

**Study on Solar-light-driven P/Ag/Ag<sub>2</sub>O/Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub>  
Photocatalyst**

**January 2018**

**ZHU QI**

**Study on Solar-light-driven P/Ag/Ag<sub>2</sub>O/Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub>  
Photocatalyst**

**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  
(Doctor Program of Bioindustrial Sciences)**

**ZHU QI**

## Abstract

Recently, photocatalytic technology has been widely investigated for solving environmental pollution and energy crisis. Titanium dioxide ( $\text{TiO}_2$ ) photocatalyst was intensively developed for wastewater treatment, water splitting, disinfection and many other applications due to its relatively high photocatalytic activity, low cost, non-toxicity and bio-chemical stability. Nevertheless, the practical application of  $\text{TiO}_2$  is limited, because it can only be excited by UV light with wavelengths below 380nm, which only account for about 3-5% of the total solar spectrum. And the fast recombination of photogenerated electron-hole pairs also decrease the activity.

To create solar-light-driven  $\text{TiO}_2$  photocatalysts with higher efficiency, considerable efforts have been made by doping noble metals (Ag, Au and Pt), narrow band semiconductors ( $\text{CdO}$ ,  $\text{CdS}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$ ) or nonmetals (C, P and N) on  $\text{TiO}_2$ . It was found that  $\text{Ag}_3\text{PO}_4$  with narrow band gap energy could improve the ability of  $\text{TiO}_2$  for water splitting and photodecomposition of organic dyes. However,  $\text{Ag}_3\text{PO}_4$  is highly unstable under light irradiation. For noble metal, Ag nanoparticles dopant could extend optical absorption spectrum of  $\text{TiO}_2$  to the visible light region and inhibit the recombination of electron-hole pairs. Interestingly, with suitable treatment, metallic Ag can be easily oxidized into  $\text{Ag}_2\text{O}$ , while  $\text{Ag}_2\text{O}$  is a capable photocatalyst with narrow band gap. In addition, the present of metallic Ag could inhibit the aging of  $\text{Ag}_3\text{PO}_4$ . On the other hand, nonmetal P element was also reported that can improve the activity of  $\text{TiO}_2$ . Until now, there was no study had focus on the synthesis, optimization and utilization of P (nonmetal), Ag (noble metal) and

Ag<sub>2</sub>O, Ag<sub>3</sub>PO<sub>4</sub> (narrow band semiconductors) co-modified TiO<sub>2</sub>. Therefore, it is expected to prepare P/Ag/Ag<sub>2</sub>O/Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub> photocatalyst for wastewater treatment, water splitting processes and disinfection.

In this study, P/Ag/Ag<sub>2</sub>O/Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub> composite photocatalyst powder was firstly prepared by sol-gel method and followed by degradation test and structure analysis. The characteristics of the material were analyzed by X-ray Diffraction (XRD), UV-vis spectrophotometer, X-ray photoelectron spectroscopy (XPS), Scanning electron microscope - Energy-dispersive X-ray spectroscopy (SEM-EDS), photoluminescence spectroscopy (PL) and transmission electron microscope (TEM). The degradation tests revealed that the activity of TiO<sub>2</sub> could be highly improved by suitable amount of Ag, Ag<sub>2</sub>O (come from AgNO<sub>3</sub>) and P, Ag<sub>3</sub>PO<sub>4</sub> (come from Ag<sub>3</sub>PO<sub>4</sub>) dopant. Comparing with pure TiO<sub>2</sub>, the as prepared composite powder showed higher absorption in visible light region, narrower band gap, extremely lower recombination rate of photogenerated electron-hole pairs and higher photocatalytic efficiency for Rh B degradation. Additionally, the radical trapping experiments implied that holes and O<sub>2</sub><sup>•-</sup> radicals were the major active species for Rh B degradation.

In the application of photocatalyst powder, an adequate previous-mixing and a tedious post-separation after treatment are usually needed. To avoid this drawback, the P/Ag/Ag<sub>2</sub>O/Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub> composite photocatalyst is further optimized as thin film for large scale application. The thin film samples, which have same component with powder, were prepared by sol-gel at different temperature, time and number of coating layers. The optimal conditions and the remarkable stability of thin film were

confirmed, and the thin film demonstrated remarkable activity on disinfection. In addition, the photocatalytic reaction mechanism of thin film was clarified.

Normally, sol-gel prepared photocatalysts has low specific surface area and poor performance on water splitting. To further improve the utilization of P/Ag/Ag<sub>2</sub>O/Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub> composite photocatalyst, hydrothermal method for the material prepared under different time and temperature was investigated and the photocatalyst exhibited smaller crystal size, larger specific surface area, higher amount of P element and lower PL intensity than sol-gel prepared material. These results further supported that the hydrothermal material exposed higher activity in dye degradation and water splitting tests under solar light irradiation.

In summary, P/Ag/Ag<sub>2</sub>O/Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub> composite photocatalyst was successfully synthesized by sol-gel and hydrothermal methods. After co-modified by Ag (noble metal), Ag<sub>2</sub>O, Ag<sub>3</sub>PO<sub>4</sub> (narrow band semiconductors) and P (nonmetal), the capacity of TiO<sub>2</sub> was greatly improved. Comparing with sol-gel synthesized photocatalyst, hydrothermal material with same component showed higher photocatalytic activity and water splitting ability. Photocatalyst thin film also presented excellent performance and stability in dye degradation. As-prepared P/Ag/Ag<sub>2</sub>O/Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub> composite photocatalyst with remarkable activity and stability would become a promising material for practical applications in wastewater treatment, water splitting and disinfection of bacteria in future.