

Photocatalytic Performance of Ag modified and doped TiO₂ nanoparticles

L. H. Chang, C. P. Cho*, C. C. Lin and Y. C. Wang

Department of Applied Materials and Optoelectronic Engineering
National Chi Nan University, Nantou 54561, Taiwan, cpcho@ncnu.edu.tw

ABSTRACT

Noble metal modification is one of the most important strategies to improve photocatalytic performance of TiO₂. Ag modified TiO₂ is a more promising material in practical applications. It is generally accepted that Ag nanoparticles can function as an electron sink to accept photogenerated electrons from excited semiconductor to facilitate dioxygen reduction. In addition to surface loading of Ag, doping of Ag ions into TiO₂ nanoparticles was also investigated. It has been discovered that the TiO₂ nanoparticles modified by Ag and/or doped with Ag showed enhanced degradation ability. In this work, tetrabutyl titanate (TBOT) was used as the titanium source for preparation of the powder of raw TiO₂ nanoparticles. The raw TiO₂ nanoparticles was then used to react with AgNO₃ aqueous solution to fabricate Ag deposited and doped TiO₂ powder.

Afterwards, the Ag deposited and doped TiO₂ powder was treated with various concentrations of HNO₃ aqueous solutions to remove some Ag from TiO₂ surface. The UV and visible light photocatalytic activities of various Ag deposited and doped TiO₂ samples had been evaluated and compared by photodegradation tests under the irradiation of a 350 W xenon lamp. An X-ray diffractometer was used to examine characteristic diffraction peaks of various samples. Their size and morphology analysis was performed by a scanning electron microscope. It was found that excessive Ag loading would not be beneficial to the photocatalytic activity of TiO₂. An optimum photodegradation efficiency was achieved as HNO₃ aqueous solution of an appropriate concentration was applied to remove excess Ag from the surface of Ag deposited and doped TiO₂ nanoparticles.

It was deduced that the TiO₂ photocatalysts containing Ag showed different photocatalytic mechanisms under UV and visible light irradiation. The isolated 4d energy level of Ag in the energy band gap of TiO₂ contributes to absorption of visible light when Ag promotes effective separation of photogenerated electrons and holes, leading to high visible light photocatalytic activity. However, the doping energy level of Ag ions in the energy band gap of TiO₂ could act as the recombination centers of photogenerated carriers. This would be unfavorable for the photocatalytic performance of TiO₂ photocatalysts. More exploration will be executed and more detailed discussion will be given. This study may provide some insights into the design of novel and high-efficiency photocatalytic nanomaterials.

Keywords: TiO₂, photocatalyst, photodegradation, doping, Ag

1 INTRODUCTION

TiO₂ is one of the photocatalysts which have been extensively investigated. Hydroxyl radicals are produced, and organic pollutants are decomposed and destroyed via nonselective reactions under light irradiation. Harmless inorganic acid, carbon dioxide and water are then generated when degradation of organics occurs on TiO₂ surface. This can reduce environmental pollution [1, 2]. However, TiO₂ has not yet shown wide applications due to its limited absorption of visible light and low photocatalytic efficiency [3]. Accordingly, researches of how to enhance absorption of visible light become important in order to improve the photocatalytic ability of TiO₂. Some approaches have been developed so far, such as nonmetal (N, S, C, B) doping [4, 5], metal ion doping (Pt, Ag, Au, Fe) [6-8], and changes of morphology or structure (nanowire, nanotube, nanoparticle, hollow nanosphere, etc.) [9, 10]. Ag has superiority in lower cost as compared to other noble metals such as Pt and Au. It is believed that Ag would be more promising for doping in TiO₂ to form a more efficient photocatalyst. Doping of Ag is beneficial to enhance the photocatalytic activity of TiO₂ in the range of visible light [11, 12]. When Ag ions are deposited on TiO₂ surface, Ag can be deemed as an electron receiver under light irradiation, and redox reactions are then facilitated.

It was reported that the photocatalyst of Ag deposited and doped TiO₂ exhibited more superior photocatalytic activity [13]. In this work, we have demonstrated that the amount of Ag deposited on the surface of Ag-doped TiO₂ nanoparticles influences the adsorption of organics and thereby the effectiveness of degradation reaction. An easy preparation approach to form raw TiO₂ nanoparticles was employed here. The deposition and doping of Ag ions were accomplished by calcination at 500 °C to form Ag deposited and doped TiO₂ powders. Various concentrations of HNO₃ aqueous solutions were used to remove Ag nanoparticles on TiO₂ surface. The influence of HNO₃ concentration on the degradation rate of methyl orange under irradiation of 350 W xenon lamp has been investigated. It was discovered that the Ag nanoparticles deposited on TiO₂ surface must have an appropriate amount. Even though Ag was beneficial to visible light absorption of TiO₂, overloading of Ag on TiO₂ surface was not helpful and would reduce the UV light absorption of TiO₂ instead. Thus, how to strike a balance becomes important and is the focus of this work.

2 EXPERIMENTAL

The raw TiO₂ nanoparticles (sample A) was fabricated by adding TBOT into D.I. water and stirring for 2 hours. The aqueous solution was then allowed to stand for 24 hours, followed by filtration and rinsing several times to form wet gelatinous TiO₂ solution. It was baked at 80 °C for 8 hours subsequently, and then ground to obtain dry TiO₂ powder.

The powder of raw TiO₂ nanoparticles was added into 0.1 M AgNO₃ aqueous solution to obtain a well mixed solution by sonication for 5 min. After stirring for 2 hours, the mixed solution was baked at 100 °C, and then calcined at 500 °C for 2 hours to achieve Ag deposited and doped TiO₂, which was also ground using a mortar to form fine powder (sample B).

The Ag deposited and doped TiO₂ powder of sample B was added into HNO₃ aqueous solutions of various concentrations and stirred continuously for 2 hours. Four HNO₃ concentrations, 0.3 M, 0.9 M, 1.5 M and 2 M, were selected to form sample C, D, E and F, respectively. The impact of Ag loading on TiO₂ surface on the degradation rate of methyl orange was thereby compared. Every mixed solution was filtrated and rinsed for several times until the PH value of the solution reached 6. After filtration, baking at 60 °C for 2 hours and grind were carried out to obtain fine powder.

Various Ag deposited and doped TiO₂ fine powders (samples A to F) were added into the aqueous solutions of methyl orange with a concentration of 20 ppm. Each mixed solution had an orange color and was stirred for 10 min under dark to achieve a uniformly dispersion of TiO₂, then it was under constant light irradiation of 350 W xenon lamp for 4 hours. The distance between the lamp and solution was fixed as 15 cm. The sampling interval for degradation test was 20 min. A UV/vis spectrometer (U-3900H, Hitachi) was used for detection of light absorbance. The X-ray diffractometer (XRD-7000, Shimadzu) with a Cu K_α light source ($\lambda = 1.5406 \text{ \AA}$) was used to analyze X-ray diffraction spectra. A scanning electron microscopy (JSM-6300, JEOL) was used to examine surface morphology of each sample.

3 RESULTS & DISCUSSION

The XRD spectra of raw TiO₂ nanoparticles (sample A) and various Ag deposited and doped TiO₂ powders (sample B to F) are shown in Fig. 1. The diffraction peaks at 25.2°, 38.4°, 48.0°, 53.9°, 55.0°, 62.7°, 68.8°, 70.3° and 75.0° evidence the existence of anatase TiO₂. The peak at 38.1° can be attributed to the diffraction of Ag (111), indicating the successful Ag deposition on TiO₂ surface and doping in TiO₂. The peak at around 44.7° comes from the diffraction of Al (200), which can be ascribed to the XRD sample stage containing Al. No conspicuous crystallinity is observed in sample A since it was obtained without the calcination process. Thus besides the diffraction peak of Al (200) at 44.7°, almost no other obvious peaks can be found in the diffraction spectrum of sample A. The magnification

of the diffraction peak at around 38.0° reveals that it is actually composed of two peaks, as shown in Fig. 2. The one at 38.1° comes from the diffraction of Ag (111), and another one at 38.4° can be attributed to the diffraction of anatase TiO₂ (004).

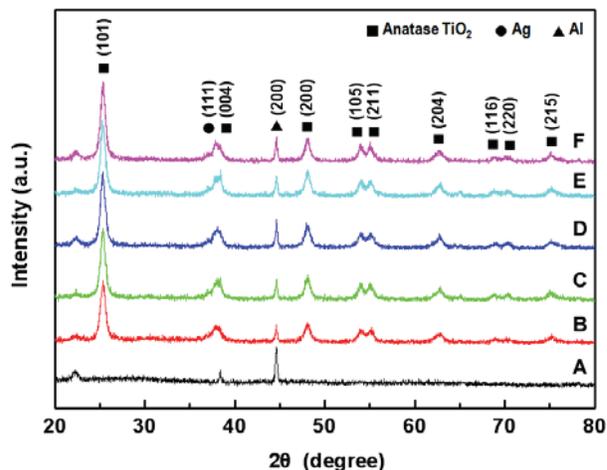


Figure 1: XRD spectra of raw TiO₂ nanoparticles (sample A) and various Ag deposited and doped TiO₂ powders (sample B to F).

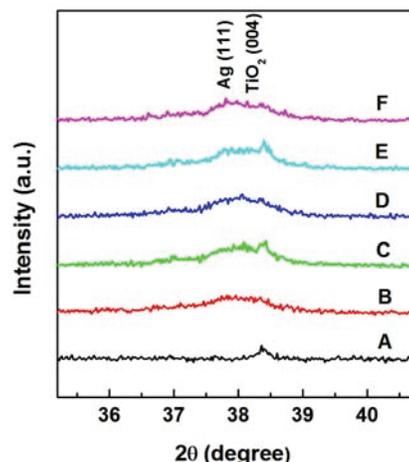


Figure 2: Magnification of the diffraction peak at around 38.0°.

The SEM images of samples A to F are displayed in Fig. 3. The diameter of raw TiO₂ nanoparticles obtained without calcination process is around 300 nm, as shown in Fig. 3A. Calcination at 500 °C makes the diameter of Ag deposited and doped TiO₂ nanoparticles increase to around 500 nm conspicuously. Many tiny Ag nanoparticles deposit on the surface of TiO₂ after the raw TiO₂ nanoparticles react with AgNO₃ aqueous solution, as revealed in Fig. 3B. Fewer and nonuniformly distributed Ag nanoparticles on TiO₂ surface

are observed after treatment of 0.3 M HNO₃ aqueous solution, as displayed in Fig. 3C. The Ag loading on TiO₂ surface goes lower as the concentration of HNO₃ aqueous solution becomes higher. Almost no Ag nanoparticles can be seen on TiO₂ surface when the concentration of HNO₃ aqueous solution is 2 M, as revealed in Fig. 3F. It has been found that the size and morphology of TiO₂ nanoparticles essentially have no noticeable changes after treatment of various HNO₃ aqueous solutions. This indicates that the concentration of HNO₃ aqueous solution only affects the amount of Ag loading on TiO₂ surface but does not influence the size, morphology and structure of TiO₂.

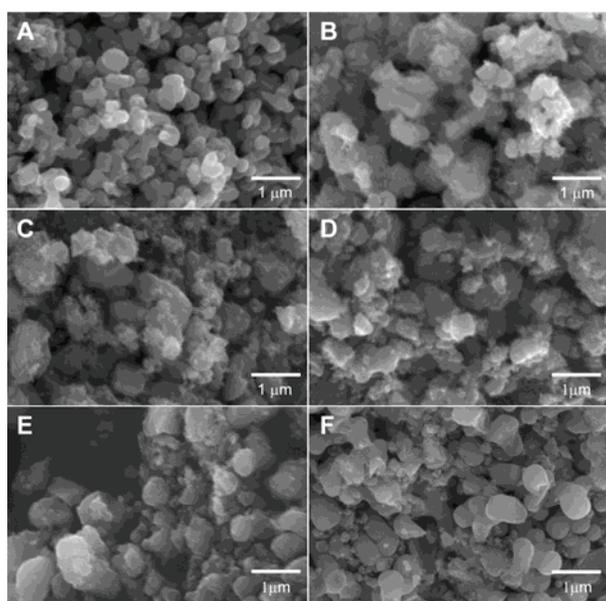


Figure 3: SEM images of samples A to F.

Fig. 4 shows the UV/vis absorption spectra of sample A to F. Apparently, the raw TiO₂ nanoparticles almost do not have absorption of visible light. The energy bandgap of TiO₂ is around 3.0 eV to 3.2 eV, so it mainly absorbs UV light in the range of 300 nm to 400 nm. Curve B shows the absorption spectrum of the Ag deposited and doped TiO₂ powder before treatment of HNO₃ aqueous solution. Its overall absorption is mainly in the range of visible light. Moreover, it has the lowest absorbance in the UV light range. This can be attributed to Ag overloading on the TiO₂ surface of sample B. Because of the light reflection and scattering by excessive Ag on TiO₂ surface, some UV light can not be efficiently absorbed by TiO₂. Curves C to F in Fig. 4 show the absorption spectra of the Ag deposited and doped TiO₂ powders obtained after treated by the HNO₃ aqueous solutions with concentrations of 0.3 M, 0.9 M, 1.5 M and 2 M. Compare to samples D, E and F, sample C is treated with less HNO₃, and the Ag loading on its surface is more than those on other three samples. Accordingly, it has

maximum visible light absorption among the four samples. The results have revealed that appropriate amount of Ag is certainly advantageous to visible light absorption of TiO₂. Excessive deposition of Ag on TiO₂ surface decreases UV light absorption of TiO₂.

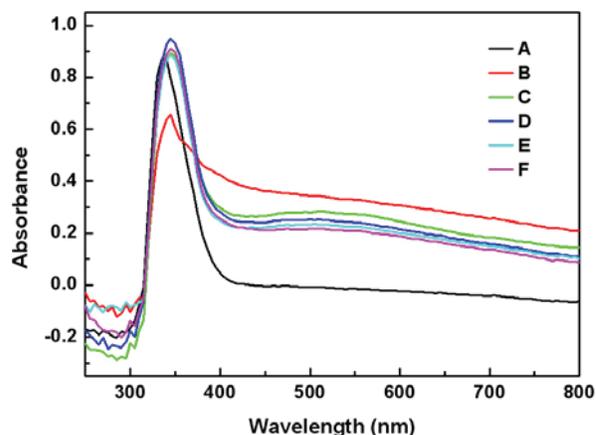


Figure 4: UV/vis absorption spectra of sample A to F.

Fig. 4 shows the degradation plots of methyl orange and samples A to F under light irradiation of 350 W xenon lamp. Curve MO reveals that methyl orange does not go self-degradation without TiO₂ photocatalyst. Curve A shows that the raw TiO₂ nanoparticles has the worst degradation rate because its light absorption is mainly in the range of UV light. Although Ag doping or deposition is favorable for enhancement of visible light absorption of TiO₂, curve B shows that excessive Ag loading on TiO₂ surface is not helpful and would reduce the degradation rate. Curve C displays that by an appropriate concentration (0.3 M) of HNO₃ aqueous solution to remove some Ag nanoparticles on TiO₂ surface, an optimum Ag loading is obtained and the best degradation efficiency can be thereby achieved. Curves D and E reveal that higher concentrations of HNO₃ aqueous solutions (0.9 M and 1.5 M) to remove more Ag nanoparticles can not further improve the degradation rate. Curve F shows that as an even higher concentration of HNO₃ aqueous solution is applied (2.0 M), the degradation rate decreases faster obviously but is still superior than that of the raw TiO₂ nanoparticles without containing any Ag. This also implies that samples B to F definitely contain Ag doping inside.

4 CONCLUSIONS

TiO₂ nanoparticles are potential photocatalyst and are worthy of attention and study, but their light absorption is only limited in the range of UV light. Ag deposition on TiO₂ surface or doping in TiO₂ could obviously enhance their visible light absorption, and photocatalytic efficiency could be thereby improved. Nevertheless, it was discovered

that excessive Ag loading would not be favorable for the photocatalytic performance of TiO₂. In this study, we has demonstrated that an optimum degradation efficiency could be achieved as HNO₃ aqueous solution of an appropriate concentration was applied to remove excess Ag from the surface of Ag deposited and doped TiO₂ nanoparticles.

[13] R. Liu, P. Wang, X. Wang, H. Yu and J. Yu, *J. Phys. Chem. C* 116, 17721, 2012.

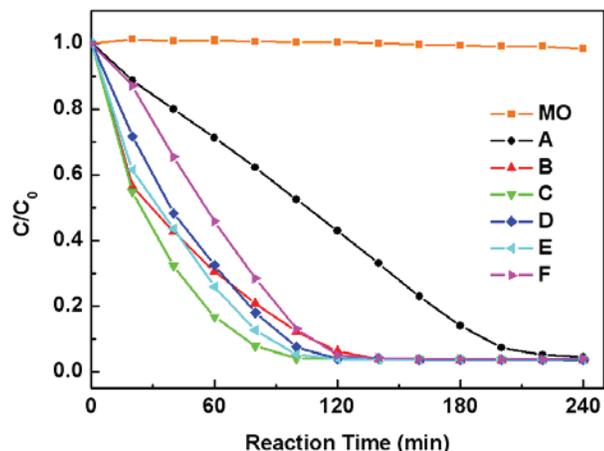


Figure 5: Degradation plots of methyl orange (MO) and samples A to F under light irradiation of 350 W xenon lamp.

REFERENCES

- [1] I. K. Konstantinou and T. A. Albanis, *Appl. Catal.* 1, 49, 2004.
- [2] S. W. Liu, J. G. Yu, B. Cheng and M. Jaroniec, *Adv. Colloid Interface Sci.* 35, 173, 2012.
- [3] A. Kudo and Y. Miseki, *Chem. Soc. Rev.* 38, 253, 2009.
- [4] L. Li, Y. Yang, X. Liu, R. Fan, Y. Shi, S. Li, L. Zhang, X. Fan, P. Tang, R. Xu, W. Zhang, Y. Wang and L. Ma, *Appl. Surf. Sci.* 36, 256, 2013.
- [5] N. Feng, A. Zheng, Q. Wang, P. Ren, X. Gao, S. B. Liu, Z. Shen, T. Chen and F. Deng, *J. Phys. Chem. C* 115, 2709, 2011.
- [6] N. R. Khalid, Z. Hong, E. Ahmed, Y. Zhang, H. Chan and M. Ahmad, *Appl. Surf. Sci.* 258, 5827, 2012.
- [7] B. Tian, Z. Shao, Y. Ma, J. Zhang and F. Chen, *J. Phys. Chem. Solids* 72, 1290, 2011.
- [8] H. Wang, J. L. Fariab, S. Dong and Y. Chang, *Mater. Sci. Eng. B* 177, 913, 2012.
- [9] S. Chu, L. L. Luo, J. C. Yang, F. Kong, S. Luo, Y. Wang and Z. G. Zou, *Appl. Surf. Sci.* 258, 9664, 2012.
- [10] J. H. Park, T. W. Lee and M. G. Kang, *Chem. Commun.* 2867, 2008.
- [11] B. F. Xin, L. Q. Jing, Z. Y. Ren, B. Q. Wang and H. G. Fu, *J. Phys. Chem. B* 109, 2805, 2005.
- [12] I. M. Arabatzis, T. Stergiopoulos, M. C. Bernard, D. Labou, S. G. Neophytides and P. Falaras, *Appl. Catal. B* 42, 187, 2003.