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審査研究科	生命環境科学研究科
学位論文題目	Synthesis of Bismuth Tungstate Based Solar-light-driven Composite Photocatalyst with High Photocatalytic Activity and Stability （高い光活性と安定性を持つ太陽光応答型タングステン酸ビスマス系光触媒の合成に関する研究）

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Abstract of thesis

In recent years, wastewater has caused numerous inconvenience due to the discharge of degradation-resistant pollutants. Semiconductor photocatalysis as an effective treatment technology for treating the wastewater has drawn wide attention due to its high efficiency, inexpensive and low toxicity. Bismuth tungstate (Bi_2WO_6), as one of the most efficient semiconductor photocatalysts, has drawn intense attention in wastewater treatment because of its narrow bandgap with visible-light-driven ability. However, the quick recombination of the electron-hole pairs in Bi_2WO_6 holds back the photocatalytic activity. After summarizing the latest developments in photocatalysts, the author highlights the details of a modification strategy that can be used to dope noble metal (Ag) and semiconductor (Ag_2O, Ag_3PO_4) in bismuth tungstate for fabrication of highly effective visible-light-driven Bi_2WO_6 photocatalysts. According to the previous studies in author's lab, $Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ nanoparticles have been synthesized. However, laborious recollection of the $Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ nanoparticles in water cleaning process has restricted its application. Herein, development of a photocatalytic thin film with high efficiency and stability is important. In Chapter 1, the author introduces that polyethylene glycol (PEG) has excellent water solubility and thermal stability, which can be an ideal structure-directing agent to form stable photocatalytic thin film. On the other hand, to further improve the photocatalytic activity, graphene oxide (GO) modified Bi_2WO_6–based composite can be used to investigate its ability in wastewater treatment. Hence, the main objective of the author's research was to synthesize bismuth tungstate based solar-light-driven composite photocatalyst with high photocatalytic activity and stability for practical wastewater treatment.

In Chapter 2, the author focused on developing photocatalytic film with enhanced photocatalytic activity and stability. The effect of PEG on the stability of photocatalytic thin films was investigated because it has not been properly studied until now. At first, $PEG/Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ thin film was synthesized by using different molecular weight ($PEG_{300,\ 2{,}000,\ 6{,}000,\ 20{,}000}$), dosage (4, 8, 12, 16, and 20 g/L), and coating layers (1, 2, 3, 4). Photocatalytic activity was determined by photodegradation of 5 ppm Rh B, and the repeatability test was carried out for 10 cycles. 2-layered thin films of $Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ modified with 12 g/L of PEG_{2000} were fabricated successfully and showed enhanced photocatalytic activity and stability. The films contained small size nanoparticles, exhibited strong visible-light absorption, low recombination, and fast charge separation of electron-hole pairs that were characterized by TEM (Transmission electron microscope), SEM (Scanning electron microscope), UV-vis (Ultraviolet–visible spectroscopy), and PL (Photoluminescence spectroscopy), respectively. The photocatalytic thin films showed higher activity and stability in 10-cycle repeatability experiments compared with the control. In addition, the author found that $PEG_{2000}/Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ thin film with enhanced

photocatalytic performance and stability was a promising alternative for wastewater treatment.

In Chapter 3, the author focused on modifying $Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ with graphene oxide (GO) to further enhance the photocatalytic efficiency. GO has been widely used as a light absorber and electron acceptor, which can reinforce light harvesting and electron-hole separation. In this chapter, Bi_2WO_6 as the base photocatalyst was synthesized in the 1st hydrothermal process, and Ag species were induced in the 2nd hydrothermal process to synthesize the $Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ composite. The $GO\text{-}Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ composite that were prepared by adding GO during the fabrication of Bi_2WO_6 (1st hydrothermal) or during incorporation of Ag dopants (2nd hydrothermal) are designated as $GO_{(I)}\text{-}Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ and $GO_{(II)}\text{-}Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$, respectively. Photocatalytic activity was investigated by photodegradation of AMX (amoxicillin), Rh B (rhodamine B), and *E. coli*. The results indicated that $GO_{(II)}\text{-}Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ showed much better photocatalytic performance compared with $GO_{(I)}\text{-}Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$, as well as with other previously reported GO modified Bi based composites. The author elucidated the mechanism according to the characterization of the GO composite by XRD (X-ray diffraction spectra), XPS (X-ray photoelectron spectroscopy), UV-vis, PL analysis, and photocurrent density. $GO_{(II)}\text{-}Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ composite possessed high crystallinity, high visible light absorption, low generated electron-hole recombination rate, and high photocurrent density for higher photo-activity. Normally, in the composite with multiple-synthesis steps, the photocatalytic performance is closely related with the crystal structure of the base photocatalyst. Adding GO during the incorporation of Ag dopants (2nd hydrothermal) did not affect crystal formation of Bi_2WO_6, while adding GO during the 1st hydrothermal process could affect the formation process of multiple-layer structure of base photocatalyst (Bi_2WO_6). Therefore, $GO_{(II)}\text{-}Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ possessed significantly enhanced photocatalytic property and high photocatalytic activity in degradation of multiple pollutants.

In summary, the author has shown in this thesis that novel $PEG_{2000}/Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ photocatalytic thin films and $GO_{(II)}\text{-}Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ composite were successfully fabricated. Both of them showed enhanced photocatalytic activity and stability, which could be promising candidates for practical water purification under solar light irradiation.

Abstract of assessment result

【Review】

Wastewater has caused numerous inconvenience due to the degradation-resistant pollutants. In this regard, the author aimed to study the wastewater treatment by using photocatalytic technology under solar light irradiation. The author synthesized Bi_2WO_6 based photocatalytic composites by modification with Ag species, PEG and GO, as well as elucidated the mechanism. The results indicated that the novel $PEG_{2000}/Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ photocatalytic thin films were synthesized successfully with an enhanced photocatalytic stability. The author also achieved remarkable organic pollutant removal efficiency by using the developed photocatalytic films, which indicated the novel thin films could be a leading candidate for practical applications. Moreover, the newly developed $GO_{(II)}\text{-}Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ photocatalyst exhibited excellent photocatalytic activity in degradation of AMX, Rh B and *E. coli*. Based on the results, the author provides reasonable and practical insights into the use of Bi_2WO_6 based photocatalytic composite for wastewater treatment.

【Result】

The final examination committee conducted a meeting as a final examination on 22 Jan, 2021. 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).