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# Photocatalytic Mechanism and Performance Improvement of $Ti_3C_2$ for the Treatment of Tetracycline Antibiotics

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## Abstract

**Compared to traditional wastewater treatment processes, advanced oxidation processes (AOP) can more effectively and environmentally friendly remove harmful substances from wastewater. Among these, photocatalytic oxidation (PCO) has garnered significant attention due to its ability to utilize solar energy for pollutant removal. With the rapid development of industry and medicine, tetracycline (TC), an antibiotic detectable at various levels of the aquatic and terrestrial ecosystems' food chains, poses long-term environmental pollution and biological toxicity risks due to its persistent residues. Conventional treatment processes are ineffective in addressing this issue. Therefore, in recent years, research related to PCO in wastewater treatment has flourished, and numerous researchers have reviewed its recent progress.However the main challenges and future directions of PCO are still not fully analyzed. In this paper, we first review the catalytic mechanism and various control factors of PCO. Then, we discuss the current development status of the main photocatalyst-$Ti_3C_2$ and summarize their commonly used evaluation criteria and systems. Finally, on this basis, we analyze the main challenges faced by $Ti_3C_2$ in theoretical studies and practical applications and propose the optimization and improvement of $Ti_3C_2$ to meet the feasibility in industrial applications. We believe that the research in this paper will provide important guidance and reference for enhancing $Ti_3C_2$ as a photocatalyst in the field of wastewater treatment.**

## Keywords

**Photocatalysis; Photocatalytic Mechanism; $Ti_3C_2$; Antibiotics.**

## 1. Introduction

Currently, about half of the world's population faces severe water shortages for at least part of the year. A quarter of the world's population is under high pressure of water scarcity, and water utilization in these regions exceeds 80%. TC is currently the most commonly used antibiotic in the world. Due to its low production price and therapeutic effect, it has a wide range of applications in human treatment, aquaculture and animal husbandry[1]. Despite the multiple health benefits of TC for humans and animals, only a small fraction of TC is metabolized or absorbed in the body. In contrast, up to 75% of TC is released into the environment through human or animal excreta, and it is difficult to degrade TC accumulation in ecosystems. Therefore, treatment of TC in wastewater is imperative[2, 3].

Growing water pollution and increasing demand for freshwater urgently require the planning and implementation of wastewater treatment measures. Wastewater treatment technology has also become the only option to ensure the world's future freshwater supply. In recent years, the world's research topics have been dealing with organic pollutants as an important research object,the main methods of removing organic pollutants in water include toxic, difficult to biodegrade organic pollutants is an important factor in causing water pollution. Various techniques have been widely investigated for the removal of organic pollutants from

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wastewater, including bioprocess coagulation[4], precipitation[5, 6] and adsorption.[7, 8]Several methods have been reported for the degradation of TC such as advanced oxidation[9], biological methods[10], membrane treatment[11], adsorption[12]. However, traditional methods are ineffective in removing TCH from wastewater. As one of the most promising means of environmental remediation, photocatalysis has been widely studied and developed in recent years, especially in the field of photocatalytic degradation of organic pollutants in wastewater, due to its advantages of high efficiency, economy, and greenness[13, 14].

However, the above methods are often faced with the problems of secondary pollution to the environment and high cost in practical use. Photocatalytic advanced oxidation process (PCO)[15-17] shows great potential and prospect in pollutant degradation by virtue of the advantages of simple operation, low cost, greenness, high degradation efficiency and fast reaction rate[18-20]. Based on the current "carbon neutrality target" and energy supply needs, the development of a low-cost, green and efficient photocatalyst is therefore the key to this technology, making photocatalytic wastewater degradation more promising[21].

In this paper, the catalytic mechanism and the main influencing factors of PCO are firstly introduced comprehensively. Then, the physical and chemical properties of $Ti_3C_2$, which is currently a commonly used photocatalyst, are discussed, followed by a discussion of the principle of photocatalytic activity of $Ti_3C_2$, including its electronic behavior and ability to generate active oxide species under light. Finally, the main challenges faced in theoretical analysis and practical applications are presented, and feasible optimization and improvement strategies are proposed to enhance the photocatalytic efficiency of $Ti_3C_2$. This review will provide valuable insights to promote the further development of $Ti_3C_2$ as a photocatalyst in wastewater treatment.

## 2. Introduction to Photocatalysis

### 2.1. Photocatalytic Mechanism

Photocatalytic reactions typically consist of three main sequential processes [22]: (i) mass transfer processes (e.g., transfer of reactants from and products from the photocatalyst surface); (ii) interfacial processes (e.g., adsorption of reactants to and desorption of products from the photocatalyst surface, photon absorption, carrier reorganization, and non-homogeneous electron transfer for inducing redox reactions); and carrier internal photocatalyst Migration[23, 24].

### 2.2. Physical and Chemical Properties of $Ti_3C_2$

Currently, the search for efficient and low-cost photocatalysts is a hot research topic both at home and abroad. 2011, with the successful isolation of $Ti_3C_2$, the door to two-dimensional layered MXene was opened, which has been attracting more and more attention from researchers[25-27]. MXene refers to a family of two-dimensional (2D) materials consisting of atomic layers of transition metals, carbides, nitrides or carbon-nitrides. Due to its large surface area, tunable surface-terminal groups, and excellent electrical conductivity, MXene shows exciting potential in photocatalysis, energy conversion, and many other areas[28, 29]. Among many 2D MXene, $Ti_3C_2$ is the most studied due to its availability, low cost, easy modification and excellent electronic properties. Photocatalytic technology is a promising approach to alleviate environmental pressure and energy crisis. However, most of the reported photocatalysts show low conversion efficiency[30-33].

As a representative of MXenes, $Ti_3C_2$ has been used in photocatalysis due to its good surface hydrophilicity, metal conductivity and structural stability. When $Ti_3C_2$ is used as a co-catalyst to construct heterojunctions with other substances, photogenerated carriers can be effectively separated. It has been shown that different compositions, structures and processing conditions of MXene may result in having different properties. Nanocomposites of 2D MXene have recently attracted much attention, especially in the fields of energy storage and catalysis, due to their stable and easily tunable microstructures, high electrical conductivity, large chemically active surfaces, and hydrophilicity[16, 34, 35]. Among many MXene, $Ti_3C_2$ has been most studied for its high availability, low cost, easily tunable interlayer and excellent electronic properties, especially in the photocatalytic field showing great potential for application[31, 36, 37].

## 2.3. Current Development of Photocatalyst-$Ti_3C_2$

In the current application of $Ti_3C_2$ in the photocatalytic field[38, 39] researchers believe that the abundant functional groups and unique layered structure of $Ti_3C_2$ Mxene produced during its preparation by the wet chemical method[40] give $Ti_3C_2$ good adsorption properties for heavy metals and organic pollutants, but $Ti_3C_2$ does not have the same photoexcitation ability as semiconductors, and it can't be used as a photocatalytic material It cannot be used purely as a photocatalytic material[37, 41, 42]. Constructing heterojunctions by compounding $Ti_3C_2$ with semiconductor materials is an effective way to enhance photocatalytic materials. The recent research progress of $Ti_3C_2$ with semiconductor materials as photocatalysts is highlighted below.

With the continuous progress of individual photocatalyst enhancement technology, the use of co-catalysts to construct metal-semiconductor heterojunction systems to improve photocatalytic activity has attracted much attention. The metal-semiconductor heterojunction interface has a high density of interfacial states and allows effective energy level modulation, which provides a solid foundation for improving photocatalytic activity[43-45]. The addition of a co-catalyst to this system further facilitates the transport and separation of electrons at the interface and promotes the generation of effective photogenerated carriers.

Cao prepared Sn-Bi-MoF/$Ti_3C_2$ heterojunction catalysts by solvothermal method and investigated their photocatalytic degradation and mineralization of tetracycline under light conditions[46]. After 90 min of photocatalysis, the degradation rate of pollutants was 96.2% and the mineralization rate was 45.5%. The physical and chemical properties of the catalysts were analyzed by various methods. The effects of solution pH, co-existing anions and water quality on the catalyst performance were investigated[47-49]. Free radical burst experiments and electron paramagnetic resonance tests showed that O2- and h+ are the main active substances in the photocatalytic mechanism[47, 50]. The degradation of TC and intermediates was determined by 3D fluorescence and LCMS. The photocatalytic mechanism of Sn-Bi-MOF/$Ti_3C_2$ was proposed on the basis of free radical determination and electrochemical tests. The formation of Schottky junction accelerated the electron transfer to $Ti_3C_2$ and improved the charge separation, which led to the generation of free radicals. After four cycle experiments, the Sn-Bi-MOF/$Ti_3C_2$ catalyst still showed good catalytic performance, and the X-ray diffraction spectra before and after the reaction were basically the same, indicating the stability of the composite structure[51-54].

Development of novel photocatalysts for efficient degradation of pharmaceutical contaminants is crucial in environmental remediation[55]. In this study, LEE et al. investigated the synthesis of nanosheets derived from MXene, specifically integrated onto highly conductive $Ti_3C_2$ MXene, which was then combined with zinc sulfide (ZnS) to form heterojunctions[56]. This integration process was accomplished using a hydrothermal method followed by a self-assembly method[51, 57]. Our goal was to evaluate the effectiveness of this integrated system in enhancing the photocatalytic degradation of TC. The in situ synthesized $TiO_2$/$Ti_3C_2$(TT) has a high-energy lattice (001) facet of the $TiO_2$ layer, resulting in an exclusive heterojunction in the $TiO_2C_2$/ZTT heterojunction. The loading of zinc sulfide nanoparticles significantly increased the specific surface area and narrower band gap of the films, which enhanced the luminescence potential in the visible region. Thus, the zinc sulfide synergistically affects the ZTTx (where x = Tt%) heterojunction matrix and significantly improves the separation and transport of photogenerated carriers[58-60]. The ZTT5 heterojunction exhibited remarkable adsorption and photoreduction properties, with 97.1% total cholesterol degradation within 60 min under UV irradiation. In addition, the ZTT5 heterojunction structure exhibited an impressive TC removal rate of 93.8% within 90 min under simulated sunlight. These results highlight the effective performance of the ZTT5 heterojunction catalysts in promoting photogenerated carriers, thus enhancing the photocatalytic capability. In addition, the energy band structures and density of states of $TiO_2$, $Ti_3C_2$, and ZnS(111) were investigated using density functional theory. In addition, the photocatalytic mechanism of TC is proposed, including the photoreduction of electrons from $TiO_2$ to the MXene surface. Upon transfer, the electrons react with $O_2$ to form $O^{2-}$, which is attributed to the high electron mobility of Mxene. The results of this study emphasize the great potential of the ZTT5 heterostructure for the effective degradation of pharmaceutical pollutants in wastewater[47, 61, 62].

$Ti_3C_2$ has attracted great interest since its first discovery,[63] and $Ti_3C_2$ has been shown to be a promising photocatalytic co-catalyst, in which $Ti_3C_2$ promotes migration as well as separation of photogenerated carriers[64]. because of its strong electronic conductivity. We believe that the most efficient $Ti_3C_2$-based heterojunction should have tight 2D/2D interfacial contacts[65, 66].

Qiao prepared ultrathin 2D/2D g-$C_3N_4$/$Ti_3C_2$ heterojunctions for photocatalytic degradation of tetracycline by direct roasting of a mixture of urea and multilayer $Ti_3C_2$[67]. Among them, urea is the precursor for the generation of g-$C_3N_4$, which generates gas during the reaction process and peels off the multilayer $Ti_3C_2$ into fewer layers, solving the problem of low yield for the preparation of fewer layers of $Ti_3C_2$. The experimental results of visible-light degradation of tetracycline showed that pure g-$C_3N_4$ (UCN) had weak photocatalytic activity, while its photocatalytic performance was improved when g-$C_3N_4$ was coupled with $Ti_3C_2$[67-70]. The best sample (5TC) showed 90.1% degradation of tetracycline within 30 min. After four stability tests, the photocatalytic performance did not change significantly, indicating that the prepared 2D/2D g-$C_3N_4$/$Ti_3C_2$ heterojunction has strong photocatalytic performance and good stability[67].

## 3. Prospects for the Application of PCO in Wastewater Treatment

Looking ahead, with increasingly stringent environmental regulations and growing awareness of water resource protection, the photocatalytic advanced oxidation process will be increasingly used in wastewater treatment, and $Ti_3C_2$, as a highly efficient photocatalyst, will play a key role in this field. Potential application scenarios include the removal of organic pollutants from industrial wastewater, the degradation of antibiotic residues, and the mineralization of toxic organic waste. In addition, with the development of nanotechnology and the reduction in the cost of titanium carbide catalytic materials, the feasibility and economics of $Ti_3C_2$ in large-scale industrial applications will be further enhanced, thus promoting its widespread use in the wastewater treatment market. Therefore, the prospect of Ti3C2 as a photocatalyst in advanced oxidation process is very optimistic, which can not only meet the existing wastewater treatment needs, but also provide an important technical support for the future development of environmental protection technology.

## 4. Conclusion

Nowadays, with the increasing scarcity of freshwater resources, the field of wastewater treatment is facing the important challenge of maintaining pollution reduction, green treatment, and efficient treatment. PCO can be used with highly efficient green and low-cost photocatalysts that are clean and efficient, making it the most promising wastewater treatment technology available today. Although researchers have gained a clearer understanding of the oxidation mechanism of PCO and the performance of catalyst materials has been significantly improved, there is still a long way to go to realize the wide application of PCO in wastewater treatment. Challenges include water pH effects, improper treatment of complex water quality, catalyst material recovery, and high material costs. Therefore, it is necessary to further develop advanced characterization methods to improve the accuracy and efficiency of theoretical studies. At the same time, catalyst structures should be optimized, other processes should be integrated to meet the treatment needs of complex water quality, and wastewater purification and other coupled processes should be developed. All these initiatives can improve the efficiency of wastewater treatment, reduce treatment costs, save energy, reduce carbon emissions, and effectively meet the demand for carbon neutrality. This paper analyzes the current research status and challenges of $Ti_3C_2$, the main catalyst for PCO, and proposes strategies to deal with them in order to guide the strategy of PCO in catalyst development.

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