Novel Photocatalytic Ag/TiO\textsubscript{2} Thin Film on Polyvinyl Chloride for gaseous BTEX Treatment

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Abstract. This study aims to provide the photocatalytic approach for treatment of some hazard air pollutants such as benzene, toluene, ethylbenzene and xylene (BTEX) under visible light. Silver doped titanium dioxide (Ag/TiO\textsubscript{2}) thin films with various molar ratios (0.01, 0.05, 0.1 and 0.2 mol) were synthesized via sol-gel method and dipped on polyvinyl chloride (PVC) sheet before curing with UV lamp. The X-ray diffractograms showed the composite of TiO\textsubscript{2} anatase and nanosilver. The effect of silver doping on decreasing of band gap energy of TiO\textsubscript{2} was observed from the absorption edge shift to higher wave length, analyzed by UV-visible spectrometer. The results from hydrophilicity test indicated that hydrophilicity of TiO\textsubscript{2} thin film was increased by doping silver. The morphology of the Ag/TiO\textsubscript{2} thin film studied by Scanning Electron Microscope equipped with an Energy Dispersive Spectrometer revealed well dispersed nanosilver on the smooth thin film. The BTEX degradation was carried out in a batch reactor with the initial concentration of mixed BTEX gas [25 ppm]. The remaining BTEX was examined by Gas Chromatography equipped with flame ionization detector. Among Ag/TiO\textsubscript{2} thin films, the 0.1 Ag/TiO\textsubscript{2} thin films exhibited the best performance for gaseous BTEX degradation under visible light. The maximum degradation efficiency was belong to xylene (89%), followed by ethylbenzene (86%), toluene (83%) and benzene (79%).

Introduction

There has been a growing concern related to the environmental damage and health impact due to volatile organic compounds (VOCs). The presence of volatile organic compounds especially in group of gaseous benzene, toluene, ethylbenzene and xylene (BTEX) in the atmospheric environment is a consequence of the developing in industrialization and transportation. These
substances are accumulative and persistent in environment which can cause adverse effects on the human nervous system and carcinogenic risk [1-5]. US EPA list determined VOCs as hazard air pollutants. According to the American Conference of Governmental Industrial Hygienists (ACGIH) and the World Health Organization (WHO) recommended 5 ppm as standard maximum level of BTEX [6]. Therefore, it is necessary to develop innovative and cost-effective technologies for safe and complete degradation of gaseous BTEX from the environment. A lot of research revealed that the photocatalytic oxidation (PCO) using titanium photocatalyst is an efficient abatement technology for the degradation of many pollutants [6-9]. Because it involves reactive free radical species for complete mineralization or decomposition of toxic organic compounds to harmless end products (CO$_2$ and H$_2$O). Moreover, TiO$_2$ photocatalyst has good chemical stability, relative low price, and non toxicity [10-13]. However, the application of TiO$_2$ photocatalysts is limited in the visible-light region because its wide band gap energy of 3.2 eV can be activated under UV irradiation [13-17]. In viewpoint of efficient utilization of solar light, the development of visible-light-responsive photocatalyst has been attractive. Various studies attempt to make the visible-light-responsive photocatalyst with transition metal [18-19] or noble metal ion doping [20-22]. Among noble metals, Ag is one of the most suitable for doping due to its characteristic with retarding the recombination of photogenerated electron-hole pairs and decreasing energy band gap [23-27]. To avoid the disadvantage of using powder photocatalyst, thin film coating has been applied on many substrates such as glass, tile, ceramic, plastics etc. [22-23, 28-30]. However, there are only few studies pointing on development of photocatalytic thin film coated on plastics. Calcination process can not be used to booth the active phase of catalyst due to relatively low thermal stability of plastic substrates [31]. This is a limitation of using plastic as a substrate for photocatalyst coating.

This study introduced a new method for preparing silver doped titanium dioxide thin film coated on polyvinyl chloride (PVC). This visible-light-responsive photocatalyst was characterized via many analytical instruments and the photocatalytic reactivity of the prepared thin film was examined by photocatalytic decolorization of methylene blue dye (MB) and the degradation of gaseous BTEX under visible light. Additionally, the influence of silver content on the reaction kinetic has been proposed.

**Experimental Procedures**

**Preparation of TiO$_2$ and Ag/TiO$_2$ thin film**

The precursory titanium solution (TiO$_2$) was prepared with the molar ratios of Ti (C$_4$H$_9$O)$_4$: C$_2$H$_5$OH: C$_6$H$_5$O$_2$: H$_2$O: HNO$_3$ as 1:18:0.5:2:0.2 [16] via sol-gel technique. Silver nitrate (AgNO$_3$) was used as a source of Ag dopant. The various concentrations of the Ag/TiO$_2$ gel were prepared by dissolving silver nitrate solution with 0.01-0.2 mol of Ag content into the TiO$_2$ solution. Then, the mixture was stirred vigorously for 1 h before refluxed at 80°C for 8 h until the gel was homogeneous and transparent. Polyvinyl chloride (PVC) sheets (1x20x30 mm) were used as thin film substrates. The PVC sheet was cleaned with ethanol and rinsed with deionized water and dipped into the ready-mixed gel using automatic dip coater. The withdraw speed was controlled at 10 cm min$^{-1}$. After that the TiO$_2$ and the Ag/TiO$_2$ thin films were cured with 125-W UV lamp for 20 min to activate the photocatalytic reactivity of the film and improve the adherence between the film and the substrate.

**Characterizations**

The crystalline patterns of TiO$_2$ and Ag/TiO$_2$ thin films deposited on the PVC substrates were recorded by X-ray diffraction spectrometer (XRD) with the model D8 Advance with Eulerian Cradle; Bruker using Cu Ka radiation at a scan rate of 20-80°. The accelerating voltage and the applied current were 40kV and 40 mA, respectively. The UV-vis spectra of thin films obtained by UV-vis NIR spectrophotometer (Hitachi U-4100) was used to measure the wavelength absorption
of samples in a range of 300-800 nm. The water contact angle measurement, following the ASTM F22–02 method, was used to determine the hydrophilicity of the thin film [32]. The morphology of the thin films coupled with energy dispersive X-ray analysis (EDX) used for the determination of the presence of the elements Ti and Ag, was investigated by using JEOL JSM-5410 scanning electron microscope.

Photocatalytic activity

The visible-light photocatalytic reactivity of the prepared thin films was determined by the decolorization of methylene blue solution under fluorescence irradiation (18 W fluorescence lamp, Philip). The 6 cm² TiO₂ and Ag/TiO₂ thin films deposited PVC substrates were placed in petri dishes, containing 15 mL of 10⁻⁵ M methylene blue solution. The 5 mL of methylene blue solution was sampled every 60 min and measured by UV/vis spectrophotometer (Genesys 10-S, Thermo Electron Corporation) at maximum wavelength absorption intensity (λ_max) 664 nm. Then the solution sample was taken back into the same container for continuous measuring. The photodecolorization rate was examined from the relationship between ln C₀/C and times, which is in accordance with first order reaction, as shown in Eq. 1.

\[ \ln \frac{C_0}{C} = kt \]  

Where: C₀ and C are the initial concentration and the concentration at time (t), respectively, t is an irradiation time and k is the first-order rate constant.

The Ag/TiO₂ thin film which provides the best performance for decolorization of methylene blue was then selected for the photodegradation of gaseous BTEX. The experiment was carried out in a batch reactor (23×32×13 cm), coated with Ag/TiO₂ thin film on the inner covers. The size of PVC sheets (0.1x8x25 cm) were used as thin film substrates. The reactor was equipped with two 8 W fluorescence lamps and two blowers. The mixed BTEX gas with the concentration of 25 mg L⁻¹ was flown into the reactor. Afterward the lamps were turned on and the 0.5 mL of gas was collected every 30 min for measuring the remaining concentration of BTEX by gas chromatography/flame-ionization detector (GC/FID, Shimadzu GC-14B). The injection temperature of 100°C, column temperature of 100°C and detection temperature of 150°C were set up for GC analysis. The schematic diagram of this process is shown in Fig.1.

![Fig. 1, Schematic diagram of experimental procedure.](image-url)
Results and Discussion

Characterizations

The XRD pattern of the pure TiO\textsubscript{2} exhibits the peaks of anatase TiO\textsubscript{2} at 2θ equal to 25º (1 0 1), 37º (1 1 0), 48º (2 0 0), 54º (2 1 1), and 62º (2 0 4), as shown in Fig. 2. No rutile TiO\textsubscript{2} is observed in all samples. The Ag/TiO\textsubscript{2} thin films shows the peaks of nanosilver (Ag\textsuperscript{0}) at 2θ equal to 38º (1 1 1), 44º (2 0 0) and 64º (2 2 0). This result confirms that the prepared Ag/TiO\textsubscript{2} thin films are the composite between Ag and anatase TiO\textsubscript{2}. Furthermore, it is noticed that the growth of anatase TiO\textsubscript{2} crystal with the hkl planar (1 1 0) and (2 0 4) is tentatively disturbed when Ag is doped on the TiO\textsubscript{2} thin film.

![XRD patterns of TiO\textsubscript{2} and Ag/TiO\textsubscript{2} thin films coated on PVC.](image)

The UV-vis diffused speectra of the pure TiO\textsubscript{2} and Ag/TiO\textsubscript{2} thin films with different Ag contents are displayed in Fig. 3. It is obviously seen clear that doping Ag on TiO\textsubscript{2} thin film causes bathochromic effect, a shift of a spectral band to higher all the samples doping Ag reveal the red shifts of wavelength, or commonly called “red shift” absorption edge upon increasing content of Ag. This effect has an advantage in lower band gap energy of TiO\textsubscript{2}, in other words, lower energy required for electron excitation from valence band to conduction band. The band gap energy (eV) of each samples were calculated by using Eq. 2.

\[
E = \frac{hC}{\lambda}
\]

Where, \(\lambda\) is a cut-off wavelength (m), C is a speed of light (3.0 x 10\textsuperscript{8} m/s) and h is the Planks constant (6.626 x 10\textsuperscript{-34} Js).
According to Table 2.1, the band gap energy values of Ag/TiO$_2$ samples are lower than that of TiO$_2$ thin film. The band gap energy values of Ag/TiO$_2$ thin film are decreased from 2.84 to 2.65 eV when Ag contents are increased from 0.01 to 0.2 mol. This result is in agreement with the result from the UV-VIS spectroscopy. Some studies reported that doping Ag in the TiO$_2$ thin film resulted in more electron excitation due to surface plasmon resonance [33-34]. Some researchers suggested that the role of Ag is not only reducing band gap energy but also retarding the charge recombination that advantages for the photocatalytic performance [15, 26, 33-36].

The 1 mL of water droplet was dropped onto the surface of the thin film and the contact angle of that water droplet was then measured from the optical images as presented in Fig.4. The lower water contact angle, the more hydrophilicity. The water contact angles of the PVC substrate and TiO$_2$ thin film are 84º and 78º, respectively. While the water contact angles of the 0.01, 0.05, 0.1 and 0.2 Ag/TiO$_2$ thin films are 74º, 72º, 67º and 85 º, respectively.

It is obviously seen that the hydrophilicity of the TiO$_2$ thin film can be enhanced by Ag doping due to surface plasmon resonance. Interestingly, the 0.1 Ag/ TiO$_2$ thin film exhibits the highest hydrophilicity among all thin films. Theoretically, the addition of noble metal to a photocatalytic
A semiconductor can improve the hydrophilic property. A major role of Ag corporate in TiO\textsubscript{2} is to generate oxygen anion radicals (O\textsubscript{2}\textsuperscript{-}) and reactive center (Ti\textsuperscript{3+}) as shown in the following reactions [27].

\[
\begin{align*}
e^- + \text{Ag} & \rightarrow \text{Ag}^- \\
\text{Ag}^- + \text{Ti}^{4+} & \rightarrow \text{Ag} + \text{Ti}^{3+} \\
\text{Ag}^- + \text{O}_2 & \rightarrow \text{Ag} + \text{O}_2^-
\end{align*}
\]

Therefore, increasing of Ag content can increase O\textsubscript{2}\textsuperscript{-} and Ti\textsuperscript{3+} particles which have the advantage on the prevention of electrons-holes pairs recombination. When, the 0.2 mol Ag content was incorporate in TiO\textsubscript{2} thin film, the hydrophilicity of the film was decreased dramatically due to the excess Ag. The agglomerated particles of the excess Ag can become recombination centers, resulting in the retardation of electron localization along the surface [38]. This phenomenon causes the adverse effect on the photocatalytic reactivity of the catalytic film.

The self-cleaning application is a co-benefit of increasing hydrophilicity of the film. The dirt can be removed by sheeting water caused by the hydrophilic surface. Highly hydrophilic surface has a potential to adsorb much water, in the other words, many hydroxyl radicals (\textsuperscript{•}OH) are generated and acts as active oxide species in the photocatalytic reaction [26]. In addition, it attributes the increasing of oxygen anion radicals (\textsubscript{O}2\textsuperscript{-}) which can degrade some adsorbed pollutants on the substrate surface.

**Fig. 4.** Water droplets photos on (a) PVC, (b) TiO\textsubscript{2}, (c) 0.01 Ag/ TiO\textsubscript{2}, (d) 0.05 Ag/TiO\textsubscript{2}, (e) 0.1 Ag/ TiO\textsubscript{2}, and (f) 0.2 Ag/ TiO\textsubscript{2} thin films.

**Photocatalytic activity: Decolorization of methylene blue solution (MB)**

The photocatalytic performance of the catalytic thin films on the decolorization of MB solution under fluorescence irradiation was presented in Fig. 5. It is clear that the photolysis and the photocatalysis of MB solution did not occur when using the bare PVC sheet (without any coating). However, the concentration of the MB solution was decreased gradually when the TiO\textsubscript{2} and Ag/TiO\textsubscript{2} thin films were used as photocatalytic thin films. The MB decolorization efficiency of TiO\textsubscript{2} thin film is 30% and can be increased by doping with Ag. The maximum decolorization efficiency belongs to the 0.1 Ag/TiO\textsubscript{2} thin film (82%). The photocatalytic degradation efficiencies of TiO\textsubscript{2} and 0.1 Ag/TiO\textsubscript{2} thin film per unit area are 5% and 14% per cm\textsuperscript{2}. The plots of the first-order reaction of MB decolorization using TiO\textsubscript{2} and Ag/TiO\textsubscript{2} thin films are displayed in Fig. 6. The reaction kinetics of all films are fit well with the first-order reaction model. The rate constants (k) of TiO\textsubscript{2} and Ag/TiO\textsubscript{2} thin films at the molar ratio of Ag as 0.01, 0.05, 0.1 and 0.2 are 0.0282, 0.062, 0.0894, 0.1417 and 0.1168 (h\textsuperscript{-1}), respectively as shown in Fig 7. It is demonstrated that the optimal Ag doping into TiO\textsubscript{2} thin film is 0.1. More than its optimum, the agglomeration of Ag particles occurs, leading to the electron and hole recombination problem [38]. The mechanism of MB decolorization under fluorescence by the TiO\textsubscript{2} catalytic thin film can be explained by the ionic reaction between the positive charges of dissolved MB molecules and the negative charge species such as hydroxyl radical (\textsuperscript{•}OH) and oxygen radicals (\textsubscript{O}2\textsuperscript{-}). When the optimal Ag content is doped into the TiO\textsubscript{2} thin film, the quantity of free electrons are significantly increased and then the surface plasmon resonance occurs. Thus, it can be said that the roles of Ag are not only decreasing band gap energy but also promote charge separation efficiency.
Fig. 5, Photodecolorizations of MB using TiO$_2$ and Ag/TiO$_2$ thin films coated on PVC under fluorescence irradiation.

Fig. 6, Plots of the first order reaction of MB photodecolorization by TiO$_2$ and Ag/TiO$_2$ thin films under fluorescence irradiation.

Fig. 7, First-order reaction rate constants (k, h$^{-1}$) for photodecolorization of MB by Ag/TiO$_2$ thin films with different Ag contents.
Photocatalytic activity: Degradation of gaseous BTEX

The comparisons of photocatalytic degradation of gaseous BTEX between TiO$_2$ and 0.1 Ag/TiO$_2$ thin film are illustrated in Fig. 8 (a) and (b), respectively. TiO$_2$ thin film has much lower degradation efficiency than 0.1 Ag/TiO$_2$ thin film. The maximum degradation efficiencies of TiO$_2$ thin film for all BTEX gases are less than 20%. In contrast, the degradation efficiencies of benzene, toluene, ethylbenzene and xylene achieved by 0.1 Ag/TiO$_2$ thin film are 79, 83, 86 and 89%, respectively. The calculated photocatalytic degradation efficiency per unit area is in a range of 0.40-0.45% per cm$^2$. The plots of first-order reaction of gaseous BTEX degradation using 0.1 Ag/TiO$_2$ thin film are presented in Fig. 9. All plots are linear relationship with high coefficient of determination ($R^2$). The first-reaction rate constants determined from the slope of the plot are 0.0062, 0.0072, 0.0082 and 0.0098 min$^{-1}$ for the photodegradation of benzene, toluene, ethylbenzene and xylene, respectively. It is noted that among BTEX gases, the degradation of xylene is the easiest but the degradation of benzene is the most difficult. This is due to two possible reasons. The dipole moment of each gas plays an important role when reacted with other reactive species. For example, benzene itself has no dipole moment which leads to its lowest reactivity for photocatalytic reaction compared with the others. Another reason is difference of adsorptivity of each gas onto the film surface. The more gas adsorption, the higher potential to be degraded by reacting with hydroxyl radicals generated from the photocatalytic surface. This is in agreement with Ao C. H. (2003) [35].

Fig. 8, Photocatalytic degradation of gaseous BTEX under fluorescence irradiation by (a) TiO$_2$ thin film and (b) 0.1 Ag/TiO$_2$ thin film.
**Fig. 9.** First order reaction rates of gaseous BTEX degradation by 0.1 Ag/TiO$_2$ thin films under fluorescence irradiation.

**Fig. 10.** SEM and EDX mapping images of thin films coated on PVC (x 20,000) (a) TiO$_2$, (b) 0.1 Ag/TiO$_2$.

Fig. 10 shows the surface morphology analyzed by scanning electron microscope of typical undoped TiO$_2$ (a) and 0.1 Ag/TiO$_2$ thin films (b) at the same magnification of 20,000. It is obviously seen that the undoped TiO$_2$ has smoother and more homogeneous film surface than the Ag doped TiO$_2$. Some cracks and aggregates of element particles are found in the Ag doped TiO$_2$ thin film. Interestingly, it can be said that the Ag doped TiO$_2$ thin film is porous thin film with well pore size distribution and the approximate pore size of 0.2 nm. The EDX mapping indicates the evidences that both TiO$_2$ and Ag atoms are well dispersed throughout the film surface.

The thickness of the TiO$_2$ and 0.1 Ag/TiO$_2$ thin films are determined from the cross-section image analysed by scanning electron microscope as illustrated in Fig 11 (a) and (b), respectively. According to the definition of thin film [37], both prepared films are defined as thin film (thickness < 100 nm). The estimated thickness of the 0.1 Ag/TiO$_2$ thin film is 87 nm, a bit thicker than that of TiO$_2$ thin film (82 nm). Moreover, it can be seen that the treatment of the Ag/TiO$_2$ film coated on PVC by UV curing can enhance not only the crystallization but also the adhesion of the catalytic thin film.
Conclusions

The visible-light responsive Ag/TiO$_2$ thin film coated on PVC material can be achieved via sol-gel method followed by dip coating. UV curing technique can be applied for activating anatase TiO$_2$ photocatalytic reactivity of the prepared film without any damage of plastic materials. The cured thin film possesses good surface properties such as good adhesion, high porosity and good Ag distribution onto the TiO$_2$ thin film. The optimal Ag doping (0.1 mole) to TiO$_2$ thin film provides the synergistic effect on the photocatalytic reactivity. Ag plays an outstanding role in increasing hydrophilicity as well as extending the light absorption spectrum toward the visible region which are beneficial for photocatalytic activity.

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