

**Study on Water Sterilization by Using TiO₂-based Composite
Photocatalyst under Visible Light Irradiation**

July 2020

Na LIU

**Study on Water Sterilization by Using TiO₂-based Composite
Photocatalyst under Visible Light Irradiation**

**A Dissertation Submitted to
the Graduate School of Life and Environmental Sciences,
the University of Tsukuba
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in Biotechnology
(Doctoral Program in Bioindustrial Sciences)**

Na LIU

Abstract

In recent years, a growing number of countries around the world have clean drinking water supply problems, both in developed and developing countries. WHO reported that 12,600 deaths per day in children below 5 years are caused by virus or bacteria present in polluted water. Therefore, the drinking water must be disinfected before use. Usually, the traditional water disinfection methods, including chlorination, ozonation and ultraviolet, have several disadvantages related to the formation of potentially hazardous disinfection byproducts (DBPs), with carcinogenic and mutagenic potential. Furthermore, these methods are often chemically, energetically, or operationally expensive, limiting their practical application.

Among the processes that are being developed, semiconductor photocatalysis has emerged as a very attractive technology for water disinfection. According to the previous studies, a novel P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst, firstly synthesized by my lab, has demonstrated as a promising material with remarkable photocatalytic efficiency in decomposing organic matter under visible light irradiation. However, regarding its photocatalytic disinfection ability, there is no research being conducted. Therefore, the main purpose of this study is to investigate the water sterilization ability of P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst in real water environment under visible light irradiation.

Firstly, the photocatalytic disinfection activity of P/Ag/Ag₂O/Ag₃PO₄/TiO₂ composite was investigated by the inactivation of *Escherichia coli* under different environmental conditions. The results showed that this novel visible-light-driven composite photocatalyst possessed remarkable bacterial disinfection ability and could completely inactivate 10⁸ cfu/mL of *E. coli* within just 40 min under the optimum catalyst loading of 0.5 g/L. Better bactericidal activity of P/Ag/Ag₂O/Ag₃PO₄/TiO₂ was achieved under higher light intensity (750 W/m²), shorter light wavelength (465–470 nm), ambient temperature (30–37°C) and natural or slightly alkaline condition. The existence of different inorganic ions under normal environmental level had no significant impact on the bactericidal performance. All these results indicated the novel P/Ag/Ag₂O/Ag₃PO₄/TiO₂ composite photocatalyst possessed remarkable bacterial disinfection ability under different environmental conditions and can be applied for real water environment.

Correspondingly, the bacterial inactivation mechanism of P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst was systematically investigated. The result showed that the destruction process of the bacterial cell is progressive from the cell membrane to the inner cellular components, leading to the final collapse of bacterial cells. There was negligible amount of Ag⁺ released from P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst. This result confirmed that

the remarkable disinfection activity of the composite should result from the major reactive species: $\cdot\text{O}_2^-$ and h^+ from photocatalytic process instead of the leakage of Ag^+ , indicating this composite photocatalyst was a safe candidate for practical application.

Furthermore, considering in real water environment, different types bacteria are usually coexistent. Hence, the disinfection efficiency of $\text{P/Ag/Ag}_2\text{O/Ag}_3\text{PO}_4/\text{TiO}_2$ on different types microorganisms (Gram-positive and Gram-negative) was comparably investigated. The results showed that this novel composite could effectively inactivate both Gram-positive and Gram-negative bacterium under visible light irradiation either in single or mixed bacteria system. The inactivation of Gram-positive bacterium was more resistant to the photocatalytic treatment than that of Gram-negative bacterium. This was mainly due to the different cell structure between the two types bacteria, as Gram-positive bacterium has a thicker cell wall than the Gram-negative bacterium. In addition, to solve the post-separation problem by using the photocatalyst powder for disinfection, a glue-immobilized photocatalytic reactor was successfully developed based on the novel visible-light-driven $\text{P/Ag/Ag}_2\text{O/Ag}_3\text{PO}_4/\text{TiO}_2$ photocatalyst. It was observed that the developed reactor could be recyclable applied for water disinfection with easy operation and there was no obvious loss of photocatalytic activity observed even after five cycles. This result indicated that the developed glue-immobilized photocatalytic reactor with

excellent stability and reusability holds great potential for actual large-scale water sterilization application in the future.

Therefore, based on the advantages of its remarkable disinfection ability, low cost, energy-saving and environment friendly, the novel visible-light-driven P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst has great potential for the actual water sterilization and could facilitate water disinfection system.