

Photocatalytic Activity and Hydrophilicity of Immobilized Nano-TiO₂ Thin Films Prepared with Surfactants

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Abstract. We have immobilized titanium dioxide (TiO₂) thin films on glass substrates using TiO₂ sol-gel solution with cationic and non-ionic surfactants. The prepared films were characterized using field emission scanning electron microscope (FE-SEM), thermogravimetry and differential thermal analysis (TG-DTA), and x-ray diffraction (XRD). The films' photocatalytic performances were tested in terms of its ability to degrade of an organic dye, methylene blue. Aside from its photocatalytic performance, the photo-induced hydrophilicity of thin TiO₂ films surface was also studied. Characterization of the thin film showed that the addition of surfactant gave rise to characteristic patterns on the surface of the TiO₂ thin film which eventually affects the photocatalytic activity as well. All of the TiO₂ multilayer thin films were able to degrade MB, but the films with prepared with surfactant showed better performance than the TiO₂ thin film prepared without the surfactant. However, in the case UV light-induced surface hydrophilicity of the TiO₂ thin films, the effect of the addition of surfactant become only significant at the end of irradiation.

Keywords: Photocatalysis, surface hydrophilicity, surfactant, TiO₂ thin films

1. Introduction

Titanium dioxide-based photocatalysis is a type of advanced oxidation process that can be used to completely degrade and mineralize organic pollutants [1], [2]. 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. However, TiO₂ is commonly used in slurry form and the post treatment recovery of TiO₂ poses a problem because it entails a separate process for the sole purpose of recovering TiO₂ catalyst.

Besides the usual photocatalytic oxidation property, the photo-induced hydrophilicity of thin TiO₂ films is an interesting property that can give rise to other applications such as self-cleaning surfaces, particularly glass or mirrors. The mechanism for photo-induced hydrophilicity of TiO₂ thin film is different from the mechanism that gives rise to its photocatalytic properties. A photocatalyst semiconductor oxide would not always exhibit photo-induced hydrophilicity under UV light, as much as a semiconductor photocatalyst which exhibits photo-induced surface hydrophilicity would show photo-oxidation properties [3].

Acetic acid assisted sol-gel strategy was used in this research. Use of acetic acid and alcohol has yield better results in the synthesis of TiO₂ sol [4], [5] because they trigger slow hydrolysis reaction that will lead to formation of finer, uniform TiO₂ particle size. Non-ionic surfactant Triton X-100 and cationic surfactant, cetyltrimethylammonium bromide (CTAB) were added to the dipping solution as to further improve the characteristics of the immobilized TiO₂ thin film. Addition of surfactants or polymer templates can possibly

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improve the structure stability of the film structure and create a mesoporous structure that can improve its catalytic properties [6], [7]. 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 TG-DTA and its photocatalytic activities of were tested in the degradation of a model organic pollutant, methylene blue (MB). Aside from the photocatalytic activity of the TiO₂ films, its hydrophilicity under UV light was also studied.

2. Experimental and Methodology

TiO₂ thin films were prepared using a TiO₂ sol with 10 mol% of surfactant, or combination of surfactants with respect to TiO₂. A non-ionic surfactant, Triton X-100, and cationic surfactant, CTAB were used in the preparation of thin TiO₂ films. Microscope glass slides were utilized as substrates and TiO₂ was deposited by dip-coating method. After dipping into the TiO₂ sol-gel, the glass substrates were calcined at 450 deg C for minimum of 1 hr. The thickness of the TiO₂ thin film was increased by repeating cycles of dipping and calcination of the glass substrate. A total of six layers of TiO₂ were deposited on the substrate. Characterizations of the TiO₂ thin films were done using FE-SEM, XRD and TG-DTA.

Photocatalytic activity was evaluated by decomposition of methylene blue. A TiO₂ thin film area of approximately 0.135 cm² was in contact per ml of MB solution. UV black light blue lamps with peak intensity at 352 nm were used in the experiment. The absorbance of MB solution is analyzed at 665 nm using UV-Vis spectrophotometer (UV 1800, Shimadzu Corp., Japan).

The hydrophilicity of TiO₂ thin film under UV light was evaluated by measuring surface contact angle using a commercial contact angle meter (DM-500, Kyowa Interface Science Co., Ltd.) by the sessile drop method. Stearic acid was coated on the surface of the films as contaminant and then the films were exposed to UV light while measuring the change in the water contact angles.

3. Results and Discussion

3.1. Characterization of TiO₂ Thin Films

All of the TiO₂ thin films showed anatase crystal structure and the surface morphology as examined by XRD and the FE-SEM images are shown in Fig. 1. The type of surfactant affected the type of morphology of the TiO₂ thin film. TG-DTA results showed that surfactants were burned off at 450 deg C.

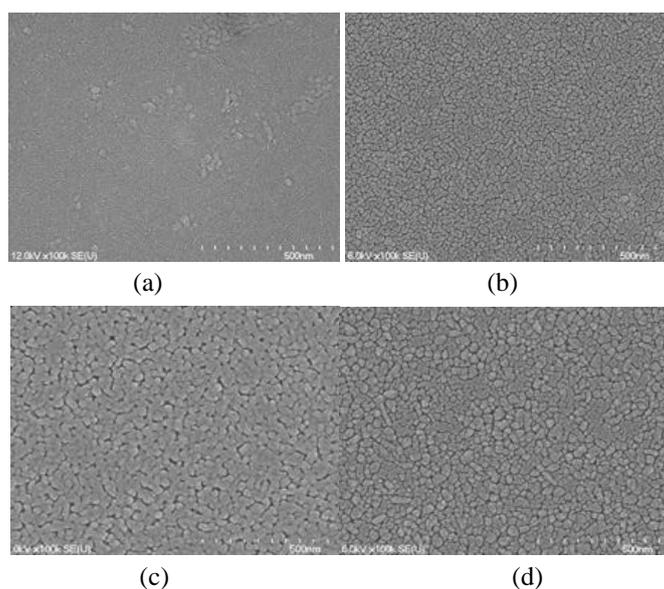


Fig. 1: FE-SEM images of the surfaces of the TiO₂ thin films coated six times :(a) with no surfactant (NS), (b) CTAB, (c) Triton X-100 (TX100) and (d) CTAB and TX100 (CTAB+TX100)

3.2. Photocatalytic Activity of TiO₂ Thin Films

The result of the activity test as showed in Fig. 2, proves that the TiO₂ immobilized on the glass slide was able to degrade the organic dye, methylene blue (MB). The type of surfactant used also affected the photocatalytic activity because the morphology of the TiO₂ thin film is greatly related to its surface area.

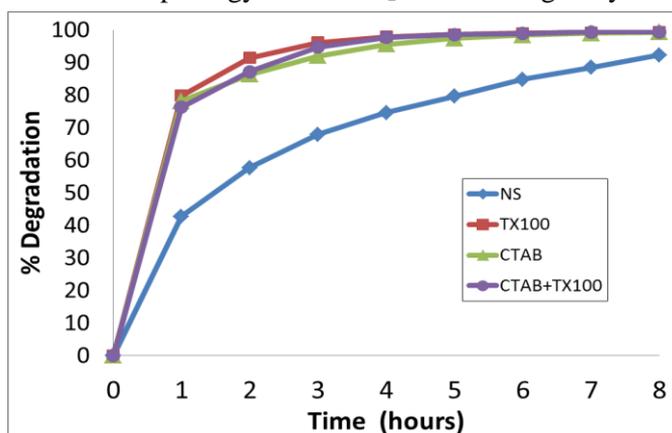


Fig. 2: Photocatalytic activity of immobilized TiO₂ films during MB degradation

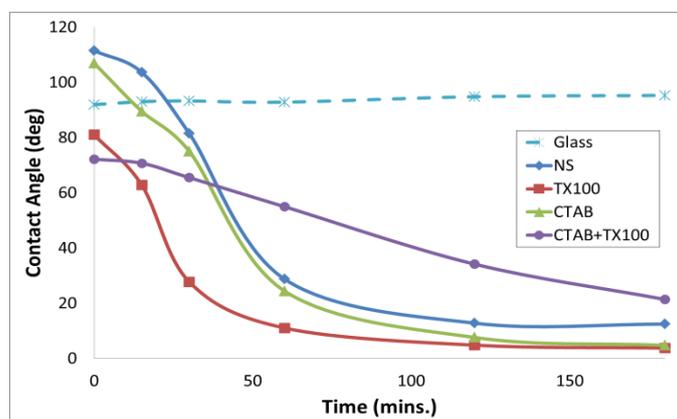


Fig. 3: Change of water contact angle of TiO₂ thin film with different surfactants

3.3. Hydrophilicity of TiO₂ Thin Films

Fig. 3 gives the plot of the data of six layers of TiO₂ films per surfactant that was used in the experiment. This indicates that the factor affecting hydrophilic property of the TiO₂ thin film is only affected by the changes that happened on the few topmost layers of the TiO₂ immobilized onto the glass slides. Even though the initial contact angles are different, the surface of NS, TX100 and CTAB turned hydrophilic after 3 hours of UV irradiation. This might be related to the type of the surface morphology formed when CTAB and TX100 are used, which can be seen in Fig. 1. However, in this experiment we used glass substrates and reports about the effect of Na⁺ ions diffusion to the TiO₂ films indicates that there might be deleterious effect on the structure of the TiO₂ immobilized on the surface of the glass [8].

Although all of the films become hydrophilic after 3 hours of UV irradiation, the final contact angle values are different. Except for the CTAB+TX100 film, which seems it still has not reach its equilibrium state, the films prepared with surfactant showed lower contact angle than the film without surfactant. Both TX100 and CTAB reached a final contact angle of 5 degrees, which is already considered as superhydrophilic and already posses anti-fogging property [9]. This result can be explained by the rougher or texturized surface that was induced by addition of surfactant into the dipping solution. As rougher TiO₂ surfaces tends to have lower contact angle than smoother TiO₂ surfaces [10].

4. Conclusions

Sol-gel dip coating process is a simple way to deposit TiO₂ thin films onto glass substrate. Surfactants also aid in the immobilization process by serving as a templating agents or possible structure directing agents. Different surfactant gave different surface morphology. Characterization of the glass slides showed that TiO₂ in the form of anatase was successfully deposited on the glass slides. The result of the activity tests showed that the TiO₂ on the glass slide was able to degrade MB. The number of times that TiO₂ was coated on the glass slide also affected the rate of MB degradation, showing that as the thickness of the TiO₂ film increased, the photocatalytic activity also increased because of the increased availability of reactive sites.

The ability to induce photocatalytic oxidation of target pollutants and surface hydrophilicity are two distinct properties of TiO₂ which are based on the same photo-induced electronic transition. However, increasing the thickness of the TiO₂ layer would not always enhance the hydrophilic property of the TiO₂ thin film.

5. Acknowledgements

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6. References

- [1] U. Cernigoj, L. Stangar, P. Trebse, P. Ribic, *Acta Chim Slov*, 53 (2006) 29.
- [2] C.Turch, D. Ollis, *J. Catal.*, 122 (1990) 178.
- [3] T. Watanabe, S. Fukuyama, M. Miyauchi, A. Fujishima, K. Hashimoto, *J. Sol-Gel Sci. Technol.*, 19 (2000) 71.
- [4] H. Choi, E. Stathatos, D. Dionysiou, *Thin Solid Films* 510 (2006) 107-114
- [5] T. Venkatachalam, K. Sakthivel, R. Renugadevi, R. Narayanasamy, R. Rupa, *AIP Conf. Proc.* (2011) 1391.
- [6] J. Pan, X. Zhao, W. Lee, *Chem. Eng. J.*, 170 (2011) 363.
- [7] S. Patil, B. Hameed, A. Skapin, U. Stangar, *Chem. Eng. J.*, 174 (2011) 190.
- [8] P. Novotna, J. Krysa, J. Maixner, P. Kluson, P. Novak, *Surf. Coat. Tech.*, 204 (2010) 2570-2575. A. Gray. *Modern Differential Geometry*. CRE Press, 1998.
- [9] F. Cebeci, Z. Wu, L. Zhai, R. Cohen, M. Rubner, *Langmuir* 22 (2006) 2856.
- [10] M. Miyauchi, N. Kieda, S. Hishita, T. Mitsuhashi, A. Nakajima, T. Watanabe, K. Hashimoto, *Surf. Sci.* 511 (2002) 401.

