

SURFACTANT-ASSISTED IMMOBILIZATION OF TiO₂ ONTO GLASS SUBSTRATES FOR PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE

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Abstract

Titanium dioxide-based photocatalysis is a type of advanced oxidation process that can be used to completely degrade and mineralize organic pollutants. The semiconductor titanium dioxide (TiO₂) is used as a photocatalyst and is activated when it absorbs photon energy equal or greater than its band gap energy. The activation of TiO₂ as a photocatalyst leads to the formation of active sites on its surface that can trigger series of oxidative-reductive reactions to mineralize the pollutants. In most cases, TiO₂ is commonly used in slurry form and the recovery of the catalyst after water treatment often requires another separate process.

To address this concern, TiO₂ photocatalyst have been immobilized on the surface of soda borosilicate glass slides with the aid of a commercial non-ionic surfactant, under the trade name Triton X-100. The TiO₂ thin film was prepared using sol-gel process and immobilized on the glass surface at different number of coatings using the dip coating technique. The TiO₂ thin films were characterized using FE-SEM, XRD and TGA and its photocatalytic activities were tested in the degradation of a model organic pollutant, methylene blue (MB).

Characterization of the prepared samples by XRD showed that TiO₂ in the form of anatase was successfully deposited on the glass slides. The addition of surfactant created thicker TiO₂ thin films that showed better performance during photocatalytic activity test. The result of the activity tests showed that the TiO₂ on the glass slide was able to degrade MB and the number of times that TiO₂ was coated on the glass slide also affected the rate of MB degradation.

Keywords: Dip-coating, Surfactant, TiO₂ Immobilization, TiO₂ Sol-Gel

Introduction

Titanium dioxide is a known photocatalyst and is often employed in advance oxidation processes for the complete degradation and mineralization of organic pollutants. The destruction of the organic pollutant on the surface of the TiO₂ photocatalyst is usually brought about by the series of oxidative-reductive reactions on the surface of the TiO₂ initiated by the generation of electron-hole pairs when the semiconductor TiO₂ absorbs energy equal or greater than its band gap energy. The energy is usually supplied by a UV light source. In the UV-TiO₂ system, TiO₂ is commonly used in slurry form. Even though the use of TiO₂ in slurry form is very effective in pollutant degradation in water, post treatment recovery of TiO₂ powder poses a problem because it entails a separate process for the sole purpose of recovering TiO₂ catalyst.

Researchers have studied different ways to immobilize TiO₂ photocatalyst so that post-treatment recovery of the catalyst will be easier. In our study, TiO₂ photocatalyst have been immobilized on the surface of soda borosilicate glass with the help of a non-ionic surfactant, Triton X-100. Surfactants or polymer templating technique has been applied in the sol-gel process to prepare mesoporous TiO₂ thin films. It was reported by some researches such as Chen et al. (2008) that surfactants are potential structure directing agents that can improve the transparency and photocatalytic activity of the TiO₂ films. The deposited TiO₂ films were tested in a photocatalytic degradation of a model organic pollutant, methylene blue (MB), a cationic dye.

Materials and Methods

Chemicals

Titanium tetraisopropoxide, min. 95.0% purity, acetic acid, min. 99.9%, ethanol (ethyl alcohol), 99.5%, and 1 N nitric acid solution, 99.8%, all from Wako Chemicals were used as received in the experiments. Laboratory-grade Triton X-100 from Sigma Aldrich was used as the surfactant. Methylene blue C.I. 52015 from Merck Chemicals was used in the test of the catalyst activity. The procedure to immobilize TiO₂ onto glass slides was outlined in the following section.

Preparation of TiO₂ Thin Films

The thin film was prepared using sol-gel process and immobilized on the glass surface using dip coating technique. Titanium tetraisopropoxide, acetic acid and ethanol were combined to make the TiO₂ sol that was used as the dipping solution. Borosilicate microscope slides were used as the glass substrate. The surfactant, Triton X-100, at 10 mol% with respect to TiO₂, was also added to aid in the dispersion and immobilization of TiO₂ onto the microscope slides. The dipped glass slides were calcined at 450 deg C. for 1 hour. The number of coatings was varied to one, three and six coatings of TiO₂ thin film deposited on glass slides and labeled TX101, TX103, and TX106, respectively. For comparison NS6 or a sample with six coatings of TiO₂ film without surfactant was also prepared. All of the films that were produced were transparent even after undergoing numerous dip-calcine cycles.

Photocatalytic Activity Test

In the photocatalytic activity testing of the thin films, TiO₂ glass slides were dipped in 10 ppm solution of methylene blue. An area of approximately 0.135 cm² of the TiO₂ thin film was in contact per ml of MB solution, and irradiated using 15 W UV lamps with peak wavelength at 360 nm. The activity of the TiO₂ immobilized without surfactant and the film that was immobilized using Triton X-100 are compared. A blank, consisting of methylene blue solution only exposed to UV light was included as a control. The methylene blue was allowed to be adsorbed on the glass slides for 30 minutes before turning on the UV lamp. Samples were taken every hour and the absorbance of MB solution at 665 nm were analyzed using UV-Vis spectrophotometer (UV 1800, Shimadzu Corp., Japan)

Results and Discussion

Characterization of TiO₂ Thin Film

FE-SEM Images

The morphology, surface structure, and thickness of the films were studied using FE-SEM. Figure 1 shows the difference between the morphology of the TiO₂ films that was deposited with surfactant Triton X-100 (TX106) compared to the other that did not use the surfactant (NS6). Both of the films underwent dip-calcine cycles until TiO₂ layer reaches six. When surfactant was added, the characteristic of the TiO₂ film surface changed, creating a patterned surface compared to the relatively smooth and fine surface of the TiO₂ film that was immobilized without the surfactant.

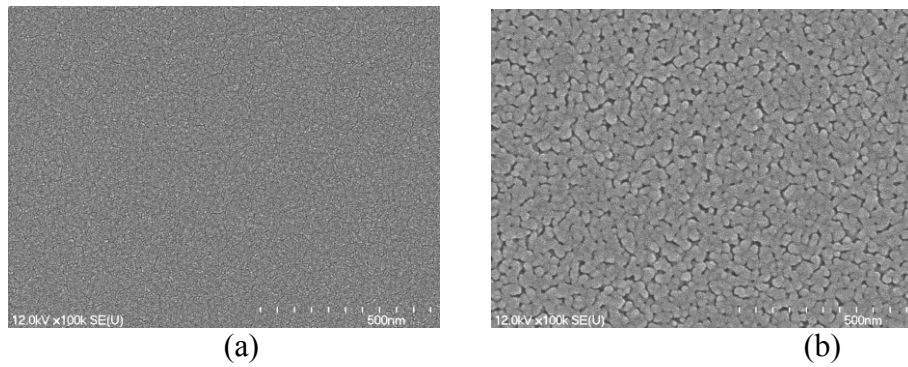


Figure 1. FE-SEM Images of TiO₂ films of NS6 and TX106

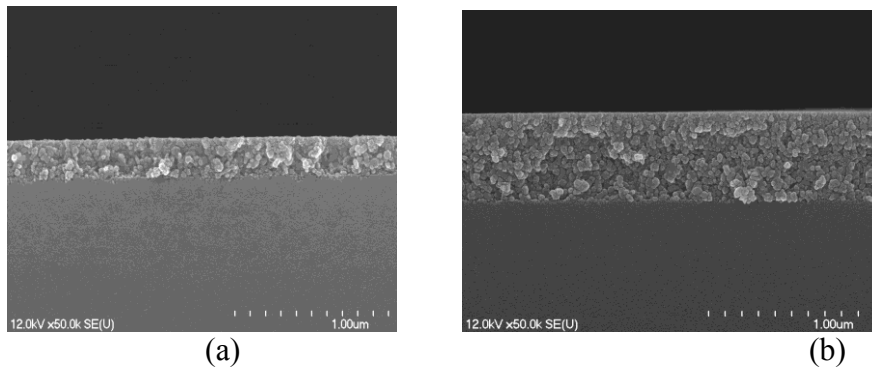


Figure 2. Cross-sectional FE-SEM Images of TX103 and TX106

Table 1. Thickness of the Film Deposited on the Glass Substrate

Film	Thickness (nm) (approx.)	Film Description
NS6	270	No Surfactant, 6 coatings
TX101	110	10 wt% Triton X-100, 1 coating
TX103	250	10 wt% Triton X-100, 3 coatings
TX106	530	10 wt% Triton X-100, 6 coatings

Cross-sectional images of three coatings and six coatings of TiO₂ film deposited with surfactant (Figure 2) showed that repeating the dip-calcine cycle increased the thickness of the films deposited in the glass. The thickness of TiO₂ film increased as the number of coatings increased. The thickness of the deposited film is given in Table 1. Furthermore from the values in the table, it can be seen that thicker TiO₂ films can be deposited if Triton X-100 was added to the dipping solution. The thermal properties of films were analyzed using thermogravimetry or TG-DTA (Rigaku Thermo plus TG 8120). The TG-DTA plot in Figure 3 showed that surfactant generally burned at 450°C so the calcination temperature was high enough to burn the surfactant.

As for the determination of the crystal phase of the immobilized TiO₂, x-ray diffraction patterns were obtained using Multiflex X-Ray Diffractometer (Rigaku Corporation) which was plotted in Figure 4. The plot shows that TiO₂ on the glass slide is pure anatase and as the film thickness increase, the intensity of the anatase peak also becomes higher. Only a small peak was observed even after six coatings because only small amounts of TiO₂ deposited as a thin film, is present on the glass substrate.

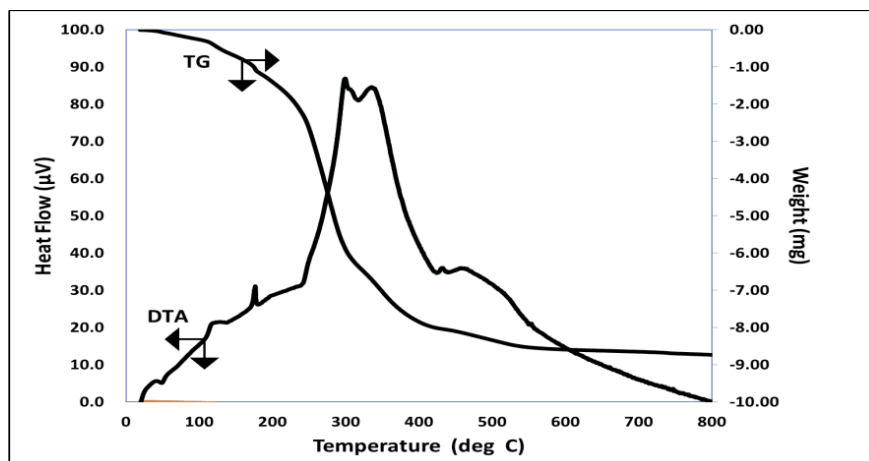


Figure 3. TG-DTA diagram of TX10 thin film

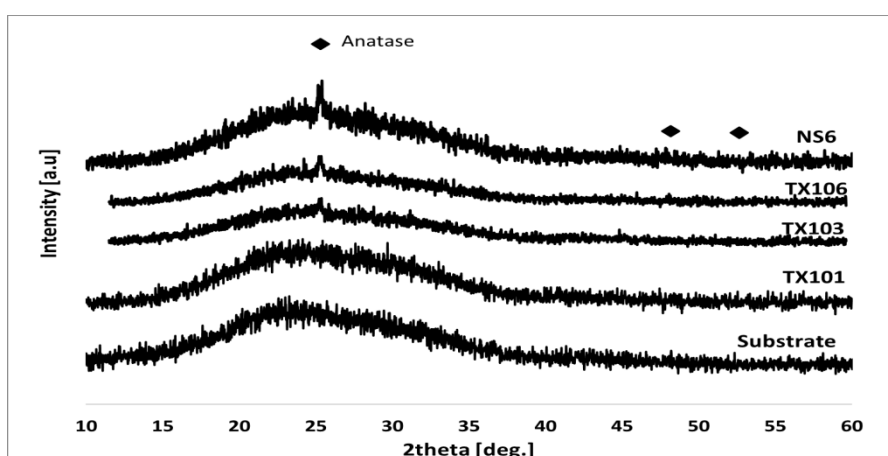


Figure 4. XRD plot of TiO₂ thin films

Activity Test of TiO₂ Thin Film Photocatalyst on MB Degradation

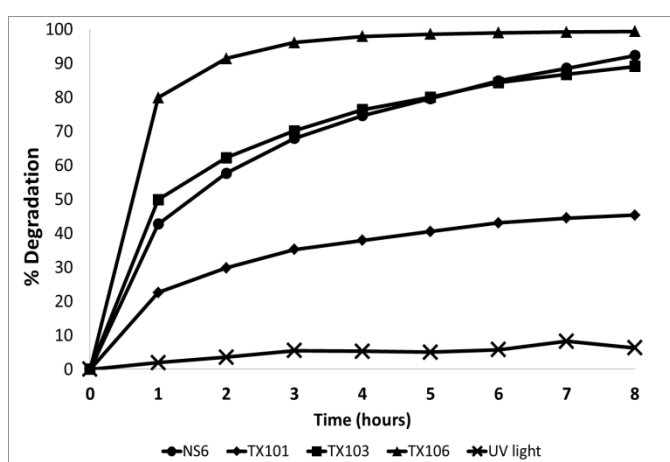


Figure 5. Activity of TiO₂ thin film as photocatalyst

The result of the activity test (Figure 4) shows the comparison between the activity of TiO₂ immobilized with and without surfactant. The blank run shows minimal change on the methylene blue in the solution. As for TiO₂ films, it can be seen that the number of times that TiO₂ was coated on the glass slide also affected the rate of MB degradation. The thicker TiO₂

film was able to degrade MB faster because more TiO₂ are available as photocatalytic site. However, the surface morphology also affected the activity, the unique patterned surface created on the film deposited using a surfactant helped to increase the photocatalytic activity by increasing the availability, possibly through increasing the accessibility, of the active sites for oxidation of methylene blue. Furthermore, the TiO₂ film deposited on the glass substrate was identified as anatase, which is also advantageous for photocatalytic reactions.

Conclusions

In summary, sol-gel dip coating process is a simple technique that can be used to immobilize TiO₂ in a glass substrate. The film thickness can be increased by repeating the dip-calcine cycle and also through addition of surfactant. Surfactant aids in immobilization process by serving as a templating agents or possible structure directing agents. The TiO₂ films remained transparent even after multiple layers of coating and were shown to have pure anatase crystalline structure. Its photocatalytic activity was tested on the degradation of an organic dye, methylene blue. The methylene blue degradation was faster as the TiO₂ film becomes thicker because there are more active sites that can breakdown the dye. Aside from that, the addition of surfactant in the dipping solution produced a more characteristic TiO₂ thin film surface that has also promoted the increase of its photocatalytic activity.

Acknowledgements

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