

氏名（本籍）	LIU NA （ 中国 ）		
学位の種類	博 士（ 生物工学 ）		
学位記番号	博 甲 第 9700 号		
学位授与年月日	令和 2 年 9 月 25 日		
学位授与の要件	学位規則第 4 条第 1 項該当		
審査研究科	生命環境科学研究科		
学位論文題目	Study on Water Sterilization by Using TiO ₂ -based Composite Photocatalyst under Visible Light Irradiation (可視光照射条件におけるTiO ₂ 系複合光触媒を用いた水の殺菌に関する研究)		
主査	筑波大学教授	博士（生物工学）	楊 英男
副査	筑波大学教授	博士（農学）	北村 豊
副査	筑波大学教授	博士（理学）	内海 真生
副査	筑波大学准教授	博士（理学）	山田 小須弥

Abstract of thesis

In recent years, a growing number of countries around the world have clean drinking water supply problems. 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. Unfortunately, all the conventional water disinfection methods, including chlorination, ozonation and ultraviolet, have some disadvantages, such as high cost or formation of by products with potential carcinogenicity and photoreactivation. The author also reported that the traditional water disinfection methods are often chemically, energetically, or operationally expensive. Therefore, development of more effective water disinfection technologies that are low-cost, energy-saving and safe for humans, has become an urgent issue.

As a “green” advanced oxidation technology, semiconductor photocatalysis has emerged as a very attractive technology for water disinfection due to its relatively high photocatalytic oxidation ability, low cost and non-toxicity (Chapter 1). According to the previous studies in author’s lab, a novel visible-light-driven P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst has been successfully developed with remarkable photocatalytic efficiency in decomposing the organic matters. However, its ability on water disinfection has not yet been assessed. Hence, the main objective of the author’s research was to investigate the water sterilization ability of the novel visible-light-driven P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst in actual water environment.

In Chapter 2, the author focused on investigating the P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst disinfection activity under different environmental conditions (including different light intensity, light wavelength, temperature, pH, and existence of different ions). In this Chapter, the author chose *Escherichia coli* as the target microorganism. The results showed this photocatalyst possess notable photocatalytic antibacterial capability for *Escherichia coli* under visible light irradiation. The bacterial inactivation by this photocatalyst was more favorable under high light intensity, shorter light wavelength, ambient temperature and natural or slightly alkaline condition. The author also found that the existence of different inorganic ions under normal environmental level had no significant impact on the bactericidal performance, suggesting that this novel photocatalyst can be applied for actual water environment.

In Chapter 3, the author elucidated the bacterial inactivation mechanism of P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst. The results showed the destruction process of the bacterial cell was 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 resulted 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.

Previously, the author had reported in Chapter 2 and Chapter 3 that this novel photocatalyst possessed notable photocatalytic disinfection capability for *Escherichia coli*. Considering in real water environment, different types bacteria are usually coexistent. Hence, in Chapter 4, the author further comparably examined the disinfection efficiency of P/Ag/Ag₂O/Ag₃PO₄/TiO₂ on different types microorganisms (Gram-positive and Gram-negative). The author found that the novel photocatalyst 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, the author developed a new glue-immobilized photocatalytic reactor based on the novel visible-light-driven P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst. The results showed that the developed reactor could be recyclable and applied for water disinfection with easy operation and there was no loss of photocatalytic activity observed 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.

In summary, the author has shown in this thesis that the novel visible-light-driven P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst possessed remarkable bacterial disinfection ability under different environmental conditions for different types bacterium. The disinfection mechanism study confirmed this novel photocatalyst was a safe candidate for practical application. Furthermore, the new developed glue-immobilized photocatalytic reactor based on this novel photocatalyst exhibited excellent stability and reusability. The author suggested that the P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst with the advantages of remarkable disinfection ability, energy-saving and environment friendly, can be a promising alternative to facilitate present water disinfection system.

Abstract of assessment result

【Review】

Pathogenic microorganisms in drinking water pose both direct and indirect risks to water quality and threaten the health of human beings. In this regard, the author aimed to study the water sterilization by using a novel P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst under visible light irradiation. The author focused on assessing the photocatalytic disinfection ability under different environmental conditions for different types bacterium as well as elucidating its disinfection mechanism. The experimental results indicated that the novel P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst possessed remarkable bacterial disinfection ability under different environmental conditions and could effectively inactivate both Gram-positive and Gram-negative bacterium. The author also observed the remarkable disinfection activity of the novel photocatalyst resulted from the major reactive species: $\cdot\text{O}_2^-$ and h^+ instead of the leakage of Ag^+ , indicating this novel photocatalyst was a safe candidate for practical application. Moreover, the newly developed glue-immobilized photocatalytic reactor based on this novel photocatalyst exhibited excellent stability and reusability. From these results, the author provides practical and actionable insights into the use of P/Ag/Ag₂O/Ag₃PO₄/TiO₂ photocatalyst for actual water sterilization to facilitate present water disinfection system.

【Result】

The final examination committee conducted a meeting as a final examination on 24 July, 2020. The applicant provided an overview of dissertation, addressed questions and comments raised during Q&A session. All of the committee members reached a final decision that the applicant has passed the final examination.

【Conclusion】

Therefore, the final examination committee approved that the applicant is qualified to be awarded the degree of (Doctor of Philosophy in Biotechnology).