Effect of Ag loading content on morphology and photocatalytic activity of Ag-TiO₂ nanoparticulate films prepared via simultaneous plasma-enhanced chemical and physical vapor deposition

Dianping Jiang, K Kusdianto, Masaru Kubo and Manabu Shimada

1 Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan
2 Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember (ITS), Kampus ITS Sukolilo, Surabaya 60111, Indonesia

E-mail: smd@hiroshima-u.ac.jp

Keywords: PECVD, PVD, annealing, morphology, photodegradation

Abstract

Ag loading is known to enhance the photocatalytic performance of TiO₂; however, the correlation between Ag and the resulting changes in TiO₂ morphology and particle size is not well understood. A plasma-enhanced chemical vapor deposition (PECVD) and physical vapor deposition (PVD) were used to prepare Ag-TiO₂ nanoparticulate thin films; the prepared films were annealed at 500°C under N₂ atmosphere. The Ag content was adjusted by the furnace temperature of the PVD system. Well-dispersed Ag nanoparticles on the surface of TiO₂ nanoparticles were observed and analyzed using transmission electron microscopy (TEM). The morphology, particle size, and photocatalytic activity of the films were evidently affected by the Ag content. TEM images showed that the TiO₂ nanoparticle size increased with increasing Ag content. Evaluation of the photocatalytic activity based on the degradation of methylene blue under ultraviolet (UV) light irradiation demonstrated that an Ag content of 2.2 wt% yielded the highest photocatalytic activity (5.5 times higher than that seen in a pristine TiO₂ film). This fabrication method has advantages because it adds Ag in a more controlled manner compared to the liquid-phase methods. Furthermore, our fabrication method can provide a way to vary the Ag content while considering the relationship between the photocatalytic performance and the Ag content.

1. Introduction

Ag-TiO₂ nanoparticles heterogeneous photocatalysts are known to have higher photocatalytic activity than TiO₂ because the metal-semiconductor junction between TiO₂ and Ag acts as an electron acceptor, reducing the rate of electron-hole recombination during the photocatalytic reaction [1]. To prepare Ag-TiO₂ nanoparticles, various routes have been taken, and can be categorized as liquid-phase and gas-phase methods. However, commonly used liquid-phase methods that include the sol-gel process [2], microwave-assisted hydrothermal reaction [3], and the photoreduction-thermal treatment [4] have several disadvantages, such as having multiple preparation steps, a long reaction time, and a laborious residues/impurities removal process. However, a few gas-phase methods regarded as one-step processes, such as ultrasonic spray pyrolysis [5] and flame spray pyrolysis [6], involve significant agglomeration of nanoparticles owing to the high temperatures that arise during reaction and deposition. Moreover, it should be noted that the preparation process of most of these methods involves the photoreduction of Ag ions to metallic Ag nanoparticles by TiO₂ [4], other reducing agents [7], or thermal decomposition from silver nitrate [5, 8]. Thus, the Ag ions introduced into the TiO₂ matrix can influence the morphology [9] and the crystallization [10] of TiO₂ during reduction and heat treatment.

To the best of our knowledge, our fabrication method of preparing Ag-TiO₂ nanoparticulate films involving simultaneous plasma-enhanced chemical vapor deposition (PECVD) and physical vapor deposition (PVD), is the first to use Ag nanoparticle aerosols [11]. In this method, the content of metallic Ag nanoparticles in the films
can be easily controlled by the furnace temperature through a change of the amount of Ag vapor. Moreover, the morphology of the nanoparticles generated during PECVD can also be altered by adjusting various factors, such as the RF (radio frequency) power (supplied to the plasma reactor), gas flow rate, and the precursor content [12]. In our previous research, wherein we used the PECVD-PVD system, showed that the presence of Ag nanoparticles not only increases the photocatalytic activity but also influences the morphology and phase transformation of the TiO2 nanoparticles. After loading the Ag nanoparticles and annealing the films, the TiO2 nanoparticles exhibited a larger size, and the photocatalytic performance of the Ag-TiO2 film was observed to be better than that of a pristine TiO2 film [11].

Our findings were consistent with those of numerous reports that explained the influence of the added Ag on the morphology [2, 10, 13], phase growth [2], and phase transformation of TiO2 [10]. According to a few researchers, the diffusion and agglomeration of Ag nanoparticles during heat treatment can inhibit the growth of the anatase phase and increase the total boundary energy, thereby influencing the morphology and phase transformation of TiO2 from the anatase to the rutile phase [2, 13]. A few researchers proposed that Ag doping increases the oxygen vacancies in the TiO2 lattice, thereby promoting the anatase-to-rutile transformation [10, 14, 15]. In addition to the doping effect, the loading effect of Ag nanoparticles on the TiO2 surface was also investigated. Since most of the TiO2 nanoparticles were well crystallized, it was deduced that the loaded Ag nanoparticles did not have a significant effect on the morphology and the crystal structure of TiO2 [4, 16–18]. On the other hand, a study by Garcia-Serrano et al [9] showed that silver oxide and metallic Ag have the opposite effect on the phase transformation of TiO2. This result was obtained by preparing Ag-TiO2 nanoparticles using the sol-gel method and conducting a heat treatment under different ambient gases to obtain silver oxide-TiO2 and metallic Ag-TiO2 nanoparticles. Therefore, despite previous research, the influence of the addition of Ag (especially through loading) on the morphology and crystal structure of TiO2 nanoparticles during heat treatment, very important to the photocatalytic activity of the prepared Ag-TiO2 nanoparticles, remains unclear.

In this study, we investigated the effects of the loading content of metallic Ag nanoparticles on the morphology, crystallinity, and the photocatalytic activity of the Ag-TiO2 nanoparticulate films prepared using simultaneous plasma-enhanced chemical vapor deposition (PECVD) and physical vapor deposition (PVD).

2. Materials and methods

2.1. Materials and experimental set-up

The set-up used for the synthesis of the Ag-TiO2 nanoparticulate thin films that were prepared using PECVD and PVD consisted of a PVD apparatus (used for generating Ag nanoparticles), plasma reactor (used for generating TiO2 nanoparticles), and a deposition chamber. A similar process was described in our previous reports [11, 19, 20].

In our study, the Ag nanoparticles were generated through PVD that involves the process of evaporation and condensation. High-purity Ag (Nilaco Corp.) was evaporated in a ceramic crucible placed in a tube furnace (TMF-300N, AS ONE). The generated Ag vapor was transported to a water-cooling system where it condensed to form Ag nanoparticles. An argon gas stream of 700 sccm was used as the carrier. To obtain Ag contents of 0, 0.5, 0.6, 2.2, 4.7, and 7.4 wt%, the heating temperature of the furnace was set to 25 °C, 1040 °C, 1080 °C, 1100 °C, 1160 °C, and 1200 °C, respectively. We have used this experimental system to prepare Ag-TiO2 films in our pervious study [11]. In this study, we improved the system so that the Ag content of the fabricated film was mainly adjusted by the number density of Ag nanoparticles. The number density significantly increased with an increase in the furnace temperature. This is because more amount of Ag vapor is produced at a higher furnace temperature, which increases the nucleation rate in the formation of Ag nanoparticles [21].

On the other hand, the TiO2 nanoparticles were synthesized through the plasma reaction of titanium tetraisopropoxide (TTIP; Kanto Chemical Co., Inc.) that was diluted using an argon carrier gas-stream of 300 sccm. To vaporize TTIP, a flow of argon carrier gas (3 sccm) was fed into a stainless steel, laboratory-made bubbler that was set to a temperature of 50 °C. Subsequently, the argon carrier gas, which was saturated with the TTIP precursor, was transported to a cylindrical plasma reactor that was connected to a RF power supply (100 W, 13.56 MHz, AX–1000IP; Adtec Plasma Technology Co., Ltd) and a matching network.

In the deposition chamber, a silicon substrate was placed on a support, which was placed perpendicular with respect to the direction of the main flow. The support was supplied a positive voltage of 500 V. The time for the deposition was set to 30 min. The samples were annealed at 500 °C for 3 h under a nitrogen atmosphere. The annealed films were measured based on the weight of the substrate by using a digital lab scale (MSA6.6S0TRDM01; Sartorius) and were selected based on the similarity of their weight (0.07 mg ± 5%) to avoid errors during the photocatalytic experiment.
2.2. Characterization
The crystal structures of the prepared films were analyzed by x-ray diffraction (XRD, MiniFlex 600, Rigaku) measurements performed in the 20°–60° range. The x-ray diffraction unit was equipped with a Copper Kα radiation (λ = 1.5406 Å) source. The surface morphologies of the prepared films were observed by using scanning electron microscopy (SEM, S-5200; Hitachi High-Technologies) and transmission electron microscopy (TEM; JEOL JEM-2010). An energy dispersive X-ray spectroscopy (EDX) equipped with TEM was employed for elemental analysis. Furthermore, geometric mean diameters (GMDs) of the nanoparticles were calculated from TEM images by using equation (1) [19, 20]:

\[
\log (\text{GMD}) = \left( \frac{1}{n} \sum \log d_i \right) / n, 
\]

where \( n \) is the number of measured particles, and \( d_i \) is the diameter of \( i \)-th particle.

Inductively coupled plasma optical emission spectrometry (ICP-OES, SPS 3000; Hitachi High-Technologies) was used to analyze the elements quantitatively. Firstly, the prepared films were dissolved in 3 ml HNO₃ solution (Kanto Chemical Co., Inc.) at 200 °C. Subsequently, the solutions containing Ag ions were cooled down and filtered through a 0.45 µm polytetrafluoroethylene (PTFE) filter (RephiLe Bioscience, Ltd). Finally, the filtered samples were analyzed by using ICP-OES, and the mass concentrations of Ag (mg l⁻¹) were determined from the calibration curve that were constructed using Ag standard solutions; the content of the Ag standard solutions ranged from 0 to 10 mg l⁻¹. The mass fractions (\( \omega \)) of Ag in the Ag-TiO₂ nanoparticulate thin films were estimated using equation (2):

\[
\omega = \rho \frac{V}{m},
\]

where \( \rho \) is the mass concentration obtained from ICP-OES, \( V \) is the diluted volume of HNO₃ solution, and \( m \) is the weight of the film after annealing.

2.3. Photocatalytic experiment
The photocatalytic activities of the Ag-TiO₂ nanoparticulate thin films were evaluated by monitoring the photocatalytic degradation of a methylene blue (MB) aqueous solution under UV irradiation. To evaluate the photocatalytic activity in individual samples, we tested the photocatalytic decomposition of methylene blue (MB) in solution under a UV light as a function of the irradiation time. The thin films were placed in a cuvette cell with 3 ml of MB aqueous solution (2 mg l⁻¹). The photocatalytic experiment was performed in a dark chamber that was irradiated by a UV lamp (365 nm, 1 W cm⁻²). The absorbance of the MB aqueous solution at 664 nm was determined by using a UV–vis spectrophotometry (V-650, Jasco). The absorbance was recorded before as well as during irradiation; during irradiation the observations were recorded after every 1 h with the last reading carried out at the 5th hour. A calibration curve for MB was used to convert the absorbance to MB concentration [MB concentration = 3.23 \times MB absorbance (mg l⁻¹)]. The photocatalytic activities of the films were evaluated based on the rate constant of the MB degradation (\( k \)) at a given time by using equation (3):

\[
\ln(C_0/C_t) = kt,
\]

where \( t, C_0, \) and \( C_t \) stand for the irradiation time, the initial MB concentration, and the MB concentration after irradiation time \( t \), respectively.

3. Results and discussion
3.1. Characterization of Ag-TiO₂ nanoparticulate films by x-ray diffraction (XRD)
Figure 1 shows the XRD patterns in the 2θ range of 20–60° for a pristine TiO₂ nanoparticulate film and 0.5 wt%, 0.6 wt%, 2.2 wt%, 4.7 wt%, and 7.4 wt%-Ag-TiO₂ nanoparticulate films. The peaks observed at 25.4°, 38.3°, and 48.5° correspond to the (101), (004), and (200) planes of the anatase phase of TiO₂ [19]. Only the anatase phase is observed in the XRD patterns. The absence of Ag peaks can be ascribed to the small size and low amount of Ag nanoparticles in the Ag-TiO₂ nanoparticulate thin films, which is in agreement with the findings of our previous work [11]. Generally, a small crystallite size in small nanoparticles leads to broad peaks in XRD patterns. As a similar case, Zhang et al. [22] and Zhang et al. [23] stated that peaks of Au were hardly detected in the XRD patterns of silica nanotubes and TiO₂/ZnO nanofibers with small (3–10 nm) and well dispersed Au nanoparticles. The absence of Au peaks was ascribed there to the size of the Au nanoparticles. In this study, the low amount of Ag is considered to have led to small signals, which can also be a reason for the absence of Ag peaks.
3.2. Characterization of Ag-TiO₂ nanoparticulate films by using SEM

Surface morphologies of the films were investigated by using SEM. The SEM images of the pristine TiO₂ and Ag-TiO₂ nanoparticulate films after annealing are shown in figure 2. We observed that the porous matrix is formed through the connection of TiO₂ nanoparticles. The inner structure and porosity of the films are apparently unaffected by the Ag content.

3.3. Characterization of Ag-TiO₂ nanoparticulate films by using TEM and EDX

Figure 3 shows the TEM images of the Ag nanoparticles prepared by PVD at different furnace temperatures. The deposition time of the Ag nanoparticles on the TEM grid was 10 s. Dark, spherical spots, indicating the presence of Ag nanoparticles, are clearly observed in figures 3(a)–(c).

Furthermore, variations in the particle size and the morphology of TiO₂ in the pristine TiO₂ and Ag-TiO₂ nanoparticulate films corresponding to the different Ag contents, were observed by using high-resolution TEM (figure 4). In figure 4(a), the pristine TiO₂ nanoparticles coalesce to form a fiber-like structure after annealing. The darker areas that appear in the TEM image are due to overlapping TiO₂ nanoparticles. The morphology of
the Ag-TiO2 nanoparticles does not change significantly when the Ag content is below 2.2 wt% [figures 4(b)–(c)]. However, when the Ag content is between 2.2 wt% and 7.4 wt%, several small dark spots are evidently seen (∼2 nm) on the surface of the TiO2 nanoparticles. These nanoparticles show an increase in density with the increase in Ag content [figures 4(d)–(f)]. The dark spots [shown by arrows in (d), (e), and (f)] are Ag nanoparticles that are uniformly dispersed in the TiO2 matrix. In contrast, these dark spots are absent on pristine TiO2. This confirms that Ag peaks cannot be detected in the XRD pattern because of the uniform and extremely small dispersion of Ag nanoparticles in the TiO2 matrix.

Further component analysis of figures 4(a) and (f) was carried out, and the results are shown in figures 5(a) and (b), respectively. In figure 5(a), the characteristic peaks corresponding to Ag and centered at around 3 keV do not appear in the EDX spectrum of the pristine TiO2 film. However, the characteristic Ag peaks appear in figure 5(b), confirming the existence of Ag in the Ag-TiO2 nanoparticulate film.

Figure 6 shows the high-resolution TEM image of small and dark Ag nanoparticles in the Ag-TiO2 nanoparticulate film that has 7.4 wt% Ag. The nanoparticles have sizes below 3 nm and are uniformly dispersed on the surface of the TiO2 nanoparticles.

The GMDs of the TiO2 nanoparticles in the Ag-TiO2 nanoparticulate films are shown in figure 7. This parameter increases with the increasing Ag content, especially above 2.2 wt% of Ag. The influence of the added Ag nanoparticles on the particle size of a supporting material was confirmed in our previous study [11]. Dehimi et al. reported that, after annealing, the average particle size of ZnO particles increases with increasing Ag content of up to 0.5 at.% [24]. He et al. also reported that as the Ag dopant content in the Ag-TiO2 nanoparticles...
increases, the anatase grain size increases [2]. Thus, it is considered that the existence of Ag nanoparticles influences the crystallization of TiO$_2$ nanoparticles during heat treatment.

3.4. Photocatalytic activities of Ag-TiO$_2$ nanoparticulate films
The photocatalytic activities of the pristine TiO$_2$ and Ag-TiO$_2$ films were indicated by monitoring the decomposition of MB solution under UV light as a function of the irradiation time. The relationship between Ag content and photocatalytic activity was determined by calculating $k$ from the plot of the logarithm of $C_0/C_t$ against irradiation time $t$, as shown in figure 8. The photocatalytic activity initially increases with increasing Ag content, reaches the maximum at 2.2 wt% Ag, and then dramatically decreases with a further increase in the Ag content (up to 7.4 wt% Ag). The highest photocatalytic activity achieved by the Ag-TiO$_2$ films is about 5.5 times higher than that achieved by the pristine TiO$_2$ film. However, the activity decreases with higher Ag content: the Ag-TiO$_2$ film with 7.4 wt% Ag has lower photocatalytic activity than the pure TiO$_2$ film.

Generally, photocatalytic activity depends on factors such as the phase structure, particle size, efficiency of electron-hole separation, and the specific surface area [25–27]. Several researchers have reported that Ag acts as an electron trap that captures photoinduced electrons from TiO$_2$, and this process reduces the rate of electron-hole recombination [2, 5, 17]. The effect of the presence of Ag on the photocatalytic activity of Ag-TiO$_2$ films is prominently seen at Ag contents below 2.2 wt%.

On the other hand, the inhibitory effect of higher Ag content on the photocatalytic activity can be explained as follows. As shown in figures 5(a)–(d), the particle size of the TiO$_2$ nanoparticles increases with increasing Ag

![Figure 5. Elemental analysis using the TEM-EDX data of (a) pristine TiO$_2$ and (b) Ag-TiO$_2$ film with 7.4 wt% Ag.](image)

![Figure 6. TEM image of Ag nanoparticles on the surface of TiO$_2$ nanoparticles.](image)
content; however, the specific surface area of the TiO\textsubscript{2} matrix decreases. Lin et al reported that the photocatalytic activity of large particles is compromised by the relatively low specific surface area \cite{28}. The size of TiO\textsubscript{2} nanoparticles increases significantly when the Ag content exceeds 2.2 wt\%, which coincides with the dramatic decrease in the photocatalytic activity. Thus, we can deduce that, at Ag contents above 2.2 wt\%, the particle size of the TiO\textsubscript{2} nanoparticles is the key determining factor for photocatalytic activity.

Moreover, the presence of Ag nanoparticles on the surface of TiO\textsubscript{2} can block the penetration of light into the TiO\textsubscript{2} matrix. This reduction of light absorption can also decrease the photocatalytic activity of the Ag-TiO\textsubscript{2} films, especially when the Ag content is at its highest. Therefore, the Ag-TiO\textsubscript{2} film with 7.4 wt\% Ag has a lower photocatalytic activity than the other films owing to the two inhibitory effects described above.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7.png}
\caption{Geometric mean diameter of Ag-TiO\textsubscript{2} nanoparticulate films after annealing as a function of Ag content.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure8.png}
\caption{Rate constant $k$ for methylene blue degradation by Ag-TiO\textsubscript{2} nanoparticulate films under UV light irradiation for 5 h as a function of Ag content.}
\end{figure}
4. Conclusions

We investigated the effects of the loading content of metallic Ag nanoparticles on the morphology, crystallinity and particle size of TiO₂ and the photocatalytic activity of Ag-TiO₂ films, which were synthesized via simultaneous PECVD and PVD. Post heat treatment at 500 °C, the morphology of the Ag-TiO₂ films significantly changed with varying contents of highly dispersed Ag nanoparticles. The GMD of the TiO₂ nanoparticles in the films became larger as the Ag content increased, especially above 2.2 wt% Ag. Extremely small dispersion of Ag nanoparticles was observed in the Ag-TiO₂ nanoparticle films. The photocatalytic activity of Ag-TiO₂ was strongly influenced by the Ag content through the combined effects of morphology and particle size of TiO₂ and reached its optimum value at 2.2 wt% Ag. This study is expected to have an important implication on the fabrication of not only Ag-TiO₂ nanoparticle films but also on metal-semiconductor materials with notable applications in photocatalysis, dye-sensitized solar cell, and antibacterial aspects.

Acknowledgments

We would like to thank M. Maeda for his supervision and assistance in the TEM experiment. This work is partly supported by the Japan Society for the Promotion of Science [KAKENHI grant; grant numbers JP16H04553, JP18K18979]. We would also like to thank Editage (https://www.editage.jp) for providing English language editing services for this manuscript.

ORCID iDs

Dianping Jiang © https://orcid.org/0000-0002-5353-0617
Manabu Shimada © https://orcid.org/0000-0002-3877-5376

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