

SILVER MODIFIED TITANIUM DIOXIDE THIN FILMS FOR EFFICIENT PHOTODEGRADATION OF METHYL ORANGE

May Thu Aung¹, Aye Aye Thant² and Pho Kaung³

Abstract

Silver-modified titanium dioxide thin films have been prepared via a two-step dipping method. Optimization of the photocatalyst's performance as a function of dipping time, irradiation time and concentration of dipping solution was performed. The optimum concentration of silver nitrate was found to be 0.001 M. UV-irradiation process of the films were examined for their catalytic activity towards photodegradation of methyl orange (MO). The modified materials presented enhanced photocatalytic efficiency and managed to decompose the organic pollutant. Its pollutant rate was faster than that of undoped original films (TiO₂). The increase in Ag⁺ ion concentration in the dipping solution resulted a decrease in the film's photocatalytic efficiency due to a shading of available semiconductor surface by the silver layer. Moreover, the lower the average particle size, the higher is the photodegradation percentage. UV analysis indicate the decomposition of M.O.

Keywords: titanium dioxide, thin films, photocatalyst, photodegradation

Introduction

Titanium dioxide heterogeneous photocatalysis has been the subject of numerous investigations in recent years as it is an attractive technique for the complete destruction of undesirable contaminants (pollutants) in both liquid and gaseous phases by using solar or artificial light illumination. TiO₂ photocatalysis are oriented towards the photocatalyst immobilization in the form of a thin film. Titania photocatalysis with advantages, such as low operation temperature, low cost, significantly low energy consumption, have led the relevant applications to the stage of commercialization. A proficient way to enhance photocatalytic reaction rate is addition of transition metals to semiconductor. This research work aimed to develop a new composite, immobilized photocatalyst consisting of silver particles photochemically deposited on rough and high surface area nano crystalline TiO₂ films with

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increased efficiency. The photodegradation of the well known organic azo-dye methyl orange (MO), a typical pollutant in the textile industry, was investigated as a model compound under near UV irradiation.

Experimental Procedure

Preparation of Titania Film

TiO₂ thin film was prepared on optically transparent microscopy glass substrates using doctor-blade method. The schematic diagram of preparation is shown in Figure 1. 10ml of vinegar (or dilute acetic acid) and 6g of titanium dioxide were mixed and stirred with a glass rod for 5 min. the glass slide was fastened with a tape to a table as shown in Figure 1 in order to get the film thickness to be that of the scotch tape. Then, 3-5 drops of the TiO₂ solution were dropped on the glass slide. In order to deposit a uniform thin layer across the unmasked portion of the slide, a glass rod was rolled on the slide Before removing the tape, the slide had been allowed to dry for a few minutes. Finally, TiO₂ thin films were annealed in an oven at 450°C for 15 min.

Preparation of silver deposition on Titania Film

A simple single dip method was used to deposit silver on the titanium dioxide thin film. Firstly, an aqueous solution of silver nitrate (AgNO₃) 0.001M was prepared by using distilled water. Then the films were dipped in that solution for 3s. After dipping, the films were illuminated by UV light for 2 hours. The illumination process made the films to be darken due to the presence of silver compound. Finally, the modified catalyst films were immediately tested for the photodegradation of MO.

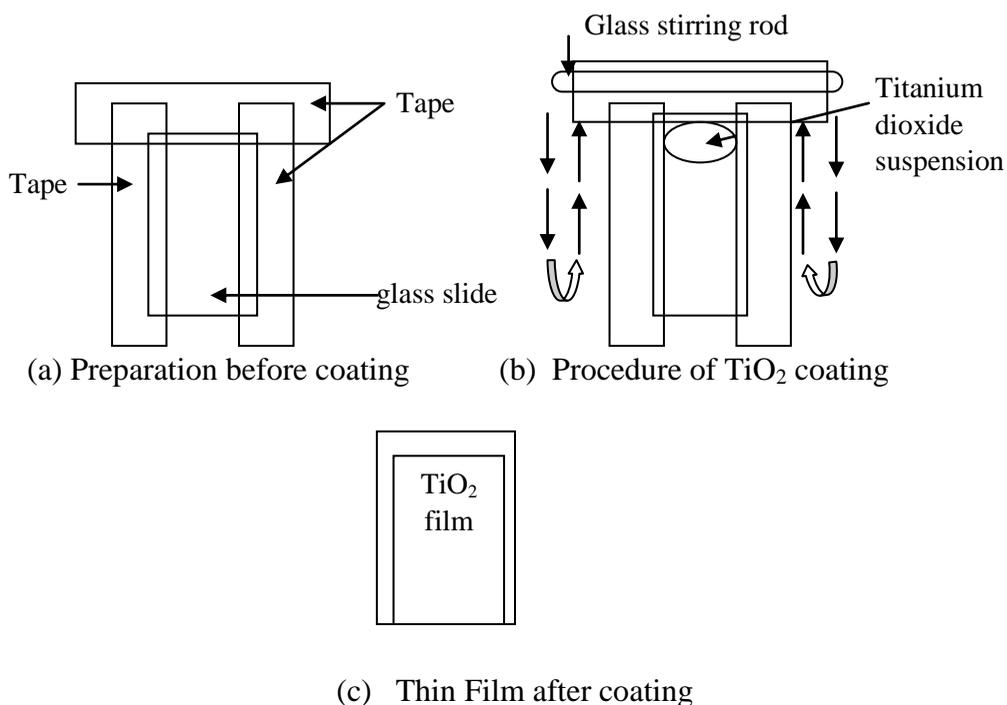


Figure 1: Schematic diagrams of preparation of TiO₂ film by doctor- blade method

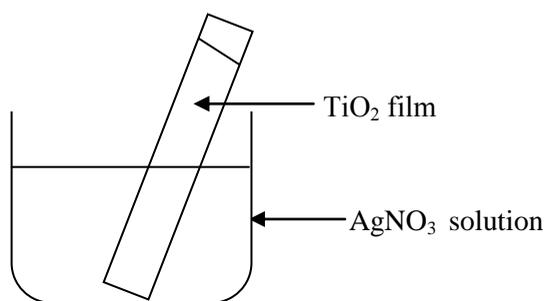


Figure 2: Schematic diagram of Silver deposition on TiO₂ thin film

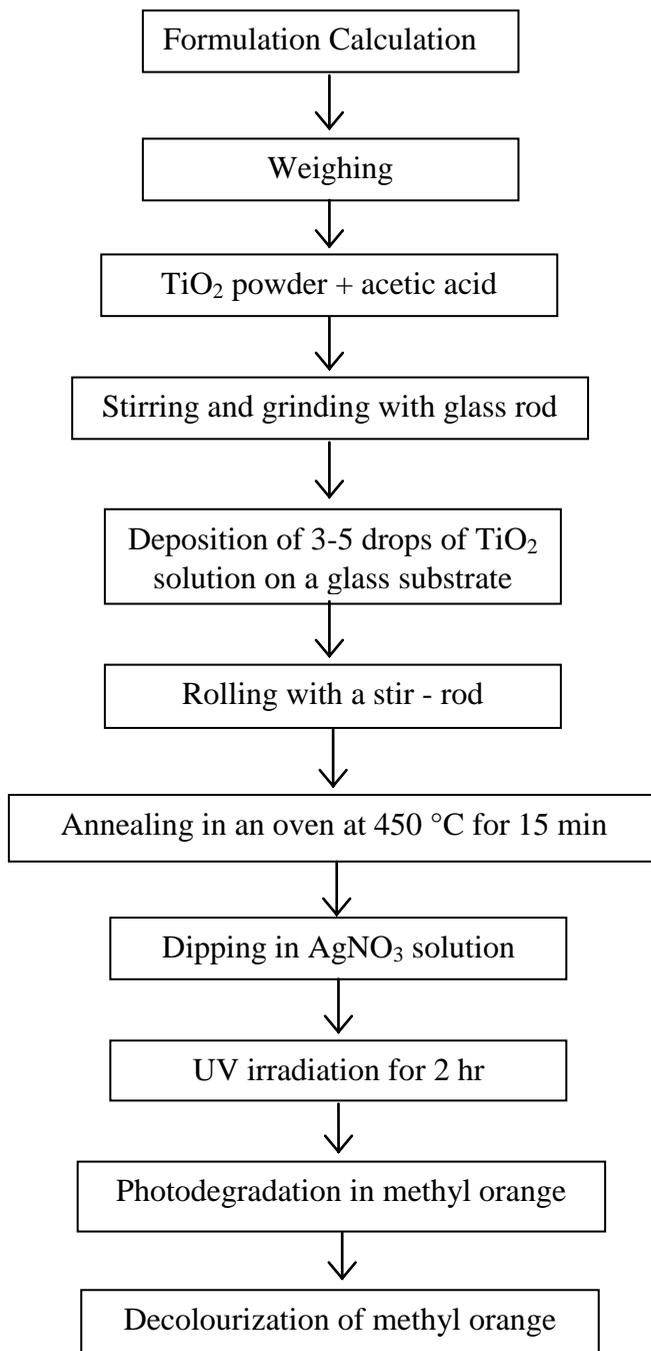


Figure 3: Block diagram for the preparation of Silver-modified Titanium dioxide thin films for efficient photodegradation

Result and Discussion

XRD Analysis of Titanium dioxide Thin Film

The XRD spectra of Ag/TiO₂ film and TiO₂ films were presented in Figure 4. According to the X-ray diffraction, well-organized crystal structure of titania particles were observed in the films. There are three phases in TiO₂: Anatase, Rutile and Brookite. In the present work, the XRD spectrum confirms that the anatase reflections are dominating where a small amount of rutile is also present. The reflections (101, 004, 200, 211, 204, 213, 116) represent anatase phase while the reflections (110, 101, 111, 210, 211, 220, 310, 112, 221) represent rutile phase. The tetragonal structure of TiO₂ was identified by using the International Centre for Diffraction Data (ICDD) file number 21-1272 (for anatase) and 21-1276 (for rutile) in Figure 4 Brookite phase is not present in TiO₂ film. It may be due to the synthesis parameters in the formation of the film.

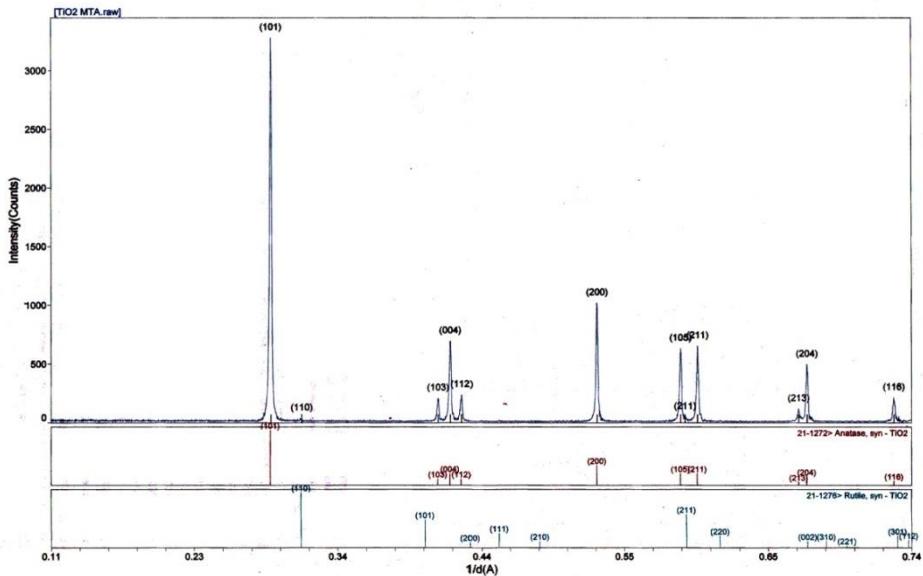


Figure 4: XRD spectrum of TiO₂ with reference patterns (Anatase 21-1272 and Rutile 21-1276)

XRD Analysis of Silver-modified Titanium Dioxide Thin Film

The XRD spectrum of silver-modified titanium dioxide thin film is shown in Figure 5. The XRD result showed that only small amount of silver percentage was observed in silver modified Titanium dioxide film. The face-centered cubic structure of Ag was identified by using the International Centre for Diffraction Data (ICDD) file number (41-1402). This observation proved to be extremely efficient for the photodegradation of methyl orange. It is also confirmed that silver oxide particles were not crystallized on TiO₂ surface as shown in Figure 5. This is probably due to the fact that the majority of the silver particles were only deposited on the surface of the TiO₂ film but not incorporated into the TiO₂ matrix.

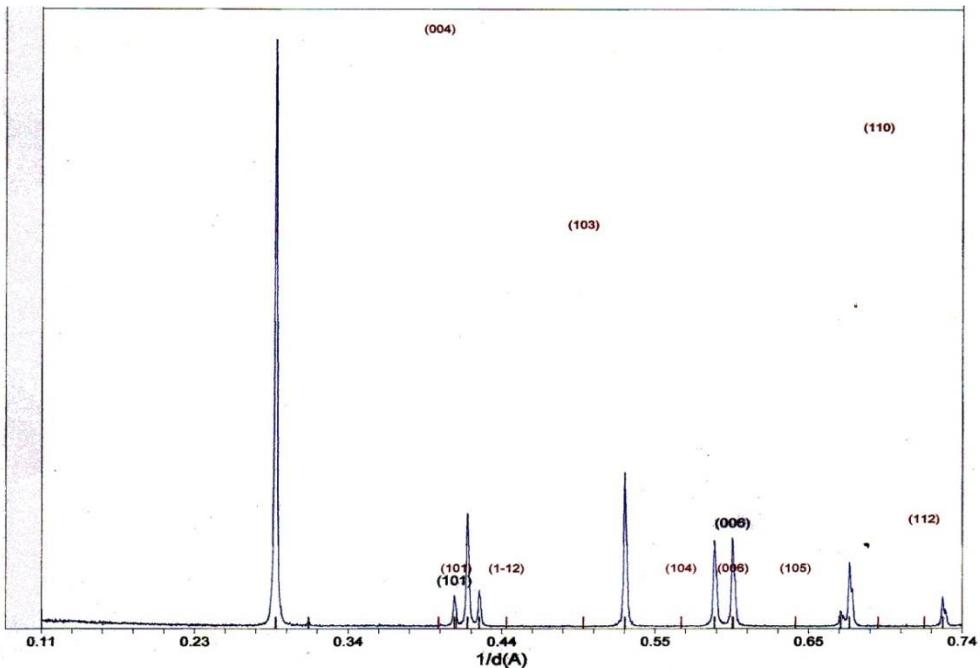


Figure 5: XRD spectrum of Ag/TiO₂

Photocatalyst Surface Properties

The morphology of the silver layer deposited on the titania surface plays a crucial role in catalytic efficiency. The surface morphology of the Ag/TiO₂ films for 0.1 M AgNO₃ and 0.001 M AgNO₃ were characterized by Scanning Electron Microscope (SEM) and shown in Figure 6 and 7 respectively. Both microstructures present a porous, sponge like network of high roughness and complexity in general. Moreover, there is no crack in the film showing that the viscosity of the solution is optimum. The film deposited from the lower concentration of the Ag⁺ solution exhibits surface characteristic of higher roughness in comparison with those resulting from higher concentration. This might be one reason for the higher photocatalytic behavior in the film with 0.001 M Ag⁺.

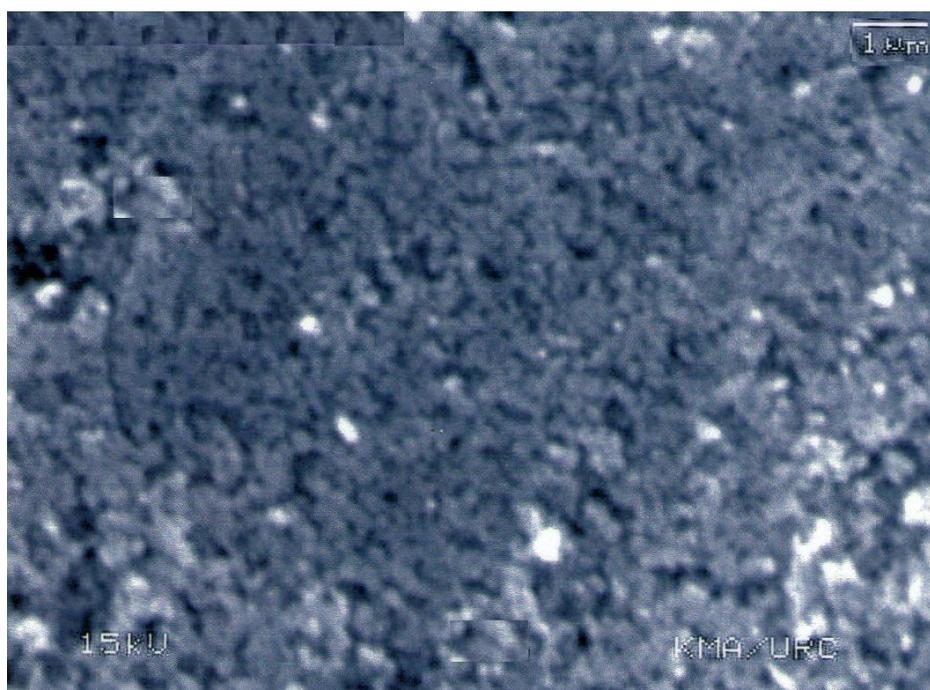


Figure 6: SEM picture of silver-modified TiO₂ film: dipping in 0.1 M AgNO₃

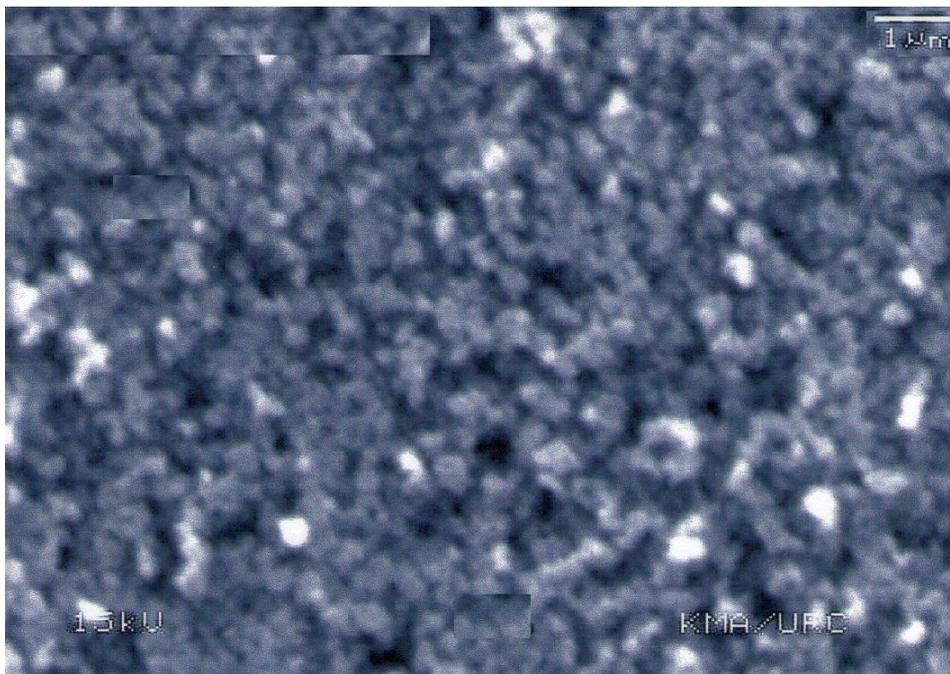


Figure 7: SEM picture of silver-modified TiO₂ film: dipping in 0.001 M AgNO₃

Photocatalytic Activity

The experiments on photocatalysis was done with an aqueous solution of methyl orange to evaluate the films activity. The photocatalytic activity was evaluated as the percentage of pollutant disappearance. The mixture solution of UV irradiated TiO₂ with and without AgNO₃ and MO was prepared prior the absorbance measurement. After degradation of MO, the photocatalyst TiO₂ was filtered out to obtain the clear solution of degraded MO. Then, The absorbance of MO solutions before and after degradation were measured at different degradation times. Measurements were carried out using Shimadzu UV - 1800 spectrophotometer in the photon energy range of wavelength 190 nm to 600 nm and with aid of quartz cells. The percentage of degradation was calculated from the following equation (1).

$$\text{Degradation \%} = \left(1 - \frac{A_t}{A_0} \right) \times 100 \quad (1)$$

Where, A_t is the absorbance after time t and A_0 is the dye initial concentration before degradation. The photocatalytic efficiency of TiO_2 with different reaction time for the MO decomposition is illustrated in Figure 8 and presented in Table 1. A maximum degradation (58%) was observed for the reaction time of 2 hours. It was also found that the percentage of decolorization and photodegradation increase with the increase in reaction time. Again, a maximum degradation (65%) was observed for AgNO_3 (0.1M) modified TiO_2 , shown in Figure 9 and presented in Table 2. The photodegradation efficiency of photocatalyst TiO_2 is lower than that of Ag modified TiO_2 . Therefore, it is concluded that the presence of Ag do enhance the degradation percentage. To confirm this finding, the experiment was repeated for AgNO_3 concentration (0.001M) and the results are shown in Figure 10 and presented in Table 3. A high maximum degradation of (82%) was found for AgNO_3 (0.001M) modified TiO_2 . The results show that the decrease in concentration of AgNO_3 can increase the photocatalytic efficiency. In order to observe the effect of Ag concentration on photocatalytic behavior, the measurement were conducted at 2 min reaction time for different concentration of AgNO_3 which shown in Figure 11 and presented in Table 4. A maximum (96%) was observed for the TiO_2 film immersed in 0.001 M AgNO_3 solution. Further increase in the Ag concentration results a considerable decrease in efficiency. All the result confirm the dependence of degradation on the reaction time. Further more these observation also show that the TiO_2 photocatalyst modified with less amount of Ag do enhance the photocatalytic efficiency via the decomposition of organic pollutant.

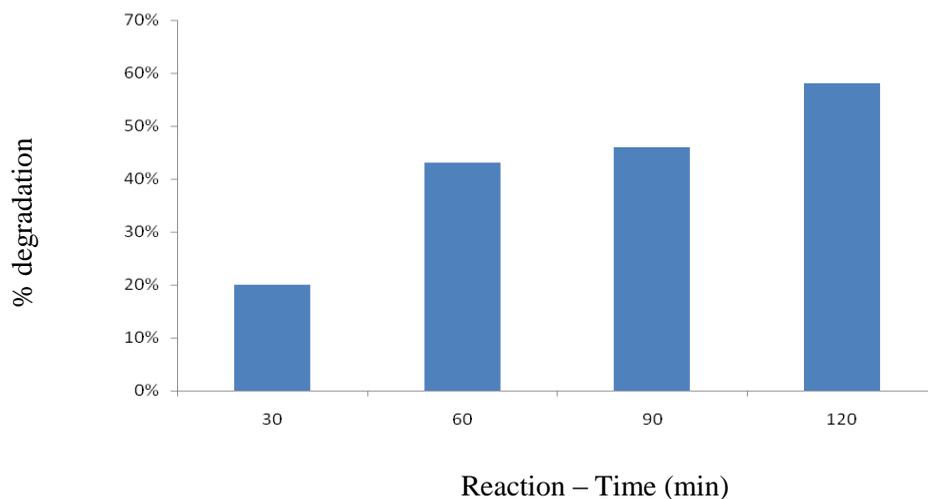


Figure 8: % degradation of methyl orange by TiO_2 film with reaction time 2 hours .

Table 1: Variation in % degradation of methyl orange via TiO_2 film with reaction time 2 hours.

Time (minute)	%degradation	Absorbance
30	20%	1.517
60	43%	1.079
90	46%	1.032
120	58%	0.800

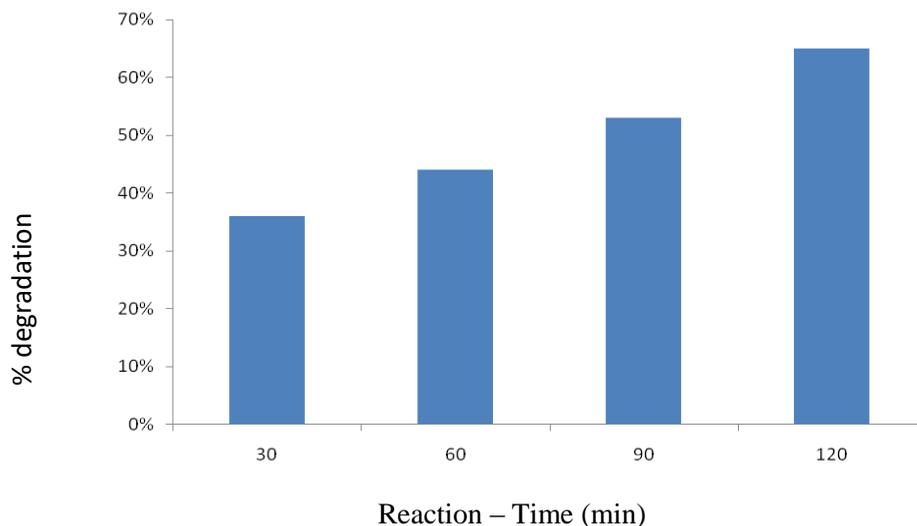


Figure 9: % degradation of methyl orange by Ag / TiO₂ film after dipping for 3s in 0.1 M of silver solution with reaction time 2 hours .

Table 2: Variation in % degradation of methyl orange via Ag / TiO₂ film after dipping for 3s in 0.1 M of silver solution with reaction time 2 hours.

Time (minute)	%degradation	Absorbance
30	36%	0.605
60	44%	0.535
90	53%	0.454
120	65%	0.341

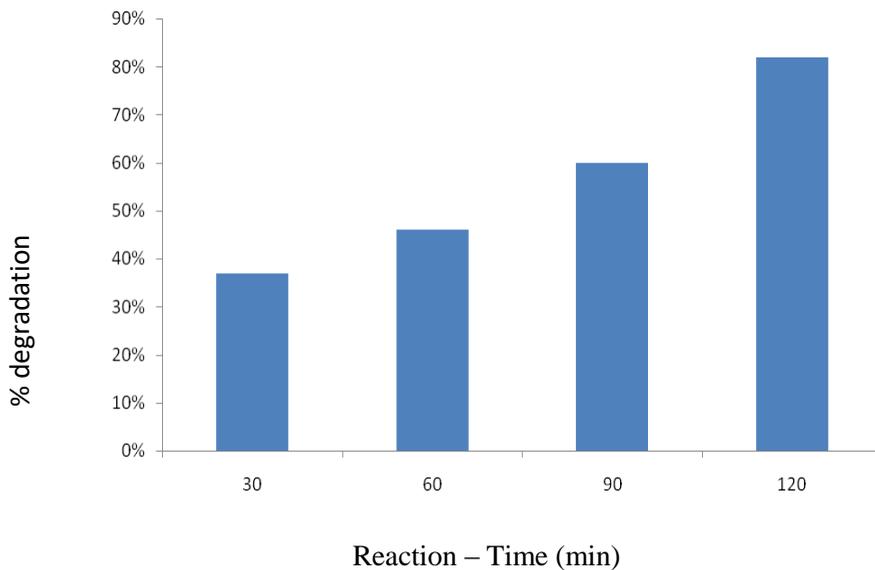


Figure 10: % degradation of methyl orange by Ag / TiO₂ film after dipping for 3s in 0.001 M of silver solution with reaction time 2 hours .

Table 3: Variation in % degradation of methyl orange via Ag / TiO₂ film after dipping for 3s in 0.001 M of silver solution with reaction time 2 hours.

Time (minute)	%degradation	Absorbance
30	37%	0.600
60	46%	0.512
90	60%	0.380
120	82%	0.163

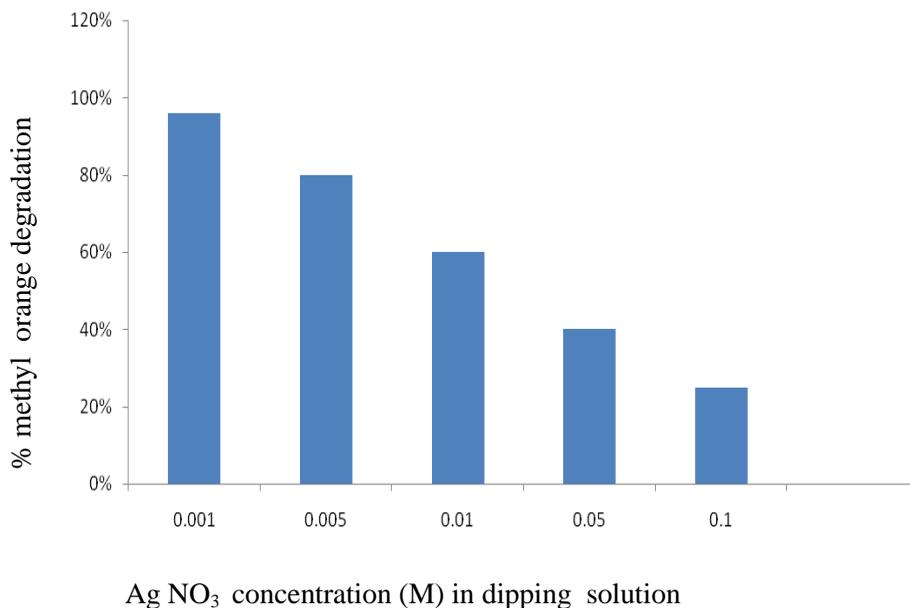


Figure 11: Photocatalytic activity of Ag / TiO₂ films as a function of the Ag NO₃ dipping solution.

Table 4: Variation in % degradation of methyl orange by Ag / TiO₂ as a function of Ag NO₃ dipping solution.

Ag NO₃ Concentration (M)	%degradation	Absorbance
0.1	25%	17.800
0.05	40%	14.250
0.01	60%	9.500
0.005	80%	4.750
0.001	96%	0.950



Figure 12: Photo of degradation of methyl orange by Ag/TiO₂ film after dipping for 3s in 0.001 M of silver solution during 2 hours.

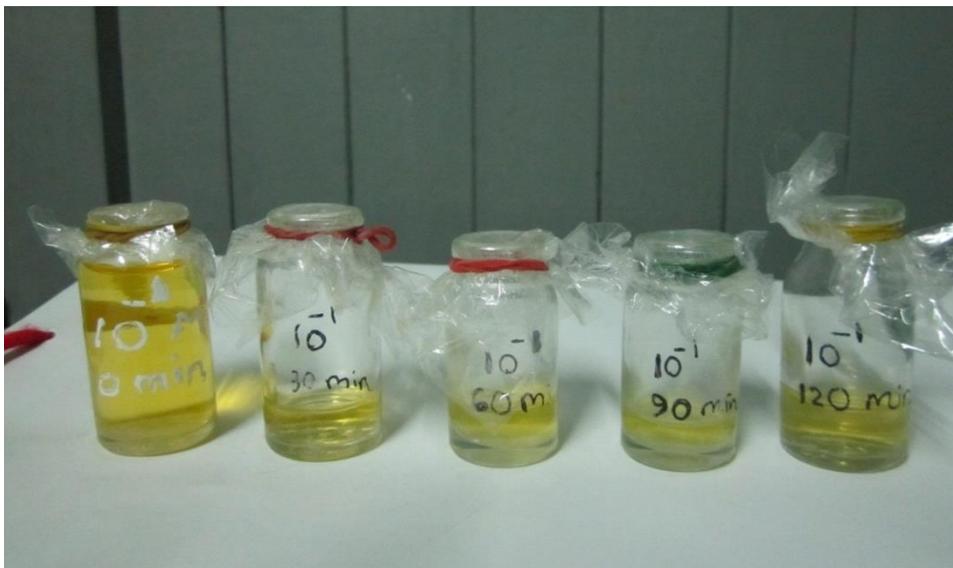


Figure 13: Photo of degradation of methyl orange by Ag/TiO₂ film after dipping for 3s in 0.1 M of silver solution during 2 hours.

Conclusion

Titanium dioxide films developed on the glass slides were modified by silver deposition and successfully tested for the photocatalytic degradation of the pollutant methyl orange. According to the SEM results, the film deposited from the lower concentration of the Ag^+ solution exhibits surface characteristic of higher roughness in comparison with those resulting from higher concentration. This might be one reason for the higher photocatalytic behavior in the film with 0.001 M Ag^+ . According to the XRD analysis the silver oxide particle were not crystallize on TiO_2 surface. According to the UV analysis, it was also found that the percentage of decolorization and photodegradation increase with the increase in reaction time due to photocatalytic activity observations. Moreover, the photodegradation efficiency of photocatalyst TiO_2 is lower than that of Ag modified TiO_2 . Therefore, it is concluded that the presence of Ag do enhance the degradation percentage. Besides, the results show that the decrease in concentration of AgNO_3 can increase the photocatalytic efficiency. Finally, all the observations in this work pointed out that TiO_2 photocatalyst modified with less amount of Ag do enhance the photocatalytic efficiency via the decomposition of organic pollutant. Therefore, it is concluded that the characterization of silver and titania surface is essential for the research of water pollution.

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