier gas, titanium alkoxide steam and water steam are introduced into the reaction zone of the reactor respectively. $Ti(OR)_4$ aerosol particles were formed by spray and nitrogen chilling of titanium alkoxide vapor, and then rapidly hydrolyzed with water vapor to form titanium dioxide ultrafine particles [2].

The chemical equation is $Ti(OR)_4+2H_2O \rightarrow TiO_2+4ROH$

(4) Laser method

The reaction is induced by the pulse laser entering the reaction chamber. The laser sources for preparing nano powder include continuous laser and pulse laser [2].

2.1.2 Liquid phase method

Nano-TiO_2 prepared by liquid phase method can be divided into colloidal method, sol-gel method and chemical coprecipitation method. Among them, the Sol-Gel method is the most utilized technique.

Sol-Gel method is a wide range of material preparation methods, which is applicable to materials from zero dimension to three-dimensional. It uses wet chemical methods to prepare materials. In this method, some precursors such as metal salts and some catalysts are mixed uniformly under liquid conditions, and a stable sol system is formed through some hydrolysis and polymerization reactions; After the sol is aged, the further slow polymerization between the colloids will form a three-dimensional network of polymer morphology with the precursor as the skeleton. The solvent that has not evaporated fills the network structure to form a wet gel system; The solvent in the structure is removed from the wet gel through drying process to form a porous dry gel system; Finally, the required materials are prepared through the heat treatment process.

In the process of preparing TiO_2, we use titanium alkoxide $Ti(OR)_4$ as the raw material and anhydrous alcohol as the organic solvent. In order to prevent the strong hydrolysis of $Ti(OR)_4$, a certain amount of anhydrous alcohol is mixed with $Ti(OR)_4$ and then the mixed solution of alcohol, water and acid is dripped into the solution in order to fully mix. After about a week of gelation, dry for several hours at 50~60°C to obtain dry gel powder with relatively dispersed shape. After that, TiO_2 particles with different morphologies were obtained by heat treatment at different temperatures [2].

The chemical equation is $Ti(OR)_4+4H_2O \rightarrow Ti(OH)_4+4ROH$ $Ti(OH)_4+Ti(OR)_4 \rightarrow 2TiO_2 +4ROH$ $2Ti(OH)_4 \rightarrow 2TiO_2+4H_2O$

2.2. Surface coupled nano semiconductor photocatalyst

The surface coupled nano semiconductor photocatalyst improves the reaction activity of the photocatalyst by loading heavy metals on the semiconductor surface, such as CdS-ZnO, SnO-TiO_2, and CdS -SnO [4].

Wang et al. Prepared CdS-ZnO composite photocatalyst by ultrasonic sol gel deposition precipitation method. Under ultrasonic conditions, Zn $(OH)_2$ sol was prepared by sol gel method, and then CdS was deposited on it to obtain CdS-$Zn(OH)_2$ catalyst precursor. The precursor was calcined under air and nitrogen respectively to obtain CdS-ZnO composite photocatalyst. The characterization of the catalyst and the experimental results of hydrogen production from water decomposition show that both CdS/ZnO composite photocatalysts have strong absorption in the visible light region [5]. The nano-sized TiO_2 Prepared by G.L. Li [6] et al. Reacted with $TiCl_4$ solution and ammonia solution in an inverse microemulsion system to obtain a variety of amorphous products. When heated at 250°C to 750°C, the crystal type changes to anatase; When heated above 750°C, the crystal type changes to rutile type.

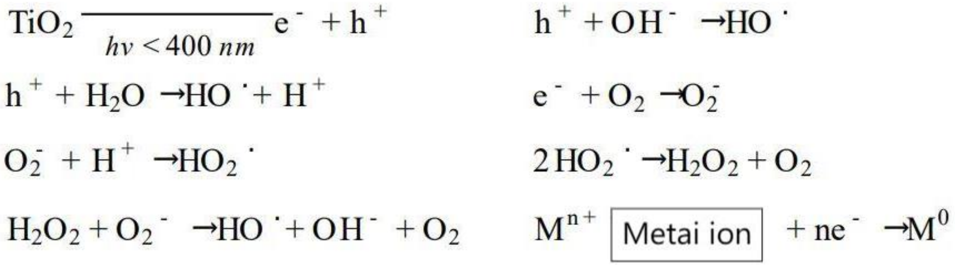
2.3. Nanophotocatalysts supported on precious metals, graphene and carbon nanotubes

It is a common method to improve the photocatalytic performance of TiO_2 by introducing precious metals onto the surface of TiO_2 by reduction, and TiO_2 has photocatalytic activity under visible light. At present, the reported precious metals mainly include Ru, Pd and Rh.

The common impregnation reduction method [7] and photo reduction method can be used to load precious metals. Zhang et al. [8] studied the effects of three loading methods on TiO_2 photocatalytic hydrolysis of acetylene: (1) H_2PtCl_6 aqueous solution impregnation method; (2) Pt $(NH_3)_4Cl_2$ aqueous solution immersion method; (3) Platinum black mixing method. The results showed that the photocatalytic activity of the photocatalysts prepared by three different loading methods was different in the photocatalytic reaction of acetylene hydrolysis.

3. Photocatalytic mechanism (TiO_2)

The essence of photocatalytic reaction is redox reaction. The N-type semiconductor material photocatalyst represented by titanium dioxide participates in redox reaction by using electrons (e^-) and holes (h^+) generated by semiconductor under the condition of light. The energy band of titanium dioxide is composed of a valence band full of electrons and an empty conduction band. The band gap is located between the valence band and the conduction band. The light shines on the surface of titanium dioxide, where the light radiation energy greater than or equal to the TiO_2 absorption threshold excites titanium dioxide to the active state. The absorbed energy of electrons on the valence band becomes excited state and moves to the high energy conduction band. Holes are formed on the valence band and electron hole pairs are formed on the surface of titanium dioxide- Unconsolidated holes migrate under the action of electric field force and move to the surface of titanium dioxide. Such holes have high electrode potential and can oxidize the substances adsorbed on the surface of titanium dioxide. The active electrons migrated to the surface of titanium dioxide have strong reducibility, which can reduce the substances adsorbed on the surface of titanium dioxide. Generally, the general formula of photocatalytic reaction is to use semiconductor as the photocatalyst and light as the source of energy to degrade organic matters into carbon dioxide and water [2]. In order to improve the performance of titanium dioxide photocatalyst, some strategies have been employed to inhibit the recombination of electrons and holes, so that more uncompleted electrons and holes can participate in the redox reaction and improve the efficiency of redox reaction.



$$TiO_2 \xrightarrow[hv < 400\,nm]{} e^- + h^+ \qquad h^+ + OH^- \rightarrow HO^\cdot$$

$$h^+ + H_2O \rightarrow HO^\cdot + H^+ \qquad e^- + O_2 \rightarrow O_2^-$$

$$O_2^- + H^+ \rightarrow HO_2^\cdot \qquad 2HO_2^\cdot \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + O_2^- \rightarrow HO^\cdot + OH^- + O_2 \qquad M^{n+}\ \boxed{\text{Metai ion}} + ne^- \rightarrow M^0$$

Figure 1. Photocatalytic reaction process of nano TiO_2 [2]

4. Applications

4.1. Wastewater treatment

At present, the situation of water pollution is becoming more and more serious, and the prevention and control of water pollution is extremely urgent. At present, the application of photocatalyst in wastewater treatment is a measure taken by many countries for water pollution. Semiconductor photocatalyst nano-TiO_2 is the most widely used one among them. Nano-TiO_2 produces electrons with strong oxidizing ability and holes with strong reducing ability under light irradiation, which can degrade most toxic inorganic and organic substances, and the CO_2 and H_2O produced by the reaction and some simple inorganic substances are non-toxic and have no damage to the environment [4].

4.1.1. Inorganic wastewater

Inorganic pollution ions in inorganic wastewater can be divided into heavy metal ions and some inorganic anions. The treatment of wastewater containing inorganic anions is relatively simple. For example, photocatalysts such as TiO_2, ZnO, Fe_2O_3, and CdS can catalyze the oxidation of highly toxic CN^- to OCN^- under oxygen environment, and OCN^- can be further decomposed into non-toxic CO_2, N_2, and NO^{3-} [9]. Hidaka et al. [10] studied the photocatalytic reaction of potassium cyanide solution and cyanide containing wastewater to generate CO_2 and N_2 through the intermediate OCN^- under the catalysis of TiO_2 photocatalyst, and proposed the idea of treating large-scale cyanide containing industrial wastewater by photocatalytic oxidation. If the wastewater contains heavy metal ions, such as Hg, Cr, Pb plasma, then CN^- is not easy to be oxidized. The treatment of cyanide containing wastewater in metallurgy, electroplating and other industries is facing the same situation. The most common carcinogenic $Cr_2O_7^{2-}$ ion can be reduced to Cr^{3+} by TiO_2, Fe_2O_3, $SrTiO_3$ and other photocatalysts, and then Cr^{3+} is removed by $Cr(OH)_3$ precipitation. The addition of hole trapping agent can improve the photoreduction rate of hexavalent chromium. Toxic $HgCl_2$ and CH_3HgCl can also be reduced to elemental mercury by TiO_2 photocatalysis, but other sacrificial electron donors such as methanol must be added in the latter process. Zhou et al. [11] added 0.7g SiO_2-TiO_2 glass as photocatalyst in the wastewater with a Cr^{6+}concentration of 80 mg/L and a volume of 100 mL, and reacted for 3h in the light system. The removal rate of Cr^{6+} reached 99%. Serpone et al. [12] studied the process of treating $HgCl_2$ and methyl $HgCl_2$ with TiO_2 as photocatalyst under simulated sunlight, and obtained good experimental results.

4.1.2. Organic wastewater

Organic wastewater mainly includes pharmaceutical, printing and dyeing, agriculture, oil refining and other fields. First of all, in pharmaceutical industry, pharmaceutical wastewater has complex components, contains a variety of organic substances, high chemicaloxygendemand value and Biochemical oxygen demand value, and contains a lot of difficult to degrade substances. It belongs to a class of organic wastewater that is relatively difficult to degrade, and it is difficult to effectively and completely remove it by common physical and chemical methods. Photocatalyst degradation will not generate substances harmful to the environment. Gong [12] and co-authors modified cerium doped nano titanium dioxide with rhodamine B, rhodamine 6G, methylene blue, bromocresol green as photosensitizers, and used fluorescent lamps to catalyze the degradation of organic chlorine pesticides such as hexachlorocyclohexane, Di6-hydroxynaphthalene disulfide and 1, 1-bis(p-chlorophenyl)-2, 2-dichloroethylene. The results showed that cerium doped nano titanium dioxide modified with rhodamine B or bromocresol green had a high photocatalytic degradation rate. Guo et al. [13] used TiO_2 as the photocatalyst to photocatalytic degradation of ceftriaxone sodium. The results showed that when the initial concentration of reactants was 500mg/L, the degradation of ceftriaxone sodium reached 93.4% at the catalyst dosage of 2.5g/L after 5 hours of reaction.

Secondly, in terms of printing and dyeing, with the improvement of people's living needs, various dye industries have emerged at the historic moment. Common treatment methods for dye wastewater include physical, chemical, electrochemical and biochemical methods. Among them, TiO_2 photocatalytic oxidation is an ideal treatment method, which can completely degrade organic substances in wastewater into small inorganic molecules such as CO_2 and H_2O. Printing and dyeing wastewater has the characteristics of high concentration, high chroma etc, and most of them contain carcinogens such as benzene ring and amino group. Sahoo et al. [14] took the commercially available particle size of about 1μM anatase TiO_2 and Ag^+-TiO_2 are used as catalysts for photocatalytic degradation of azo dye methyl red. When ultraviolet light is irradiated for 45 min, TiO_2 can degrade methyl red solution with a concentration of 2 times 10^{-6} by 85%, while Ag^+-TiO_2 can degrade it by 99%. In addition, Ag^+-TiO_2 can degrade 90% of methyl red dye under the condition of simulating solar light source after 10 hours of illumination, and 83% of the dye has been mineralized after 60 minutes of illumination. Wang et al. [15] prepared doped modified TiO_2 photocatalyst by sol-gel method, and investigated its catalytic degradation performance for scarlet dye. The effects of N, Fe, Pb doping elements on the catalytic activity were studied respectively, and then the single element doped, double element doped and three element doped TiO_2 catalysts with the best catalytic activity were prepared. It was found that the co doping of N, Fe and Pb had a synergistic effect on TiO_2 catalyst, and its absorption of visible light was stronger. The degradation rate of bright red dye under visible light could reach 99%.

Finally, in the agricultural field, nearly 1% of pesticide wastewater is discharged every year in China is 1 times 108m^3, dilution biochemical treatment method is often used to treat organic pesticide wastewater in China. However, due to the complex composition of pesticide wastewater, it is difficult to meet the national discharge standard after treatment. Yuan et al. [16] prepared TiO_2 film by magnetron reactive sputtering to study its photocatalytic degradation effect on organic phosphorus pesticide wastewater-DDVP. The results showed that nano TiO_2 was loaded on stainless steel prepared by magnetron sputtering. The film has high photocatalytic activity. The photocatalytic degradation rate of 40cm^2 nano TiO_2/stainless steel foil for 400ml initial concentration 4.52 times 10^{-4}mol/l DDVP 3 h is 81.2%, which is the best. Photocatalytic degradation rate of 20-100W irradiation power is basically linear with light irradiation intensity. The higher the initial concentration of DDVP, the lower the degradation rate. Dong [17] used a self-made photocatalytic reactor coated with TiO_2/GeO_2 composite film on the zinc sheet to photocatalytic oxidize pesticide wastewater. After the photocatalytic degradation treatment of the reactor, the COD degradation rate of pesticide wastewater can reach more than 85%, the COD value can be reduced to 57mg/L, the degradation rate of ammonia nitrogen compounds and total phosphorus can reach 96.2%, the color degradation rate can reach more than 86%, and the wastewater can meet the national first-class discharge standard.

4.2. Air treatment

With the rapid development of industry, air pollution is becoming more and more serious. Carbon monoxide, ammonia, nitrogen oxides, sulfur oxides and other pollutants are harmful to human health, and the purification of harmful gases has received increasing attention. Harmful gases can be simply divided into two categories, indoor gases and atmospheric gases. Indoor harmful gases mainly include formaldehyde, ammonia, hydrogen sulfide, etc. The harmful gases in the atmosphere mainly come from the exhaust gas from cars and sulfide and other gases from factory production. The use of photocatalysis technology can remove sulfide, nitride and other harmful gases at normal temperatures. Nano-TiO_2 photocatalyst is widely used in air treatment. Nitride is the most common harmful substance in the air. It can cause photochemical smog, acid rain and other phenomena, which are serious hazards to human beings. Zhang et al [18]. carried out many experiments and drew conclusions in order to explore the best conditions for photodegradation reaction and enable TiO_2 photocatalyst to photocatalytic degrade NO in a large area flow system. Hak - Hyoung Lin et al. [19] studied the photocatalytic reduction of NO and explored the influencing factors. When they improved the two-dimensional fluidized bed photo reactor, they finally found that the surface gas velocity, CuO load and reaction temperature would affect it. Noguchi et al. [20] used TiO_2 film for photocatalytic degradation of acetaldehyde gas. The study found that when the concentration of acetaldehyde gas is low, TiO_2 film has strong adsorption capacity for it, and acetaldehyde can be completely oxidized to carbon dioxide and water under ultraviolet light. Zhong et al. [21] used the composite photocatalyst material TiO_2/Sr_2CeO_4 to catalyze the oxidation of gaseous benzene. The experiment shows that the catalytic material fits into the first-order kinetic reaction model in the whole degradation reaction.

4.3. Antibacterial

Antibacterial means that photocatalysts inhibit or kill microorganisms in the environment under light conditions. There are various harmful microorganisms in the environment, such as bacteria, which induce human to suffer from infectious diseases and are extremely harmful to human health. Many articles have introduced examples of TiO_2 photocatalytic oxidation technology to remove bacteria and viruses. TiO_2 can be smeared on glass, and after 3h of light, it can kill Escherichia coli. After 4h of light, the toxin content can be controlled within 5% [4]. At present, there are many antibacterial products produced by photocatalysis technology, such as antibacterial fibers and antibacterial tiles. In addition, TiO_2 photocatalyst has more excellent performance, more thorough bactericidal effect and longer bactericidal time than other bactericides.

5. Conclusion and Outlook

This article reviews the preparation methods of three main types of photocatalysts, the reaction mechanism of TiO_2 photocatalyst, and the application of photocatalyst in sewage treatment, air treatment, and antibacterial sterilization.

Photocatalyst has the advantages of excellent performance, environmental protection, mild reaction, strong plasticity, etc. It is an indispensable and important partner in human production and life. Photocatalyst has broad development prospects and high research value in the fields of air purification, self purification, medical and health, agriculture, deodorization and deodorization, water purification, etc. At present, the development of photocatalyst is flourishing.

Although it has been studied for nearly a hundred years, the research on it is still not perfect. Some traditional photocatalysts still have problems such as insufficient reaction and high energy consumption. Take the most common TiO_2 as an example. Because TiO_2 has a wide band gap, its absorption range of light is limited to the ultraviolet region, and it cannot make full use of solar energy, resulting in slow transfer of photogenerated electrons and holes generated by TiO_2, high recombination probability, and serious impact on the photocatalytic efficiency. At present, the most common solution is to modify TiO_2 by doping. However, doping TiO_2 is easy to cause TiO_2 lattice defects, lead to changes in cell constants, and make the catalyst lose stability. Taking N doping as an example, different preparation methods will result in different states of N in TiO_2 lattice and different product activities. How to explore the preparation method with higher performance, low cost and good stability has become an important research content [22]. In addition, the quantum efficiency of photocatalysis is low, and it is difficult to play a key role in the treatment of wastewater with large capacity and high concentration. The separation and recovery of photocatalyst and the design of photocatalyst reactor need to be solved urgently. How to develop a better photocatalyst and how to build a more stable and efficient photocatalyst reaction system need to be actively explored and discovered by researchers.

References

[1] Ollis DF and Al-Ekabi H 1993 Photocatalytic Purification and Treatment of Water and Air (Elsevier Science Publishers B V).

[2] Zhang Mei, Yang Xujie, Lu Lude and Wang Xin 2000 Nano TiO2-- A photocatalyst with excellent performance (New Chemical Materials).

[3] Zhang, J. L, Ayusawa T, et al. 2001 Investigations of TiO2 photo-catalysts or the decomposition of NO in the flow system: the role of pretreatment and reaction conditions in the pho-tocatalytic efficiency (Journal of Catalysts) p198(1): 1-8.

[4] Lu Qiuhang, Ren Kaibin, Jiang Hao, Ma Xiaochen, Ren Yuanwen, Xia Zelin, and Liu Shimin. 2020 Research progress in the types, preparation and application of photocatalysts (China Ceramic Industry) pp9-23.

[5] Wang Yanhua, Bai Xuefeng and Zhang Lingling 2009 Preparation, characterization and Hydrogen production from water decomposition of JCdS/ZnO composite semiconductor photocatalyst (Chemistry and Adhesion) p 4-6.

[6] GL Li and G H Wang 1999 Synthesis of nanometer-sized TiO2 parti-cles by a microemulsion method (Nanostructure Materials) pp 663-668.

[7] Yang Jianjun, Li Dongxu and Li Qinglin 2001 Reaction mechanism of formaldehyde photocatalytic oxidation (Journal of Physical Chemistry) p 278-281.

[8] Zhang Jinlong and An Baozhengyi Studies on the Photocatalytic Hydrolysis of Propyne over Precious Metal Supported Photocatalysts (Journal of Chemistry of Colleges and Universities) p 733.

[9] Yan Youjun 2012 Nano-TiO2 Application of photocatalyst in wastewater treatment (Guangdong Chemical Industry).

[10] Hidaka H 1992 Heterogeneous photocatalytic degradation of cyanide on TiO2 surfaces (J Photochem Photobiol A) pp 367-374.

[11] Zhou Linbo and Wang Jian. 2003 Study on Photocatalytic Degradation of Chromium Containing Wastewater by SiO2-TiO2 Glass (Northern China Environment) p 46-50.

[12] Xiong Rongchun, Dong Xueling and Wei Gang 2001 Synthesis of green biopolymer polyaspartic acid and its scale inhibition performance (Industrial Water Treatment) p17-20.

[13] Hunier R J, Neagoe C N and Jarvelainen H A 2003 Alcohol affects the skeletal muscle proteins, titin and nebulin in male and female rats (The Journal of Nutrition) p 1154-1157.

[14] C. Sahoo, A.K. Gupta, Anjali Pal 2005 Photocatalytic degradation of Methyl Red dye in aqueous solutions under UV irradiation using Ag+ doped TiO2 (Desalination) p 91-100.

[15] Wang Jiusi, Guo Lixin, Wen Zhuoqiong and He Zhaozhao 2010 Preparation of Pb, N and Fe co doped photocatalyst and its application in the treatment of scarlet dye wastewater (New Chemical Materials) p 94-96.

[16] Yuan Shengli, Zhang Zongquan 2005 Loaded TiO2 Study on the degradation of organic phosphorus pesticide wastewater by photocatalyst (Natural Science Edition) p122-125.

[17] Dong Junming 2007 Study on degradation of pesticide wastewater by photocatalytic oxidation of TiO2/ GeO2 composite membrane (ring Journal of Environmental Engineering) p 76-79.

[18] Zhang, Jinlong and Terukazu Ayusawa 2001 Investigations of TiO2 photocatalysts for the decomposition of NO in the flow system: the role of pretreatment and reaction conditions in the photocatalytic efficiency (Journal of Catalysts) p 1-8.

[19] Tak -Hyoung lim and Sang Mun Jeong 2000 Degradation Characteristics of NO by Photocatalysis with TiO2 and CuO /TiO2 (React. Kinet. Catal. Lett) p 223-229.

[20] Noguchi T, Fujishima A and Sawunyama P 1998 Photocatalytic degradation of gaseous formaldehyde using TiO2 film (Environmental science & technology) p 3831-3833.

[21] Zhong J, Wang J and Tao L 2007 Photocatalytic degradation of gaseous benzene over TiO2/Sr2CeO4: kinetic model and degradation mechanisms (Journal of hazardous materials) p 323-331.

[22] Problems to be solved in photocatalysis PAhotocatalysis and its basis and application 2016.