Degradation of acetaldehyde by Ag/TiO$_2$ photocatalyst coated on polyester air filter

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Abstract. Acetaldehyde is a toxic mainstream in cigarette smoke. This study aims to apply Ag/TiO$_2$ coated on a polyester air filter (PET) to degrade acetaldehyde. Ag/TiO$_2$ was prepared by doping 10 mol% of silver (Ag) on TiO$_2$ via impregnation method. The crystallinity and wavelength absorption of Ag/TiO$_2$ particles were characterized by X-ray Diffraction (XRD) and UV-vis NIR spectrophotometer, respectively. Then, the Ag/TiO$_2$ particles were mixed with two different binders such as Polyethylene glycols (PEG, Mw = 6,000 g/mol) and Polyacrylic acid (PAA) before coating on PET filter by dip-coating technique. The percentages of binder were varied from 0.3, 1, 3 and 5wt% by weight of photocatalyst particles. The photocatalytic activities of PET filters coated by Ag/TiO$_2$ with different binders were examined by decolorization of 10$^{-5}$ M methylene blue (MB) solution and degradation of acetaldehyde under visible light irradiation. The XRD results indicated that Ag/TiO$_2$ had the combination of anatase phase, silver oxide (AgO) and metallic silver (Ag). After doping, the band gap energy of TiO$_2$ was reduced from 3.28 eV to 3.22 eV (red-shift effect). The PET filters coated with 5% PEG-Ag/TiO$_2$ and 3% PAA-Ag/TiO$_2$ showed the MB decolorization efficiency of 88 % and 87%, respectively. The photocatalytic degradation of acetaldehyde was carried out by 3%PAA-Ag/TiO$_2$. The degradation efficiency of acetaldehyde by 3%PAA-Ag/TiO$_2$ filter was 96% within 96 h. The concentration of CO$_2$ which was a product of photocatalysis increased simultaneously during the reaction. This was an evidence that acetaldehyde was degraded by the photocatalytic air filter.

1. Introduction

Cigarette smoke is one of the main causes of lung disease. In cigarette, there are more than 5,000 chemicals and at least 50 compounds are carcinogens [1]. Volatile Organic Compounds (VOCs) such as carbonyls, tars and aldehyde are major compounds found in cigarette smoke. The emissions from cigarette impacted on indoor air quality and increased of particulates which caused airborne diseases to not only smokers but also non smokers.

Among VOCs from cigarette smoke, acetaldehyde is the main product which can induce sensory irritation and itself is a carcinogen agent [2-3]. The reduction of acetaldehyde can be carried out in various techniques such as adsorption [4-5], immobilized activated sludge [6], ozonation [7] and plasma oxidation [8-9]. However, these methods have limitation for use and are unsustainable [10].

Recently, the photocatalytic oxidation method has been proved as a promising method to clean up air pollution. Titanium dioxide (TiO$_2$) is a well-known photocatalyst due to its non-toxic, good stability, good chemical resistance, high photocatalytic reactivity and low cost [11]. During the photocatalysis, TiO$_2$ generates reactive free radical species (OH, O$_2$) which convert various kinds of air pollutants to...
harmless end products (CO₂, H₂O) [12]. The photocatalysis of TiO₂ is preferable under UV irradiation due to its large energy band gap (3.2 eV). This mechanism leads to the limitation when TiO₂ is applied under visible light irradiation or indoor environment [13]. To overcome this problem, many researchers focused on the modification of TiO₂ by doping noble metals, which enhances the photocatalytic performance of TiO₂ under visible light irradiation [14-18]. Among those noble metals, silver (Ag) is an attractive dopant for TiO₂. Ag can reduce the band gap energy of TiO₂, promote electron-hole separation, and increase the interfacial electron transfer process due to Schottky barrier formation [8,19-20]. The photocatalytic treatment of air pollutants are commonly carried out by coating photocatalysts on substrates such as fiberglass filter [18], carbon filter [21], high efficiency particulate air (HEPA) filter and Polyester (PET) filter [20]. To increase the adhesion between the photocatalyst and the substrate, binders such as polyacrylic acid (PAA) and polyethylene glycol (PEG) are commonly used in the coating process [20,22,23].

Thus, this study aimed to synthesize Ag doped TiO₂ particles (Ag/TiO₂) by impregnation and coat the photocatalyst particles on polyester (PET) air filter by using two different binders which were PAA and PEG. The photocatalytic activity of the photocatalytic filter was examined by photocatalytic decolorization of methylene blue and acetaldehyde degradation under visible light irradiation.

2. Experimental

2.1. Materials
Titanium dioxide (TiO₂, commercial grade), silver nitrate (AgNO₃, Fluka, 99%), nitric acid (HNO₃, Merck, 65%) were used for the preparation of Ag/TiO₂. Methylene blue (MB, Merck, AR grade) was used to determine the photocatalytic performance of the Ag/TiO₂ photocatalyst. The binders used in this study were polyethylene glycol (PEG from Merck, molecular weight = 6,000 g/mol) and polyacrylic acid (PAA, commercial grade). Acetaldehyde (C₂H₄O from Alfa Aesar, 99%) was used for the photocatalytic degradation test.

2.2. Characterization
Crystallinity and phase identification of TiO₂ and Ag/TiO₂ particles were examined by X-ray diffractometer with CuKα radiation (λ=1.5406Å for the 20 range from 20-80°). The light absorption properties of photocatalyst particles were determined by UV-vis spectrometer with the wavelengths of 300-400 nm. The porosity of the photocatalyst particles was measured via the Brunauer-Emmett-Teller (BET) method.

2.3. Ag/TiO₂ particles preparation
Ag/TiO₂ particles were prepared by impregnation method. In the synthesis process, 30 g TiO₂ particles were dispersed in 100 mL deionized water and 10% of AgNO₃ was added to TiO₂ suspension. The slurry was stirred for 3 h. Then the slurry was dried in an air oven at 105°C for 12 h. The dried solids were calcined at 550°C for 5 h in a furnace.

2.4. Preparation of the photocatalytic air filter
The polyester (PET) air filters were used in this study. The air filters were cut to size 40×35 cm. The coating suspension was prepared using PAA and PEG as binders. Five grams of the photocatalyst particles (TiO₂ or Ag/TiO₂) were mixed with the binders at different concentrations of 0.3, 1, 3 and 5% by weight of the photocatalyst particles. Then the PET air filters were dipped into the coating solution for 30 min while the solution was stirring. The coated air filters were dried in the ambient air for overnight. Finally, the coating filters were dried at 65°C for 12 h.

2.5. Photocatalytic decolorization of MB solution by photocatalyst particles
The photocatalytic activity of TiO₂ and Ag/TiO₂ particles was measured by the photocatalytic decolorization of MB solution under visible light irradiation. The standard solution of MB with the
concentration of $10^{-5}$ M MB was used as an organic model for the study of photocatalytic degradation. One gram of photocatalyst particle was added to 100 mL of MB solution. The solution was kept in the dark until the adsorption of MB on the photocatalyst particles was saturated. Then, the solution was irradiated under visible light. The photocatalytic decolorization of MB was monitored using UV-vis spectrometer at the wavelength of 664 nm. The concentration of MB in the solution was determined as a function of time. The degradation efficiency was calculated using the following equation (1):

$$\text{Photocatalytic degradation}\% = \frac{C_0 - C}{C_0} \times 100$$

Where, $C_0$ represents the initial concentration of MB solution and $C$ represents the remaining concentration of MB solution at the interval time.

2.6. Photocatalytic degradation of acetaldehyde by photocatalytic air filter
The photocatalytic degradation of acetaldehyde was examined by a batch experiment with 50 cm$^3$ of a stainless reactor under visible light irradiation. The coated or uncoated PET air filters were placed inside the reactor. The visible light sources were two LED lights. The initial concentration of acetaldehyde in the reactor was 50 ppm. The adsorption of acetaldehyde gas on the air filters was carried out in the dark. After the saturated adsorption, the lamps were turned on. The decrease of acetaldehyde concentration and the increase of CO$_2$ concentration were measured by UNICSENSOR® every hour.

3. Results and discussion

3.1. XRD analysis
The XRD patterns of TiO$_2$ and Ag/TiO$_2$ particles were shown in Fig. 1. The XRD pattern of bare TiO$_2$ showed the anatase characteristic peaks at 25.3, 37.8, 48.0, 53.9, 55.1, 62.7, 68.8 and 75 degree. The peaks were indexed as (101) (004) (200) (105) (211) (204) (116) and (215), respectively. These peaks coincided with the standard JCPDS card [17]. The XRD pattern of Ag/TiO$_2$ exhibits the additional peak at 44.2, 64.4 and 77.3, corresponding to (200) (220) and (330), respectively. These peaks indicated the presence of metallic silver. The peak at 38.1 revealed the presence of Ag$_2$O due to the oxidation of Ag during the calcination [26]. The average crystallite sizes of the TiO$_2$ and Ag/TiO$_2$ were determined from the main diffraction peak and calculated using Scherrer’s equation. After doping, the crystallite size of anatase in Ag/TiO$_2$ was decreased from 24.1 and 21.3 nm. This result indicated that the growth of anatase crystal was suppressed by an Ag dopant which was in agreement with other studies [18,27-28].

![Figure 1](image-url)
3.2. BET surface area
The BET surface area, pore volume and pore diameter of TiO$_2$ particles were 12.24 m$^2$g$^{-1}$, 0.029 cm$^3$ and 9.61 nm, respectively. When doping Ag into TiO$_2$, surface area, pore volume and pore diameter were 9.46 m$^2$g$^{-1}$, 0.018 cm$^3$ and 7.93 nm, respectively. It was found that the surface area of Ag/TiO$_2$ particles was decreased after doping Ag because Ag dopant could interfere the arrangement of anatase crystallization. This result agreed with the absorption of MB solution as discussed later on.

3.3. UV-visible absorption spectra
Fig 2 shows the UV-vis absorption spectra of the TiO$_2$ and Ag/TiO$_2$. It was found that the wavelength absorption of Ag/TiO$_2$ in a range of 300-700 nm increased significantly when compared with the bare TiO$_2$. This was attributed to charge transfer transition between the electrons of Ag and TiO$_2$ which could reduce the band gap energy between the conduction band and the valence band of TiO$_2$ [29-30]. Moreover, Ag nanoparticles on TiO$_2$ can trap the electrons resulting in the prevention of the electron-hole recombination [26,31]. The band gap energy for the TiO$_2$ and Ag/TiO$_2$ sample was calculated from equation (2)

$$E_g = \frac{hc}{\lambda_{\text{onset}}}$$

Where, $E_g$ is the band gap energy (eV), $h$ is the Planck’s constant (6.626×10$^{-34}$ Js), $c$ is a speed of light (3.0×10$^8$ m/s) and $\lambda$ is a cut-off wavelength (m)

The band gap energy of TiO$_2$ was 3.28 eV. After Ag was doped into TiO$_2$, the band gap energy was reduced to 3.22 eV. This result was in accordance with the wavelength absorptions as described previously.

![Figure 2. UV-visible absorption spectra of TiO$_2$ and Ag/ TiO$_2$ particles](image)

3.4. Photocatalytic decolorization of MB solution by the photocatalyst particles
The photocatalytic activity of TiO$_2$ and Ag/TiO$_2$ particles was studied by the decolorization of MB solution under visible light irradiation. Fig 3 illustrates the adsorption capacity of MB under the dark condition. The MB adsorption capacities of TiO$_2$ and Ag/TiO$_2$ particles within 3 h were 50% and 40%, respectively. The higher adsorbability of TiO$_2$ in the dark was due to its larger surface area. Fig 4 shows the photocatalytic decolorization of MB under visible light irradiation by TiO$_2$ and Ag/TiO$_2$. It was also found that MB solution itself could be decolorized under visible light. The MB decolorization efficiency
within 8 h of Ag/TiO$_2$ (81%) was significantly higher than that of TiO$_2$ (58%). This result indicated that Ag doping could enhance the photocatalytic reactivity of TiO$_2$. The mechanism of MB degradation under visible light by Ag/TiO$_2$ particles can be explained that the electrons of Ag migrate into the conduction band of TiO$_2$. The excitation electrons react with the absorbed O$_2$ on the surface of TiO$_2$ and produce super oxide radicals (O$_2^-$). The holes ($h^+$) of Ag react with the absorbed H$_2$O and generate hydroxyl radicals (OH$^-$). Both O$_2^-$ and OH$^-$ can be powerful oxidizing agents for the degradation of MB [17]. The roles of Ag are trapping electron, inhibiting recombination of the electron-hole pair and promoting charge separation efficiency [32-33].

![Figure 3](image1.png)

**Figure 3.** The adsorption of MB by TiO$_2$ and Ag/TiO$_2$ in the dark

![Figure 4](image2.png)

**Figure 4.** The photocatalytic decolorization of MB under visible light irradiation by TiO$_2$ and Ag/TiO$_2$ particles
3.5. Photocatalytic decolorization of MB solution by the photocatalyst loaded on PET filter

The TiO$_2$ and Ag/TiO$_2$ particles were loaded on PET filters by using PAA and PEG as binders. The amount of binder was varied from 0.3, 1, 3 and 5% by weight of the photocatalyst particles. The comparison of the photocatalytic decolorization of MB by the photocatalytic filters are illustrated in Fig 5 and 6. It was noticed that Ag/TiO$_2$ filter had much higher MB degradation efficiency than TiO$_2$ filter. In the case of PAA binder, 3%PAA-Ag/TiO$_2$ filter showed maximum degradation efficiency of 87%. When the PAA content was increased up to 5%, the MB degradation efficiency was decreased. This result was attributed to the agglomeration of the photocatalyst particles, resulting in the reduction of the surface area [34]. For the PEG binder, 5%PEG-Ag/TiO$_2$ filter gave higher degradation efficiency (88%) than the 3% PEG-Ag/TiO$_2$ filter. This was because PEG can be easily dissolved in water. Thus, more amount of binder was required to increase adhesion between the photocatalyst particles and the filter.

For the next experiment, the filter coated by 3%PAA-Ag/TiO$_2$ was selected due to its high efficiency but low binder amount.

3.6 Photocatalytic degradation of acetaldehyde by the photocatalytic filter

Fig 7 shows the photocatalytic degradation of acetaldehyde by uncoated filter and 3%PAA-Ag/TiO$_2$ filter as a function of irradiation time. The initial concentration of acetaldehyde was 37 ppm. The CO$_2$ concentration produced by acetaldehyde degradation is shown in Fig 8. For uncoated filter, the acetaldehyde concentration was decreased about 15% for entire period due to the adsorption mechanism. The adsorption of acetaldehyde by the photocatalytic filter under dark condition was about 25% within 20 h. After the LED lamps were switched on, the photocatalytic degradation of acetaldehyde reached 96% within 96 h. While the concentration of CO$_2$ increased from 325 ppm to 1150 ppm. Increase of CO$_2$ concentration was caused by the degradation of acetaldehyde [20-21, 23-25]. The mechanism of acetaldehyde oxidation was explained by the following equation (3) and (4). Acetaldehyde is converted to acetic acid and then acetic acid is finally degraded to CO$_2$.

\[
\begin{align*}
\text{CH}_3\text{CHO} + \text{H}_2\text{O} + 2h^+ & \rightarrow \text{CH}_3\text{COOH} + 2H^+ \quad (3) \\
\text{CH}_3\text{COOH} + 2H_2\text{O} + 8h^+ & \rightarrow 2\text{CO}_2 + 8H^+ \quad (4)
\end{align*}
\]

**Figure 5.** The MB decolorization efficiency of the PET filters coated by TiO$_2$ and Ag/TiO$_2$ particles with different PAA concentrations under visible light irradiation.
Figure 6. The MB decolorization efficiency of the PET filters coated by TiO$_2$ and Ag/TiO$_2$ particles with different PEG concentrations under visible light irradiation

Figure 7. Photocatalytic degradation of acetaldehyde by the photocatalytic filter under visible light irradiation
4. Conclusion

The Ag/TiO$_2$ particles prepared by impregnation method exhibited higher photocatalytic reactivity than bare TiO$_2$ particles under visible light irradiation. The roles of Ag were reducing band gap energy, increasing visible light absorption and inhibiting recombination of the electron-hole pair. The photocatalytic filter prepared by coating 3%PAA-Ag/TiO$_2$ on PET filter could degrade acetaldehyde with the efficiency of 96% within 96 h under visible light irradiation. The increase of CO$_2$ during the photocatalytic reaction confirmed the complete degradation of acetaldehyde. Thus, this photocatalytic filter could be applied for cigarette smoke treatment in the future.

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