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

In recent, wastewater has caused numerous inconvenience due to the degradation-resistant pollutants. Various technologies such as physical adsorption, chemical decomposition, and biological degradation have been developed to solves these problems. Among these conventional technologies, photocatalytic treatment offers great potential in low cost and eco-friendly way for purification of wastewater. Semiconductor photocatalysis has drawn wide attention due to it high efficiency, economic and low toxicity. Bismuth tungstate (Bi_2WO_6), one of the most efficient semiconductor photocatalysis, has drawn intensive attention in wastewater treatment because of its narrow bandgap, visible-light-driven property, and high photocatalytic activity. However, the quick recombination of the electron-hole pairs in Bi_2WO_6 holds back the photocatalytic activity. To fabricate high effective visible-light-driven Bi_2WO_6 photocatalyst, considerable efforts have been taken for photocatalyst modification by doping with noble metal (Ag) and semiconductor (Ag_2O, Ag_3PO_4).

For noble metal, Ag will work as electron acceptor, and help to promote photocatalytic activity by reduce the recombination rate of electron and hole. Interestingly, Ag can be easily oxidized to Ag_2O, Ag_2O is a promising photocatalyst for degradation of hazardous organic pollutant under solar light irradiation. Meanwhile, some phosphate semiconductors also have been adopted as highly efficient photocatalysts for water purification. Ag_3PO_4 as a semiconductor photocatalyst with relatively narrow band gap can help to expand the solar light absorption of Bi_2WO_6 photocatalyst. Therefore, $Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ was fabricated with enhanced photocatalytic activity.

Photocatalysis is usually utilized as suspended powders in water cleaning process. However, laborious recollection of the powders has restricted their applications. Herein, development of photocatalytic thin film with high efficiency and stability is important for wastewater treatment. Polyethylene glycol (PEG) has excellent water solubility and thermal stability, which made it a proper structure-directing agent. Furthermore, photocatalyst doped by PEG exploits its non-toxicity and photosensitive properties.

PEG with different molecular weight and dosage manipulate nanoparticle growth of the photocatalysts. Besides, coating layers of the photocatalytic thin films were very crucial for improving the photocatalytic activity. To our best knowledge, the effects of PEG on the stability of photocatalytic thin films were not properly studied simultaneously. Herein, PEG/Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6 composite photocatalytic thin film was prepared with high stability and efficiency. At first, PEG/Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6 thin film was synthesized by 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), followed by characterization test (SEM, XRD, UV-Vis, PL, Photocurrent, XPS and TEM) and photocatalytic activity experiments. Photocatalytic activity was determined by photodegradation of 5 ppm Rh B, and the repeatability test was observed by 10 cycle's photodegradation of 5 ppm Rh B. The results showed that 2-layered of 12 g/L $PEG_{2,000}$ modified Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6 thin film was fabricated successfully, and exhibited small particle size, strong visible-light absorption, low recombination and fast charge separation of electron-hole pairs, and high photocatalytic activity. The photocatalytic thin films showed higher activity and stability in both 10-cycle repeatability experiments compared with other reported Bi based semiconductor photocatalyst. Therefore, $PEG_{2,000}$/Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6 thin film with enhanced photocatalytic performance and stability was a promising alternative for wastewater treatment.

To further enhance the photocatalytic efficiency of Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6, graphene oxide (GO) is used to synthesize Bi_2WO_6 based composite photocatalyst. GO has been widely used as a light absorber and electron acceptor, which can reinforce light harvesting and electron-hole separation. In this study, Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6 was synthesized by a two-step hydrothermal method, Bi_2WO_6 as the base photocatalyst was synthesized in the 1st hydrothermal process, and Ag species were induced in the 2nd hydrothermal process. Normally, in the composite photocatalyst with multiple-synthesis step, the photocatalytic performance is closely related with the crystal structure of the base photocatalyst. For synthesis of GO-Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6 composite, GO added in the fabrication of base photocatalyst (Bi_2WO_6) or in inducing of Ag dopants could affect crystal formation of Bi_2WO_6, finally influence the photocatalytic activity. When adding GO in the formation process of Bi_2WO_6, GO with multiple-layer structure may impact the crystal growth of Bi_2WO_6. Herein, GO adding in the fabrication of Bi_2WO_6 (1st hydrothermal) and in inducing of Ag dopants (2nd hydrothermal) of GO-Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6 were synthesized separately marked as $GO_{(I)}$-Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6 and $GO_{(II)}$-Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6. Characterization test (SEM, XRD, UV-Vis, PL, Photocurrent, XPS and TEM) and photocatalytic activity experiments were conducted to find the most optimal condition of GO modified Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6. Photocatalytic activity was determined by photodegradation

of AMX, Rh B, and *Escherichia coli*. The results indicated that $GO_{(II)}$-$Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ photocatalyst possessed high visible light absorption, low generated electron-hole recombination rate, and high photocurrent density. Clear chemical bond of GO can be observed from FT-IR and Raman spectra. Results of XRD and TEM showed that $GO_{(II)}$-$Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ were synthesized successfully. Besides, $GO_{(II)}$-$Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ had high crystallinity and integration between Ag, Ag_2O, Ag_3PO_4 and Bi_2WO_6 which benefited for photocatalyst. $GO_{(II)}$-$Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ generated high photocatalytic performance in degradation of AMX, Rh B and *E. coli*, compared to other reported GO modified Bi based photocatalyst, which proved to be an alternative in future wastewater treatment.

In summary, $Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ photocatalyst, $PEG_{2,000}/Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ photocatalytic thin film were synthesized successfully with enhanced photocatalytic activity and stability, which could be a promising candidate for practical water purification under solar light irradiation. To further develop $Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ based photocatalyst for practical application, $GO_{(II)}$-$Ag/Ag_2O/Ag_3PO_4/Bi_2WO_6$ were successfully fabricated and exhibited high crystallinity. Besides, it showed high photocatalytic activity in degradation of AMX, Rh B, and *E. coli*, which indicated high prospects for practical application in wastewater treatment.