Review of the Application of TiO₂ in the Field of Photoelectric Catalysis

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Abstract. Industrial wastewater contains many substances harmful to the human body. Many traditional treatment technologies have poor treatment effects and are difficult to meet standards. TiO₂ photocatalytic technology has the advantages of strong oxidizing ability, no selectivity and no secondary pollution. It is widely used in the treatment of high concentration, refractory and toxic and harmful organic wastewater, and has achieved remarkable results. Based on photoelectrocatalytic technology, this paper outlines the development mechanism of photoelectrocatalytic oxidation technology and photocatalytic technology, summarizes the development and application of new photoelectrocatalytic materials in recent years, and forecasts the development prospect of photoelectrocatalytic water treatment technology.

1. Introduction

With the development of modern industry, the impact of organic wastewater on the environment is becoming more and more serious. Traditional organic wastewater treatment methods often consume large amounts of energy, incomplete degradation, and even cause secondary pollution. Photoelectrocatalytic technology is an enhanced photocatalytic oxidation technology that has been proposed in recent years to effectively promote photoelectron and hole separation and utilize photoelectric synergy. When a TiO₂ photocatalyst is used as a photoanode, a certain bias voltage is applied thereto, and photogenerated electrons migrate to an external circuit, thereby suppressing recombination of photogenerated electrons and holes. The holes accumulate on the surface of the catalyst and further reactions occur to remove contaminants. The addition of voltage to the reaction system can significantly reduce the recombination of electron-hole pairs. This feature can solve the serious recombination problem of electron-hole pairs in semiconductor photocatalysis. A large number of research results show that photoelectrocatalytic oxidation technology provides an effective method for the degradation of organic pollutants in water.
2. Photoelectrocatalysis

2.1. Principle of photoelectrocatalysis
When the energy is greater than or equal to the TiO$_2$ band gap energy, TiO$_2$ absorbs photons to generate electron-hole pairs, and transfers the charge to the species from the solution or gas phase and adsorbed on its surface through the forbidden band. The holes capture electrons in the adsorbate or solvent on the surface of the particle, bind to the species that supply the electrons, cause the species (often organic contaminants) to be oxidized, and electron acceptors (usually oxygen in aqueous solution) receive surface electrons to be reduced. At the same time, however, electron-holes can be simply recombined on the surface and inside, reducing their photocatalytic efficiency. Photoelectrocatalysis can improve the photocatalytic efficiency, and the principle diagram is shown in Fig. 1. As the carrier of TiO$_2$, the electrode can avoid the separation of the catalyst and is beneficial for repeated use. The photogenerated electrons move toward the counter electrode under the action of external anodic bias, avoiding the simple recombination of photogenerated electrons and holes, and improving the photocatalytic efficiency of the wastewater.

![Fig. 1 Schematic Diagram of Photoelectric Catalysis](image)

2.2. Photoelectrocatalysis progress
Photoelectrocatalysis is an advanced oxidation technology with a broad application prospect in the field of environmental and chemical engineering. It can be seen from the previous literature review that in the preparation of photocatalysts, a lot of research work has been carried out, and the technology is relatively mature. At present, there are commercial TiO$_2$ photocatalysts, but for some new preparation technologies, such as micro In-depth study of preparation and product properties should also be carried out by emulsion method, etc.

In order to improve the utilization of light energy by TiO$_2$ photocatalyst, various modification methods of TiO$_2$ have also been studied extensively, such as manufacturing composite semiconductor, doping metal modification, surface precious metal deposition modification and the like. In addition to the manufacture of composite semiconductors, most of the current modification methods are based on the already prepared TiO$_2$ photocatalyst. Therefore, in order to obtain a high-performance, low-cost modified photocatalyst, it is necessary to further carry out technical research that is easy to realize commercial production by directly combining the preparation and modification of the photocatalyst.

There are many studies on the kinetics of photocatalytic reactions. However, most of the researches remain on the investigation of several major influencing factors, and there is rarely a kinetic model that can reflect many influencing factors. Some kinetic models are based on specific reactants and reaction systems. Without this particular environment, there is no practical value. Therefore, in the future work, we should also study some kinetic equations with universal applicability and more influencing factors.
In the research of photocatalytic reactors, in order to solve the problem of catalyst recovery, people tend to study the immobilization of photocatalysts. However, due to the immobilization of TiO\(_2\), the contact area with the reactants is greatly reduced, and there are some problems in the transmission of light. In order to take advantage of the large specific surface area of the photocatalytic suspension system, the preparation and properties of the magnetic TiO\(_2\) photocatalyst have been explored. The magnetic photocatalyst can recover TiO\(_2\) relatively easily by using a magnetic field. Therefore, while studying some reactors based on TiO\(_2\) immobilization, some new and efficient photocatalytic reactions based on suspension systems should be carried out. In short, although most of the researches on TiO\(_2\) photocatalysis technology are still in the laboratory research stage, it is believed that with the continuous research of high-performance photocatalysts and the development of new, highly efficient and easily industrialized photocatalytic reactors, TiO\(_2\) Photocatalytic technology is bound to be widely used in the near future.

2.3. Environmental photocatalysis

Environmental photocatalysis refers to a technology that uses a certain wavelength of light energy to catalyze the oxidation of pollutants at normal temperature and pressure in the presence of a photocatalyst for the purpose of environmental pollution control. According to different subjects of photocatalytic oxidation, it is mainly divided into liquid-solid phase photocatalysis and gas-solid phase photocatalysis. Among the 189 basic pollutants announced by the Environmental Protection Agency (EPA), there are 9 categories of organic matter, totaling 114 species. Among them, all kinds of main organic pollutants can be mineralized and harmlessly treated by semiconductor photocatalytic oxidation technology, and finally oxidized and decomposed into CO\(_2\), water, inorganic anions and other oxides. These organic substances include: surfactants, endocrine disruptors, antibiotics, insecticides, herbicides, colored dyes, etc [1].

3. Modification status and research results of TiO\(_2\) catalyst

Since 2000, research reports on the use of Localized Surface Plasmonic Resonance (LSPR) to improve the photocatalytic activity of semiconductors have emerged [2, 3]. In 2008, Awazu [4-6] et al. carried TiO\(_2\) on the Ag/SiO\(_2\) core-shell structure and studied its photocatalytic activity. Studies have shown that the LSPR effect has a positive effect on photocatalysis and names this phenomenon as plasma photocatalysis [7]. The introduction of this concept has greatly promoted the enthusiasm of researchers to develop plasma photocatalysts. At the same time, such catalysts also show broad application prospects in effectively utilizing solar energy to solve environmental pollution problems.

3.1. Overview of TiO\(_2\)

The core issue of photocatalysis research is to find and develop high-efficiency photocatalysts, which are related to whether the technology can be industrialized. Among the many photocatalysts currently studied, TiO\(_2\) has become the focus of attention in the field of environmental photocatalysis. As a photocatalyst, TiO\(_2\) has high stability and no photo-corrosion or chemical corrosion in the reaction; it has a suitable band gap and can be excited by ultraviolet light; the catalytic activity is high, and the photo-generated charge has a strong redox capacity. Some organic pollutants can undergo catalytic degradation and mineralization. As a practical material, TiO\(_2\) is cheap, easy to obtain, safe and non-toxic. Therefore, environmental workers' research and development of TiO\(_2\) has never stopped since 1972.

3.2. Study on modification of TiO\(_2\)

As far as TiO\(_2\) is concerned, there are still some key technical problems that constrain the industrial application of this technology. Mainly in:

1. TiO\(_2\) as an n-type semiconductor, its large band gap energy (rutile type 3.03 eV, anatase type 3.2eV) makes it effective to ignite the price only under ultraviolet light with a wavelength less than
With electronic transition to conduction band, electron-hole pairs are generated, and the utilization rate of solar energy is only 3%-5% [8];

(2) TiO$_2$ photogenerated carriers have high recombination rate and low quantum efficiency (less than 4%), which is difficult Industrial waste gas and wastewater with large processing capacity and high concentration [9].

(3) The system used for photocatalytic degradation of organic pollutants in water by TiO$_2$ is mostly a suspension system [10]. Although its photocatalytic activity is very high, due to the fine particles of TiO$_2$, there are disadvantages of difficulty in recovery and secondary pollution.

The above problems have greatly restricted the wide industrial application of TiO$_2$. In response to these problems, current research has focused on improving the utilization of visible light based on TiO$_2$ photocatalysts and reducing the recombination probability of electron-hole pairs by modification. Modification methods include: pore structure morphology control, precious metal deposition, semiconductor coupling, co-doping, and the like.

3.3. Progress in TiO$_2$ nitrogen doping

In recent years, semiconductor TiO$_2$ photocatalysts have been extensively studied in the field of advanced oxidation technology, because a large number of experiments prove that it is a very effective catalyst in environmental protection and energy conversion. TiO$_2$ can not only degrade organic matter in wastewater into CO$_2$ and H$_2$O, also oxidative decomposition to remove low concentrations of harmful gases in the atmosphere.

At present, the preparation of catalysts with strong photoreactivity under visible light by new methods has become the main research direction of many researchers. The doping of non-metallic elements N has become a research hotspot in recent years. In 2001, R. Asahi [11] reported for the first time that nitrogen-doped TiO$_2$ can shift the spectral range to the visible region and predict the electronic density of non-metallic elements N, C, F, P and S in anatase TiO$_2$. The nitrogen-doped absorption spectrum has the best red shift effect. The improvement in photocatalytic activity is usually attributed to the overlap of the N-2p level and the O-2p level above the valence band, resulting in narrowing of the TiO$_2$ band gap or the formation of some impurity compounds (NO$_x$, NH$_x$) due to the N-induced intermediate band. It has been reported that the atomic size of nitrogen and oxygen are relatively close, and the ion energy is small, which tends to form a structural center of steady state and metastable state. Pelaez et al. prepared N/F co-doped TiO$_2$ nanoparticles by sol-gel method and used them to degrade LR-cystine aqueous solution. Livraghi [12] et al. also reported that the reason why nitrogen promotes the absorption of visible light by N-TiO$_2$ is because it promotes the conduction of electrons from the fixed-state band gap guide or electron acceptor.

4. Application of TiO$_2$ in the Treatment of Refractory Organic Wastewater

The pace of global industrial production is accelerating, and the treatment of dye wastewater, surfactant-containing wastewater, halogenated organic compounds, and oily wastewater has presented us with great challenges. Nearly 90% of the priority pollutants announced by the US Environmental Protection Agency (USEPA) are organic pollutants, and photoelectrocatalysis is listed as the most environmentally-friendly high-tech.

4.1. Dyeing Wastewater

Printing and dyeing wastewater has large water content, high content of organic pollutants, deep color, large alkalinity, large water quality change and poor biodegradability. The wastewater also contains benzene ring, amine group, azo group and other poisonous substances, and some can even cause cancer. It is a highly concentrated organic wastewater that is difficult to handle. Studies [13] have shown that the use of photoelectrocatalytic oxidation process for printing and dyeing wastewater can completely destroy organic matter under normal temperature and pressure, and has the advantages of high oxidation efficiency and fast decomposition speed, and has broad application prospects.
4.2. Papermaking wastewater

The papermaking wastewater has large discharge, complex composition, high chroma, high chemical oxygen demand and poor biodegradability. Especially, it contains refractory organics such as lignin, cellulose, hemicellulose and monosaccharide. It is difficult to achieve conventional treatment methods. Satisfactory processing effect. However, TiO₂ photocatalysis can effectively treat halogenated hydrocarbons, chlorinated phenols, dioxins, cyanides, various organic acids and metal ions in papermaking wastewater [14].

4.3. Pesticide wastewater

There are many types of pesticides, such as large discharge of wastewater, complex composition, high concentration of toxic substances, high toxicity, wide pollution surface, long duration, difficult biodegradation, and bioaccumulation. In addition, organic pesticides containing chlorine and phosphorus are generally regarded as suspicious carcinogens, which are low in water and are usually difficult to remove by conventional methods, and the catalytic activity of nanomaterials can greatly improve the catalytic degradation rate. Under ultraviolet light, photoexcitation of photogenerated electrons, holes and strong oxidizing ·OH generated by TiO₂ can oxidize and degrade pesticides into simple inorganic substances such as H₂O, CO₂, PO₄³⁻ and SO₄²⁻ without causing more toxicity. Intermediate product without secondary pollution [15].

5. Conclusion and Outlook

As a new type of photocatalyst with superior performance, TiO₂ has a very broad application prospect in the treatment of refractory organic wastewater. Doping non-metal ions, metal ions, semiconductor composites and semiconductor photosensitization and other modification technologies can effectively improve the photocatalytic activity, visible light utilization rate and reaction efficiency of TiO₂, thereby improving its ability to handle a variety of difficult-to-degrade organic compounds.

Photoelectrocatalysis can be applied not only to the treatment of refractory pollutants, but also to the photolysis of water to produce hydrogen. If organic pollutants can be collected while degrading as a clean renewable energy source, it has far-reaching significance and influence. With the continuous development of technology and continuous improvement of technology, it is believed that in the near future, photoelectric catalytic technology will be more widely and more efficiently applied to wastewater treatment.

6. References

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