

Effect of Calcinations Temperature on Photo catalytic Activity of Ag-doped TiO₂ Coated on Tile Substrate

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ABSTRACT

Pure TiO₂ and Ag/ TiO₂ thin films were prepared by sol-gel method, spin coating on ceramic tile substrates via Ag content and the calcinations at the temperature range of 400-600°C in air for 1 h. Pure TiO₂ and Ag/ TiO₂ were characterized by XRD, SEM, DTA, EDS and XRF. The photocatalytic activities of the films were carried out by means of the degradation of methylene blue solutions under the UV light radiation in a dark chamber for a different time. It was seen that the Ag doping promotes the phase transformation but it has a depression effect on the anatase grain growth when temperature increase. Ag addition 0.5-2% can enhance the reaction compared to that of pure TiO₂

Key words: Nano-composite, Photocatalytic, Ag/ TiO₂, Titanium dioxide, Sol-gel Process, Coating, Thin film

INTRODUCTION

TiO₂ is widely used as a photocatalyst because it is relatively highly efficient, cheap, non-toxic, chemically and biologically inert and photo stable (Zou et al., 2005) And it has energy band gap, $E_g \sim 3.20 \text{ eV}$ (Kwon et al., 2003) TiO₂ have been applied for wastewater treatment (Priya et al., 2005) and antibacterial (Kim et al., 2006 and Maness et al., 1999) However, the efficiency of TiO₂ photocatalytic is low for its application (Zhang et al., 2005). Other factors, such as preparation process, crystallite size and anatase-rutile ratio seem to have an effect on the activity. The effective way to improve the TiO₂ photocatalytic activity is to introduce metal ions into TiO₂ (Sonawane et al., 2004 and Wu et al., 2006) Because it affects to a large surface area and prevents the electron-hole pairs recombine rapidly after excitation. Many works introduced metal ions, such as V⁵⁺ (Hou et al., 2005), Se²⁺ (Nguyen et al., 2005), N⁵⁺ (Shifu et al., 2005), Pt⁴⁺ (Sreethawong et al., 2005), Fe³⁺ (Yu et al., 2006) and Ag¹⁺ (Liu et al., 2003 and Rengaraj et al., 2006) etc., into TiO₂. Especially silver species coexisted, Ag⁺, Ag⁰ and metal Ag, the radius of Ag⁺ ion (ca. 126 pm) is much larger than that of Ti⁴⁺ ion (ca. 68 pm), the Ag⁺ ions introduced by the sol-gel method could not enter into the lattice of TiO₂ phase.

During the drying and calcining process Ag^+ ions would gradually migrate from the volume of TiO_2 grains to the surface and further to the surface of the TiO_2 powder under the action of heat (Chao et al., 2003). These Ag^+ , Ag^0 and metal Ag play the role trapping photo induced electrons and holes. So recombination of photo induced electrons and holes were effectively inhibited. Otherwise, increment of adsorbed O_2 and OH-on the surface of TiO_2 due to Ag depositing on the surface also improved photocatalytic activity of Ag/ TiO_2 (Xin et al., 2005). Besides, Ag ions effect to crystallite size and anatase to rutile phase transformation (Sen et al., 2005; and Stir et al., 2003). The aim of this work is to investigate the effect of calcinations temperature and Ag-doped content on photocatalytic efficiency of pure TiO_2 and Ag/ TiO_2 thin films coated on ceramic tile substrates which were prepared by sol-gel and spin coating processes.

MATERIALS AND METHODS

Materials

Materials used for synthesis of pure TiO_2 and Ag/ TiO_2 composite powders and thin films were Titanium (IV) isopropoxide (99%) (Fluka Sigma-Aldrich), silver nitrate (AgNO_3) and methylene blue (Fluka). Ethanol (99%) and nitric acid were both AR grade.

Synthesis and characterizations

Pure TiO_2 and Ag/ TiO_2 were prepared by sol-gel method and coated on a ceramic tile by spin coating process. Pure TiO_2 and Ag/ TiO_2 powders were prepared by adding the ethanol into titanium (IV) isopropoxide and then slowly dropping a certain amount AgNO_3 in ethanol solution together with 2M nitric acid into the mixed precursors under vigorously stirring at room temperature for 60 min. The pH value of the solution was adjusted to be about 3. This sol was kept in a room temperature for 7~20 days to allow gel form and then dried for 24 h at the temperature of 200°C followed by calcining at the temperature range of $400\text{-}600^\circ\text{C}$ for 1 h.

Thin films of pure TiO_2 and Ag/ TiO_2 were prepared from the same precursors for making powder but sol was kept in a refrigerator in stead of the room temperature for 24 h until the sol become to be a low viscosity clear gel. The gel was then coated on 7x7 cm ceramic tile substrate by spin coating method. The coated substrates were dried at the temperature of 200°C for 24 h before calcining at the different temperature for 1 h. The crystal phase of the synthesized TiO_2 and Ag/ TiO_2 powders were characterized by DTA (Perkin-Elmer, DTA 7 with the temperature range of $50\text{-}1250^\circ\text{C}$ at heating rate of $20^\circ\text{C}/\text{min}$). The surface morphology was observed with a SEM (JSM-5800 LV, JEOL). The dispersion of Ti in the film was characterized by EDS (EDS : Oxford ISIS 300) attached to the microscope and XRD (Phillips, Cu- k_α radiation of wave length 1.5418 \AA). The data were taken in the range of $5\text{-}80 (2\theta)$. The phase content was determined from XRD patterns according the following equations (Zhu et al., 2005).

$$W_a = \frac{0.884 A_a}{0.884 A_a + A_r}, \quad W_r = \frac{A_r}{0.884 A_a + A_r} \quad (1)$$

Where W_a and W_r represent the weight fractions of anatase and rutile respectively. A_a and A_r are the individually integrated intensity for anatase (1 0 1) and rutile (1 1 0).

The average crystallite size (D) were determined from the XRD pattern by Scherer's equation,

$$D = \frac{k\lambda}{\beta \cdot \cos\theta} \quad (2)$$

Where k is a constant (shape factor, about 0.9), λ is the X-ray wavelength (0.15418 nm), β is the full width at half maximum (FWHM) of the diffraction line, and θ is the diffraction angle. The values of β and θ of anatase and rutile are taken from anatase (2 0 0) and rutile (1 1 0) diffraction line, respectively. It was assumed that the FWHM of anatase (2 0 0) peak is not affected by brookite (2 3 1) peak because the integrated intensity of anatase (2 0 0).

Photocatalytic activity test

The photocatalytic activity experiments on pure TiO_2 and Ag/TiO_2 thin film for the degradation of methylene blue under radiation of a UV light of 20x3 W power with the intensity of 4.77 mW/cm² in dark chamber by using methylene blue solution concentration of 2 mg/l. The area of thin film photocatalyst used for this experiment was 49 cm². Sample of 5 ml was taken at every 1 h. And concentration of methylene blue was determined by UV-visible spectroscopy at wave length 665 nm.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of pure TiO_2 and Ag/TiO_2 powder calcined at different temperatures. Peak marked "A" and "R" correspond to anatase and rutile phases, respectively. It can be seen that the anatase single phase starts to appear when the pure TiO_2 and Ag/TiO_2 are calcined at the temperature 400°C and the crystallization increase with an increase in Ag content. Calcination at 500°C, both the pure and Ag/TiO_2 powders are well crystallized.

The crystallite size and crystal phase of anatase and rutile of pure TiO_2 and Ag/TiO_2 powder are summarized in Figure 2. For calcining at 600°C, it was found that, the phase content of anatase seems to increase with an increase in Ag addition from 0~2%. It can be seen that anatase crystallite size decreases with an increase in Ag content. For the TiO_2 powder with 1%Ag doped, the smallest crystallite size was found to be about 25.3 nm. However, the crystallite size and crystal phase increase when Ag is doped into TiO_2 more than 3%. Because, during drying and calcining process Ag^+ ions spreading on the surface anatase grains would gradually be reduced into Ag^0 effect to start oxygen vacancies occur. The concentration of oxygen vacancies at the surface of the TiO_2 powder then increases, which

facilitates the bond rupture and ionic movement necessary for the formation of the rutile phase. The anatase to rutile phase transformation is then accelerated (Chao et al., 2003)

EDX analyses confirm the presence of Ti in pure TiO_2 and Ag/TiO_2 thin film, EDX spectrum of Ti is presented in Figure 4, indicates the presence of Ti. For Ag/TiO_2 , TiO₂ and Ag were well dispersed on ceramic tile.

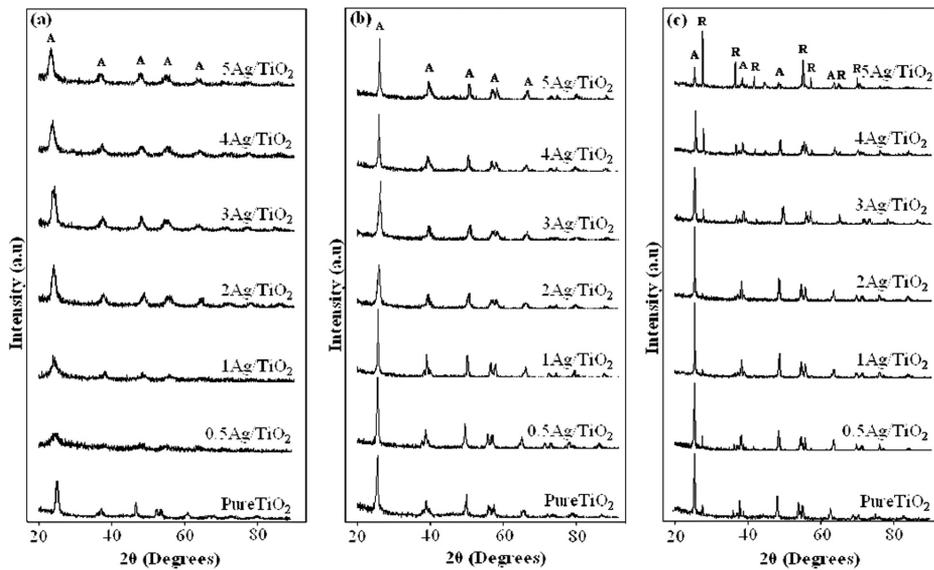


Figure 1. XRD patterns of pure TiO_2 and Ag/TiO_2 powder calcined at a) 400, b) 500 and c) 600°C.

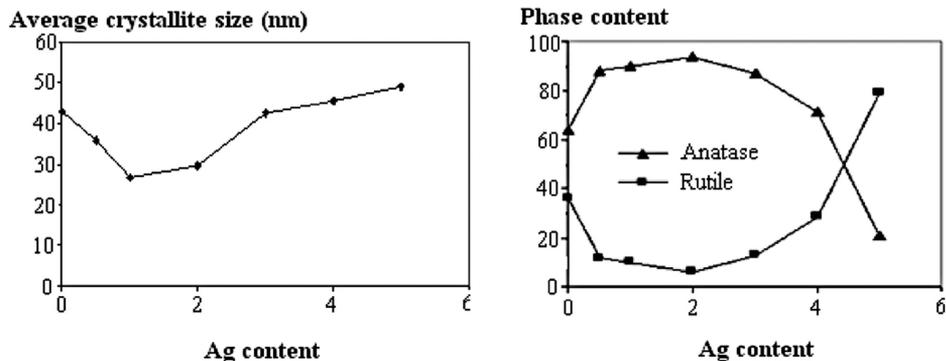


Figure 2. Phase content and of pure TiO_2 and Ag/TiO_2 powder calcined at temperature 600°C.

The result of DTA is illustrated in Figure 3. It was found that anatase phase is formed at the temperature about 420°C.

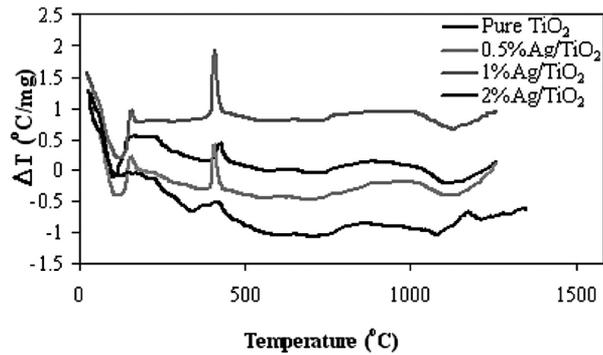


Figure 3. DTA curve of pure TiO_2 and Ag/ TiO_2 powder.

EDX analysis confirm the presence of Ti in pure TiO_2 and Ag/ TiO_2 thin film. EDX spectrum of Ti presented in Figure 4, indicates the presence of Ti. For Ag/ TiO_2 and Ag were well dispersed on ceramic tile.

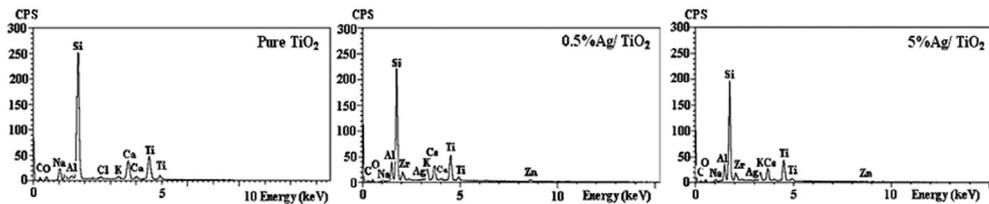


Figure 4. EDX spectrum and Mapping of pure TiO_2 and Ag/ TiO_2 thin film.

The photocatalytic activities of pure TiO_2 and Ag/ TiO_2 thin films shown Figure 5 were evaluated by the decomposition of methylene blue solution. At 400 $^{\circ}\text{C}$, it is also observed that degradation efficiency was nearly the same except for that of 1 and 3 mol%Ag doped TiO_2 . At 500 $^{\circ}\text{C}$ it also that show degradation rate of 0.5, 1 and 2mol% wear nearly the same and better than that of Ag-undoped sample. 1mol% seems to give the highest rate, that it can degrade methylene blue solution about 95%. And at 600 $^{\circ}\text{C}$, photocatalytic activity of 0.5%Ag/ TiO_2 was highest one. It was noted that the higher calcinations temperature the lower mol% of Ag doped for obtaining the highest activity.

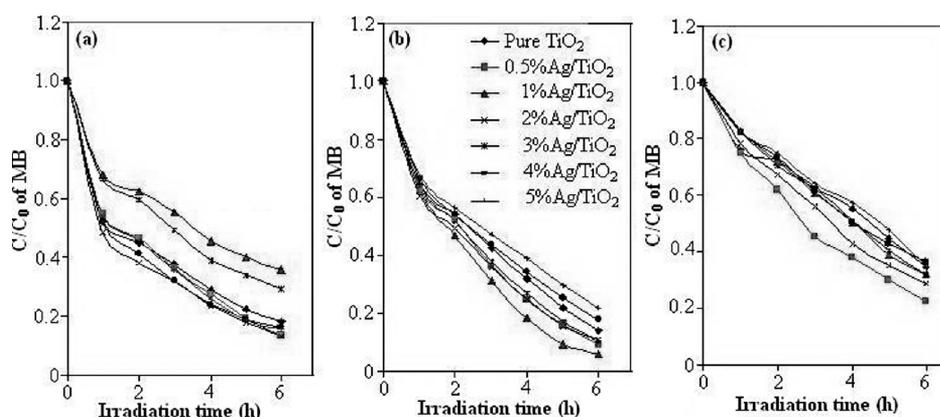


Figure 5. Photocatalytic degradation of Methylene blue with pure TiO_2 and Ag/ TiO_2 catalysts calcined at (a) 400°C , (b) 500°C and (c) 600°C .

CONCLUSION

In this work, pure TiO_2 and Ag-doped TiO_2 were synthesized by sol-gel method. It was found that temperature calcinations and Ag content affect to crystallite size, phase content and photocatalytic activity. From XRD pattern, it can be seen that anatase single phase appears at the temperature at $400\text{--}500^\circ\text{C}$. The rutile phase starts to appear at the temperature of 600°C . The phase content of anatase seems to increase with an increase in Ag addition from 0-2%Ag and tends to decrease when Ag doped into TiO_2 more than 3%Ag. The crystallite size of pure TiO_2 and Ag/ TiO_2 tends to increase with an increase in temperature. At 600°C , the crystallite size decreases with an increase in Ag addition from 0-1% Ag and the crystallite size increases when Ag addition above 2%Ag. The highest photocatalytic activity of film was obtain using 1 mol%Ag doped TiO_2 calcined at 500°C .

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