Research Paper

Fabrication and Photocatalytic Activity of Ag/TiO$_2$ Powder Immobilized TiO$_2$ Thin Film in Methyl Orange Mineralization

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Abstract: *TiO$_2$ thin film and Ag/TiO$_2$ powder immobilized TiO$_2$ thin film were synthesized by dip-coating technique on glass substrate. Fabricated thin films were characterized using X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). Photocatalytic activities of the films were evaluated by the decomposition reaction of methyl orange under UV radiation according to the first-order rate constant k. The experimental results indicated that the initial concentration of the dye solution influenced the decolourization of azo dye methyl orange and the addition of catalyst powder into the TiO$_2$ sol improved the efficiency of the photocatalytic process of pure TiO$_2$ thin film. The mineralization of methyl orange was confirmed by chemical oxygen demand (COD) and total organic carbon (TOC) measurements.*

Keywords: Ag/TiO$_2$ catalyst, methyl orange, mineralization, thin film, UV irradiation.

Introduction

Textile industry wastewater with high pollutant concentrations contains many chromophore organic compounds which possess durable, difficult biodegradable structure and is highly toxic to humans and animals. If the contamination sources are not handled, they will cause serious environmental pollution, destruction of aquatic ecosystems and destroy the self-cleaning ability of the receiving water body. Some dyes with cyclic structures containing azo groups are cancer-causing agents [1,2].

In recent years, TiO$_2$ semiconductor photocatalysis has been applied to important issues such as environmental decontamination of water and air [3-5]. When particles of TiO$_2$ semiconductor are illuminated by UV radiation with energies greater than the band-gap energy of the semiconductor, they will produce electron-hole (e$^-$/h$^+$) pairs. These e$^-$/h$^+$ pairs can move to the surface of the TiO$_2$ particles to initiate the redox reactions of organic compounds adsorbed on TiO$_2$ surface. In most cases, this redox process leads to complete mineralization of organic matter to CO$_2$ and H$_2$O [6-8]. Some techniques of metal ion and non-metal ion doping are employed to alter electronic structure and optical properties of TiO$_2$ in order to extend photoresponse of TiO$_2$ into the visible light region and slow down the recombination rate of photo-generated e$^-$/h$^+$ pairs. The metal ions often used for doping process are Fe, Zn, V, Cr, Cu, Co, Pt, Au, Ag, etc [9-11].

The oxidation method using nano TiO$_2$ photochemical catalyst revealed many advantages in the field of textile industry wastewater treatment because of the complete destruction and elimination of organic contaminants in the environment [12,13]. The use of TiO$_2$ photocatalytic powder has some disadvantages that the particles are aggregated at high concentration, the catalysts must be separated from the treated water and reuse of catalyst is complex [14,15]. The manufacture and use of catalyst film will overcome the above drawbacks thus increasing the applicability of

catalysts in practices such as self-cleaning and bactericidal surfaces manufacturing, improve the efficiency of catalyst use as the catalyst film can be employed repeatedly and eliminate the catalytic recovery stage after reaction in order to reduce wastewater treatment costs. However, the film type catalyst possesses a working surface area lower than that of the powder one. The thin film surface area in photocatalytic reaction is sufficiently high to achieve the desired efficiency. Therefore, the size of thin film reactor is larger than the suspension reactor.

In this paper, the fabrication and evaluation of the mineralization of methyl orange by using the Ag/TiO_2 powder immobilized TiO_2 thin film (Ag-TiO_2/TiO_2 thin film) to increase photocatalytic efficiency of pure TiO_2 thin film were investigated.

Material and Methods
Chemicals and apparatus
As the starting precursors, the following reagents and apparatus were employed: Tetra-nbutyl orthotitanate (TBOT, Merck, 98%), TiO_2 (Merck, 99%) as TiO_2 source, Tetraethyl ortho silicate (TEOS, Merck, 99.8%) as SiO_2 source, Silver nitrate (Sigma-Aldrich, > 99%) as dopant source, Sodium citrate dihydrate (Sigma-Aldrich, > 99%) as reductant, tetraethyl ammonium hydroxide (TEAOH, Merck, 98%), diethanolamine (DEA, Merck), acetone (Merck, > 99%) and deionized water.

The structural characterization of the TiO_2 nanoparticles and thin films were investigated by X-ray diffraction (Siemen D500 diffractrometer) analysis. The measurement conditions were as follows: CuKα radiation (λ = 1.5406 Å) at U = 30 kV and I = 25 mA, 0.2^o step size and 1 sec step time from 20 to 70°.

The morphology of the as-prepared photocatalyst powder and photocatalyst films such as crystallite particle shape and size were characterized by transmission electron microscopy (TEM, JOEL-JEM 1010) and field emission scanning electron microscopy (FE-SEM, S-4800 Hitachi).

Preparation of catalyst samples
TiO_2 sol
TiO_2 sol was prepared by the procedure described as follows. Deionized water was added to the TBOT under continuous stirring at room temperature to obtain a white precipitate. TEAOH was added dropwise to the resulting suspension and was mixed vigorously until the precipate was dissolved completely. By turning off the agitator and settling for 30 minutes, the solution was separated into two phases. The pale yellow solution layer at the top was removed, leaving the obtained white solution at the bottom. TEAOH was added to the white solution in the beaker on the agitator for 2 hours. The resulting solution was filtered to get transparent TiO_2 sol.

Preparation of SiO_2 sol
The SiO_2 solution was prepared by using TEOS as starting material. TEAOH was added dropwise to TEOS under continuous stirring at room temperature for 30 minutes to obtain a transparent SiO_2 solution.

Preparation of Ag/TiO_2 powder
Sodium citrate dihydrate was dissolved completely in deionized water. Then, silver nitrate was added to the sodium citrate dihydrate solution and the solution was stirred at 80°C until the color of solution changed from colorless to yellow, then violet-brown. Silver concentrations of 0.0, 0.1, 0.3, 0.5, 0.7 and 1.0% atom were used. TiO_2 was added into the solution and the reaction was carried out at 50°C for 24 hours. The resulting product was dried at 105°C for 24 hours and calcined at 300^oC for 3 hours.

Preparation of thin films on glass substrate
Glass plates were cut into 55 x 107 mm rectangular pieces. The plates were cleaned with detergent, rinsed with deionized water and followed by ultrasonication with acetone to remove dirt and contaminants. Finally, glass substrates were dried at 60^oC for 1 hour.

Coating solutions
TiO_2 thin film: The stock TiO_2 sol and stock SiO_2 sol were diluted by DEA and deionized water. The clear solutions were then stirred for 15 minutes to obtain working solutions for preparation of transparent films.

Ag-TiO_2/TiO_2 thin film: Ag/TiO_2 powder was dispersed in TiO_2 sol by ultrasonication with a concentration of catalyst of 15 grams per liter.

Thin films were deposited on substrate by dip coating methods. The SiO_2 layer was used to prevent the diffusion of Na^+ ions from glass substrate into the TiO_2 films. The coated glass plates were placed horizontally in enough sol solution to cover its surface. The deposited films were dried at room temperature for 24 hours and followed by 100°C for 30 min. The films were calcined at 500^oC for 1 hour with an increasing temperature rate of $5^oC/min$ in furnace. This process was repeated three. The resulting deposited substrates were immersed into water and kept in a bath type ultrasonicator for 1 hour to remove catalyst particles not adhered.

Photocatalytic mineralization experiments

Photocatalytic activity of TiO_2 in suspension and thin films was evaluated by degradation of methyl orange (azo dye). Firstly, to assess the effect of doping silver concentration on the photocatalytic activity, the Ag/TiO_2 powder catalyst with different silver amounts (0.0, 0.1, 0.3, 0.5, 0.7 and 1.0% atom) in the form of suspension was used. The experiment was performed with the following conditions: concentration of catalyst 2 g/l, methyl orange concentration of 15 mg/l, under continuous stirring condition at room temperature. In this experiment, collected samples after photocatalysis were centrifuged to separate Ag/TiO_2 particles from methyl orange solution before UV-vis measurements.

From the above experiments, the catalyst sample with the highest photocatalytic activity was selected to form a thin film on the glass substrate as described in the procedure and test the photocatalytic activity of fabricated thin films. The thin film was fixed in a tray, film area was 176.55 cm^2, methyl orange solution was pumped continuously by circulating pump, forming thin layer with a thickness of about 1 mm of film surface. The concentration of methyl orange solution was surveyed 5, 10 and 15 mg/l. The volume of solution was 1 liter.

Prior to photocatalytic experiment, the sample was stirred in the dark for 24 hours to reach an adsorption–desorption equilibrium on the catalyst surface in the absence of light radiation. After this, the film was irradiated by UVC lamp with 20W power, the lamp was 80 cm in length and 9 cm in diameter.

Samples were taken periodically and measured light absorption at wavelength of maximum absorbance $\lambda_{max} = 462$ nm to determine the concentration of the solution. Photocatalytic degradation reaction obeyed first-order kinetic $\ln(C/C_0) = -kt$ where C and C_0 are the concentration of dye at reaction time = t and 0, respectively, t is the irradiation time and k denotes as the first-order rate constant [16,17]. The degradation efficiency (%) of methyl orange was calculated as follows: Degradation efficiency (%) = (C_0 – C)/C_0x100%. The mineralization degree was assessed by total organic carbon (TOC) analysis performed on a TOC analyzer (Torch, Teledyne Tekmar) and Chemical oxygen demand (COD) determined by the dichromate oxidation method.

Results and Discussion
**Characterization of Ag/TiO_2 powder catalyst**
The crystalline phase of the Ag/TiO_2 material prepared was characterized by X-ray diffraction (Figure 1). XRD pattern of synthesized catalyst sample indicated the existence of peaks at the diffraction angle 2θ of 25.3, 37.8, 48.1, 53.9, 55 and 63° characterized anatase crystalline phase. Observation of XRD patterns of Ag doped TiO_2 and commercial TiO_2 revealed that there was not a typical peak of silver in prepared Ag/TiO_2 powder. The possible reasons for this might be the concentration of silver was too low to be detected by XRD or the diffraction peak of silver at 2θ = 37.8° was overlapped by the anatase TiO_2 peak [18].
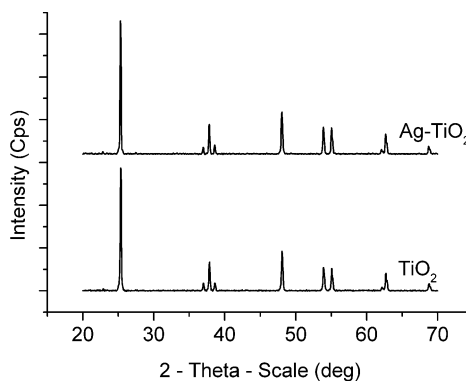
Figure 1: XRD diffraction patterns of commercial TiO_2 and prepared Ag/TiO_2 particles

TEM image of nano Ag/TiO_2 in Figure 2 elucidated the morphology of the material. TEM images presented the existence of spherical silver nanoparticles with relatively uniform size in the range of 8 to 10 nm attached on the surface of the TiO2 material with an average size range from 80 to 120 nm. TEM observation revealed the silver nanoparticles distributed with very low density and were not agglomerated.
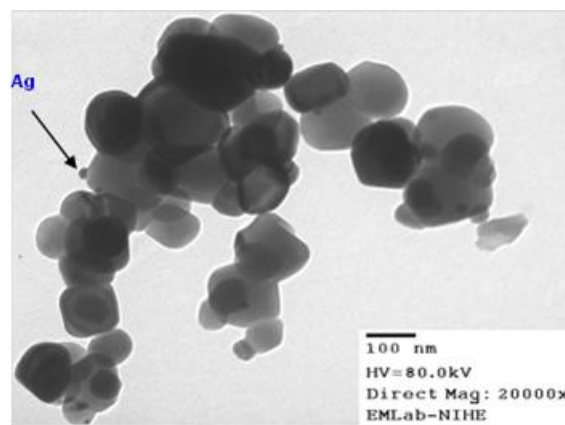

Figure 2: TEM image of prepared Ag/TiO_2 particles

Characterization of thin films
Figure 3 presented the XRD diffraction patterns of fabricated thin films. XRD pattern of TiO_2 thin film showed the presence of peak at 25.3° characterizing for the anatase structure. Observation of XRD pattern of

Ag-TiO$_2$/TiO$_2$ thin film revealed that besides the major peak at 25.3°, the peaks at 37.8, 48.1 and 54° with observable intensity could be realized. It showed that the presence of Ag/TiO$_2$ powder in TiO$_2$ thin film enhanced crystalline anatase phase confirmed by the increase of diffraction peaks intensity.
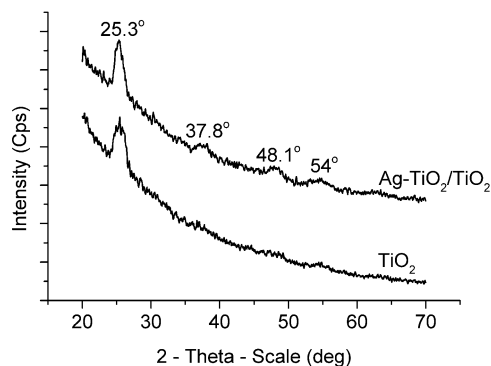
Figure 3: XRD diffraction patterns of TiO$_2$ thin film and Ag-TiO$_2$/TiO$_2$ thin film

FESEM analysis illustrated that the particles were nearly spherical with a diameter of about 20 - 100 nm. On the FESEM micrographs (Figure 4(a1)), it was found that the presence of the cracks was a result of the shrinkage process when the thin films were calcined at high temperature. The cracks of the film produced plates with variable height and the crack increased the roughness of the fabricated film. The spherical particles with relatively uniform size arranged in overlapped layers (Figure 4(a2)) and 5(a2)) or ordered on a plane (Figure 4(a3) and 5(a3)). FESEM images of Ag-TiO$_2$/TiO$_2$ thin film exhibited Ag/TiO$_2$ catalyst powder (Figure 5(a1)), it could not be observed on TiO$_2$ thin film (Figure 4(a1)).

On FESEM images of the cross-section of fabricated TiO$_2$ thin films (Figure 4(b)) showed that the thickness of films was about 4 µm and no distinction between the different coatings. Conversely, the FESEM micrographs of Ag-TiO$_2$/TiO$_2$ thin film (Figure 5(b)) displayed three distinct coatings with a layer thickness of about 4 – 5 µm.
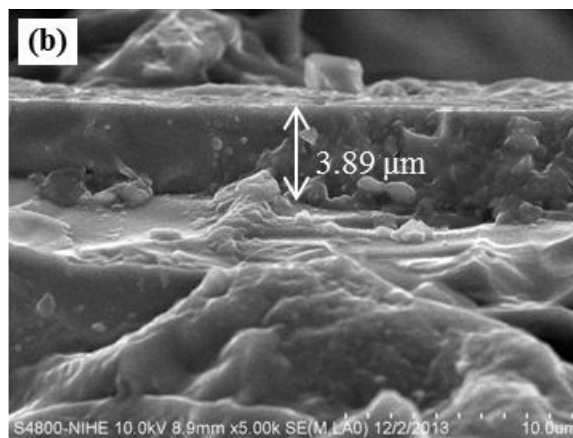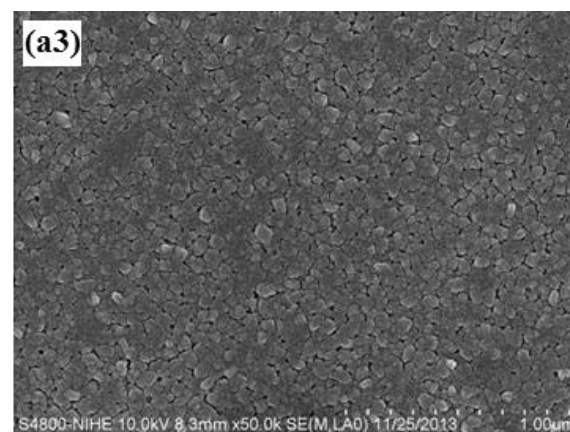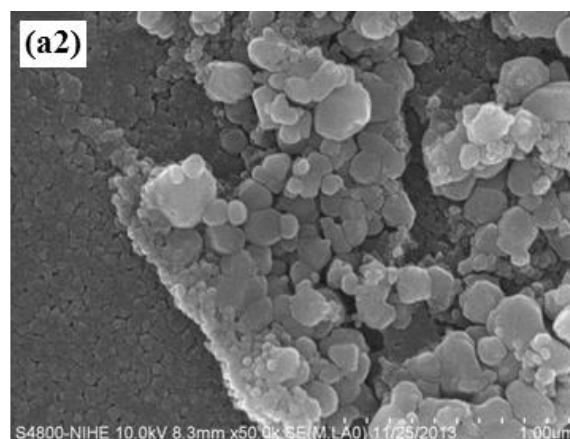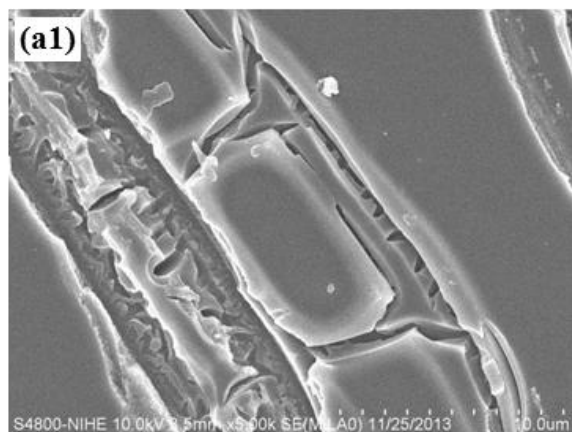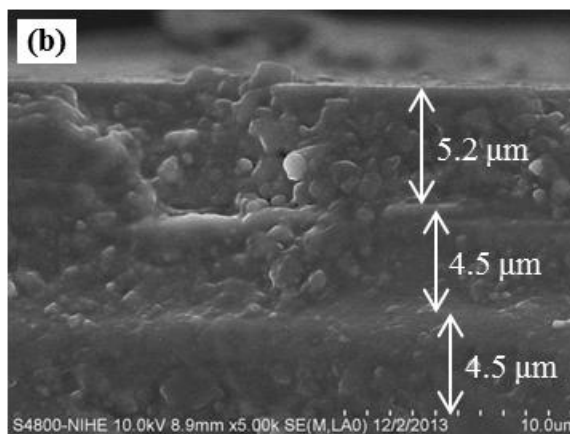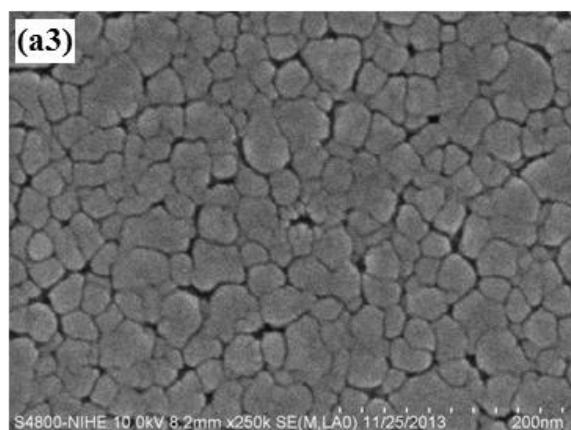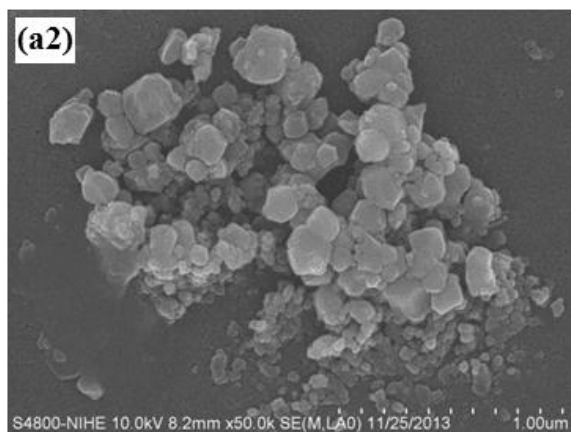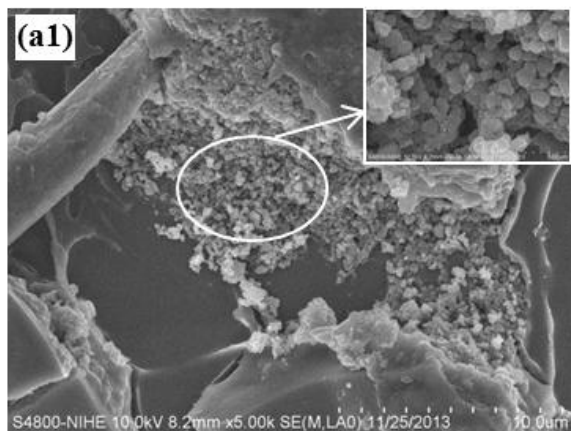

Figure 4: FESEM images of TiO$_2$ thin film. (a) Surface view, (b) Cross sectional view

Photocatalytic performance for methyl orange decomposition

Assessment procedure of catalytic activity of prepared samples was given in the experimental section. By plotting -ln(C/C$_0$) as a function of irradiation time (t), the reaction rate constant (*k*) values were obtained from the slope of the best fit lines. The rate constant of methyl orange decolourization reaction was presented in Figure 6. The silver content in catalyst samples varied from 0.0, 0.1, 0.3, 0.5, 0.7 and 1.0%, and the values of reaction rate constant were respectively 0.726,

0.750, 0.822, 1.044, 1.170 and 1.146 h^{-1}. The results showed that when the doping silver content increased from 0.0% to 0.7%, the photocatalytic activity increased gradually and reached the highest value at silver content of 0.7%. When the amount of silver was 1.0%, the rate constant decreased slightly. Compared with undoped samples, it could be seen that silver plays an important role in improving the catalytic activity of TiO_2.

As previously published [19,20], silver acts as charge separators of the photoinduced e^-/h^+ pair, thereby reducing the possibility of recombination of photo-generated e^-/h^+ pairs.

Figure 5: FESEM images of Ag-TiO$_2$/TiO$_2$ thin film. (a) Surface view; (b) Cross sectional view

However, when the silver content was in excess, it conversely served as recombination centers of photo-generated electrons and holes, so it reduced the photocatalytic activity of TiO_2 catalysts. Therefore, the optimal concentration of doping silver, specifically in this study, was 0.7% silver content for the photocatalytic activity of TiO_2.
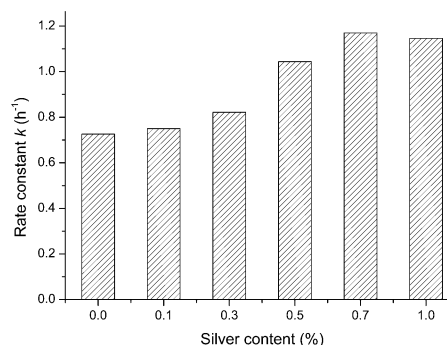
Figure 6: Rate constant values of methyl orange decolourization reaction of the Ag/TiO$_2$ catalyst samples with different amounts of silver

The 0.7% silver doped catalyst sample was selected to fabricate Ag-TiO$_2$/TiO$_2$ thin film. Comparison of the photocatalytic activity between TiO$_2$ thin film and Ag-TiO$_2$/TiO$_2$ thin film in the removal of methyl orange color was given in the Figure 7 and Table 1. It was observed that the photocatalytic activity of Ag-TiO$_2$/TiO$_2$ thin film was higher than that of TiO$_2$ thin film in all the cases the solution concentration of 5, 10 and 15 mg/l. This could be due to the fact that the presence of Ag/TiO$_2$ catalyst powder increased photocatalytic ability of Ag-TiO$_2$/TiO$_2$ in comparison to the pure TiO$_2$ thin film. In addition, FESEM images showed the presence of catalyst particles increased surface roughness and raised the contact area of the dye solution with catalyst film whereby the efficiency of the reaction increased.

Table 1: Rate constants for first order kinetics of TiO$_2$ thin film and Ag-TiO$_2$/TiO$_2$ thin film

Methyl orange concentration (mg/l)	Removal	Ag-TiO$_2$/TiO$_2$ thin film		TiO$_2$ thin film	
		Rate constant k (h^{-1})	R^2	Rate constant k (h^{-1})	R^2
5	Color	0.1510	0.9917	0.0879	0.9776
10	Color	0.1244	0.9972	0.0744	0.9796
15	Color	0.0898	0.9840	0.0546	0.9870
	COD	0.0437	0.9942	0.0286	0.9940
	TOC	0.0197	0.9972	0.0125	0.9941

As shown in Figure 7(c), by increasing the dye concentration from 5 to 10 and 15 mg/l, the rate constant of decolourization reaction in both cases of Ag-TiO$_2$/TiO$_2$ thin film and TiO$_2$ thin film declined. In the photocatalytic reaction, the ability to transmit UV radiation to the surface of catalysts was very important. The more radiation rays were absorbed on photocatalyst surface, the more interactions were performed between photons and active sites of photocatalyst. Thus, more photogenerated holes (h$^+$)

and photogenerated electrons (e$^-$) were produced. These h$^+$ and e$^-$ pairs could react with water and dissolved oxygen on the surface of photocatalyst to produce reactive oxygen species hydroxyl radicals. These radicals were powerful oxidizing agents. They continued to react with dye molecules and completely decomposed these organic compounds into harmless species such as CO$_2$, H$_2$O, etc.

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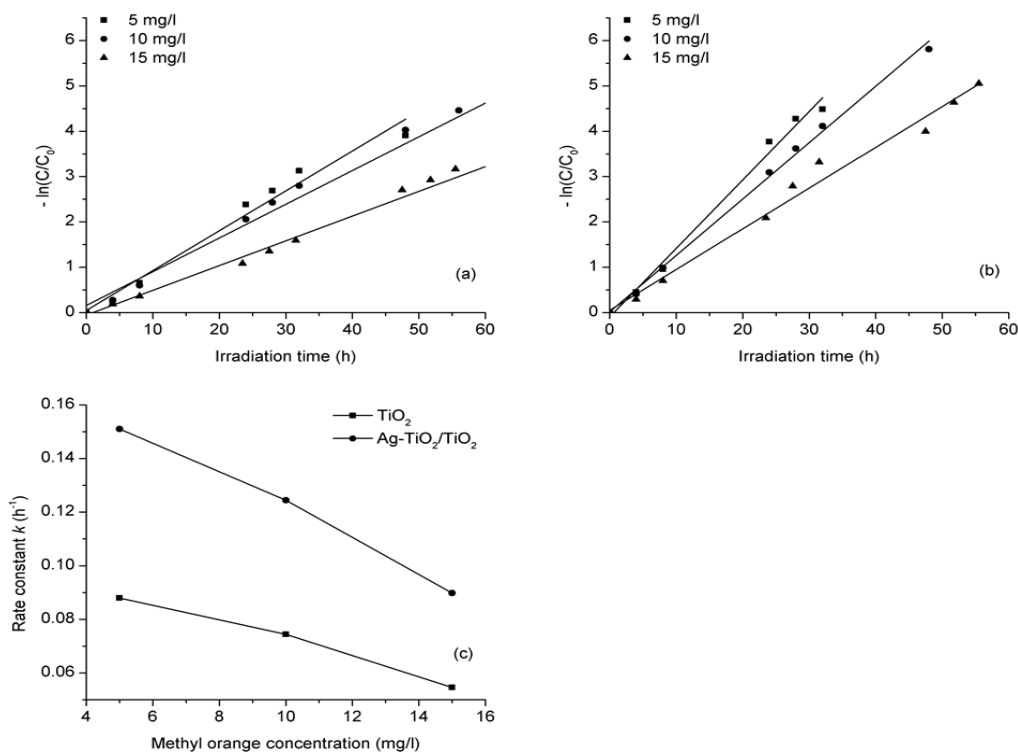
Figure 7: Rate constant of decolourization reaction of methyl orange with different initial concentration of dye: (a) TiO$_2$ thin film, (b) Ag-TiO$_2$/TiO$_2$ thin film and (c) comparison between TiO$_2$ thin film and Ag-TiO$_2$/TiO$_2$ thin film

A plot of -ln (C/C$_0$) as a function of irradiation time was shown in Figure 8(a). Data of the rate constants k

of removal reaction of color, COD and TOC in the presence of TiO$_2$ thin film and Ag-TiO$_2$/TiO$_2$ thin film

was reported in Table 1. It is obvious that the disappearance of color occurred easier than COD and TOC loss. At 72 hours after irradiation, the degradation efficiencies of color, COD and TOC of TiO_2 thin film were 97.3, 86.4 and 60.6%; respectively. Meanwhile, by using Ag-TiO_2/TiO_2 thin film, color was removed completely and degradation efficiencies of COD and TOC were 95.7 and 76.1%, respectively (Figure 8b). This indicated that chromophore group of methyl orange could be completely broken. The residual COD and TOC values demonstrated further oxidation of dye molecules into smaller molecules and the depletion of COD and TOC was slower than the color removal.
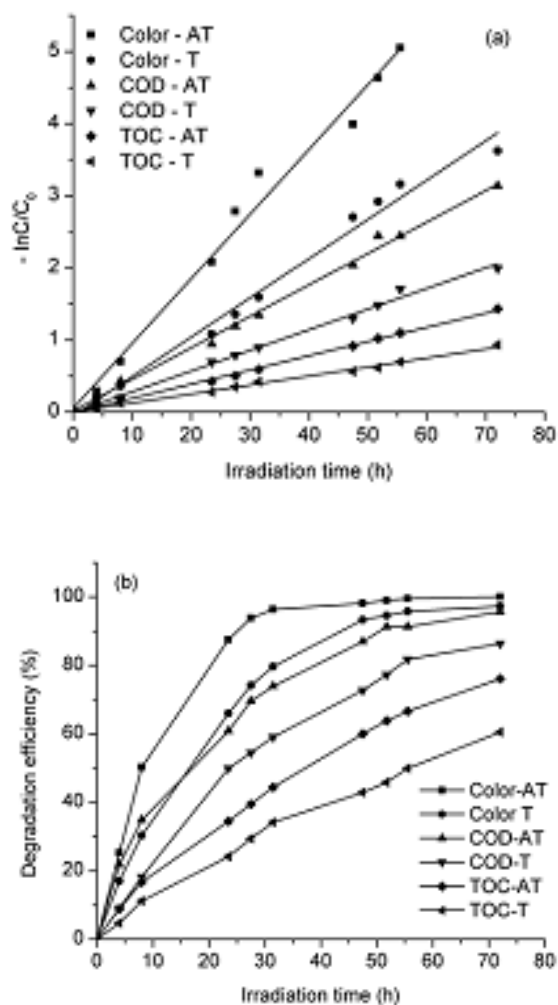
Figure 8: Kinetic plots (a) and degradation efficiency (b) for removal of color, COD and TOC of TiO_2 thin film and Ag-TiO_2/TiO_2 thin film

These results indicated that photocatalytic activity of Ag-TiO_2/TiO_2 thin film in the mineralization process of methyl orange was higher than that of pure TiO_2 thin film. Consequently, the FESEM characterization results and the photocatalytic mineralization proved the role of immobilization of Ag-TiO_2 powder catalyst on TiO_2 thin film in enhancing dye degradation efficiency.

Conclusion

The Ag/TiO_2 powder immobilized TiO_2 thin film and TiO_2 thin film coated on glass substrate were successfully fabricated. The characterization results showed that the surface of the TiO_2 thin film was uneven and rough. The presence of Ag/TiO_2 catalyst particles in the Ag/TiO_2 powder immobilized TiO_2 thin film increased not only the surface roughness but also the photocatalytic activity of this thin film.

Photocatalytic activity of as-prepared thin films fabricated was evaluated by decomposition reaction of methyl orange under UV radiation with different initial concentration of methyl orange of 5, 10 and 15 mg/l. The results showed that Ag-TiO_2/TiO_2 thin film was more active than pure TiO_2 thin film. When the initial concentration of dye was increased, the rate constant k of degradation reaction of methyl orange declined in both the TiO_2 thin film and Ag-TiO_2/TiO_2 thin film. The reason was that the increased concentration of dyes adversely affected to the capability to transmit UV light to the surface of the catalyst. The Ag-TiO_2/TiO_2 thin film displayed better photocatalytic mineralization than pure TiO_2 thin film. The residual COD and TOC analysis indicated the presence of intermediates derived from the dye decomposition process although the color was removed completely.

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