

Characterization and Bactericidal Activity of Thin-film TiO₂ Photocatalyst

Kannikar Jungsuwattananon¹, Somsak Saesoo¹, Nuttaporn Pimpha^{1*}
and Nobuaki Negishi²

¹National Nanotechnology Center, 113, Paholyothin Rd., Klong 1, Klong Luang, Pathumthani, 12120, Thailand

²National Institute of Advanced Science and Technology (AIST), Institute for Environmental Management Technology, Tsukuba-West 16-1 Onogawa, Tsukuba 305-8569, Japan

*Corresponding author. E-mail: nuttaporn@nanotec.or.th

ABSTRACT

Transparent and highly porous photocatalytic thin-films were prepared using the dip-coating method with the thermal decomposition of titanium alkoxide complex. Titanium alkoxide was coordinated with 2,4-pentanedione and diethanolamine in order to study its morphology and film formation. α -Terpineol was used as a highly viscous solvent. The phase composition and crystallinity of TiO₂ particle obtained after calcination at 480°C by X-ray diffractometer (XRD) shows 200% anatase phase and composes of well-defined crystalline. The decomposition behavior of the residual organic compound was investigated by thermogravimetric analyzer (TGA). The surface structure of the nano-sized TiO₂ crystal was determined by dynamic force microscope (DFM). The antimicrobial activity of the TiO₂ thin film against Escherichia coli ATCC 25922 showed 97% (using 2, 4-pentanedione as a ligand) and 50% (using diethanolamine as a ligand) microbial reduction under UV light. It can be concluded that this photocatalyst provided a great potential application as bactericidal film.

Key words: Thin-film photocatalyst, Dip-coating method, and Bactericidal effect

INTRODUCTION

Nanocrystalline titanium dioxide photocatalyst (TiO₂) is one of the most promising materials that have been used in various fields of environmental redemption. It was used to degrade hazardous organic/inorganic compounds, decolorization of dyeing waste water, direct decomposition of NO_x, SO_x and the photocatalytic biodegradation of microbial. Utilization of the TiO₂ photocatalysts greatly involves on oxidation and reduction reaction between UV-light generated charges (e⁻ and h⁺) and organic species on TiO₂ surface. It leads to the generation of reactive oxygen species (ROS) that cause various damages to living organisms

(Fujishima et al., 2000; Miao et al., 2004; Herrmann, 1999). Many researchers have paid attention on the preparation and characterization of TiO₂ nanoparticles as well as their applications. The TiO₂ can be prepared either in the form of particles or thin-film. A variety of coating technique has been modified and developed to produce photocatalytic TiO₂ surface. Among several techniques, the sol-gel dip coating is known to produce films with high porosity and composing small particles (Ge et al., 2006; Hu and Yuan, 2005; Li et al., 2004). It is obviously reported that the photocatalytic activities of TiO₂ strongly depend on crystal structure, surface morphology and crystallinity of the achieve photocatalysts (Yuhong et al., 2002; Liqianga et al., 2003). Moreover, the efficient TiO₂ films should be transparent. To obtain all requirements, several attempts made transparent TiO₂ films by sol-gel method using inorganic binder, such as colloidal silica, and SiO₂-TiO₂ binary system. However, silica can embedded TiO₂ particle which consequently results a lower surface area and therefore reduces photocatalytic activity. This study was aimed to prepare transparent thin-film TiO₂ without utilization of silica binder to achieve an efficient TiO₂ film. In this present work, the transparent thin film TiO₂ photocatalysts immobilizing on glass substrates were prepared by dip-coating process using the titanium tetraisopropoxide as Ti-precursor which was coordinated with 2,4-pentanedione, and diethanolamine ligands. (-Terpineol was used as a highly viscous solvent. The morphology, crystal structure, as well as the bactericidal activity of the obtained films were also reported.

MATERIALS AND METHODS

Preparation of TiO₂ sol

The TiO₂ precursor was prepared by sol-gel method which as described by Negishi et al., 2007. Titanium tetraisopropoxide (Ti(OC₃H₇)₄), propan-2-ol (2-PrOH, 99.9% purity), 2, 4-pentanedione, diethanolamine and α -terpineol (TPO) were used as a Ti precursor, solvent, ligands for TPOT and a highly viscous solvent, respectively. All chemicals were purchased from Wako Chemical Co. and of analytical grade. Titanium tetraisopropoxide was dissolved in propan-2-ol containing 2, 4-pentanedione or diethanolamine as a ligand. The resulting solution was stirred for 5 min and then slowly added (-terpineol to adjust the viscosity of the precursor.

Preparation of TiO₂ thin-film

For the preparation of the TiO₂ film, the silica-coated glass plates (200 x 150 x 1.1 mm) were cleaned thoroughly and dried before deposition. Then the substrate was dipped in the TiO₂ precursor sol with the withdrawing rate of 1.5 mm/min, and then treated at 480°C for 1 h. The TiO₂ layers on glass plates were thickened by repeating the dip-coating and sintering process for 20 times.

Material characterization

The crystallite structures of the TiO₂ films obtained from different synthesized condition were characterized by using an X-ray diffractometer (XRD; Rigaku,

TTRAX III, Japan). Phase identification was performed by comparison with the standard diffraction patterns of the Joint Committee Powder Diffraction Standard (JCPDS). The surface texture of the film was observed by tapping mode dynamic force microscopy (DFM; SPI 4000, Seiko, Japan). An experiment was performed with a tapping mode using NSG 20 cantilever with 190-325 KHz resonance frequency. All images were recorded in air at room temperature at a scan speed of 1 Hz. To further investigate the appropriated calcination temperature of the TiO₂ sample, some of the as-synthesized TiO₂ gels were subjected to a thermogravimetric analysis (TGA; SDTA851e, Mettler Toledo, Switzerland). The sample of 5-20 mg was accurately weighed into an aluminum pan. The measurement was conducted at a heating rate of 20°C/min under nitrogen purge. A scanning electron microscope (SEM; S-3400N, Hitachi, Japan) was used to measure the film thickness.

Bactericidal activity of TiO₂ thin-film photocatalysts

Modified method from Japanese Industrial Standard (JIS Z 2801) has been employed in this study. This method was considered for the determination of bactericidal ability of the thin-film TiO₂ photocatalysts against *Escherichia coli* ATCC 25922. The experimental procedures were performed by the sterilization of thin-film samples in autoclave at 121°C for 15 min. The samples were exposed to microbe at an initial concentration 20⁵ CFU/ml in 0.4 ml Nutrient Broth (NB) and then incubated under UV light (0.6 mW/cm²) for 24 h. Samples were transferred into 20 ml of TSB, diluted and cultivated on TSA at 37°C for 24 h for total bacteria count testing. Finally, the survival number of *E. coli* was obtained by colony counting (CFU/ml).

RESULTS AND DISCUSSION

Characterization of thin-film TiO₂ photocatalyst

The appropriate calcination temperature for the preparation of thin-film TiO₂ was selected from the thermal analysis profile of as-synthesized TiO₂ gel. As shown in Figure 1, a major weight loss of about 83% at the temperature below 300°C was attributed to desorption of water. The weight loss of about 11 % was observed between 300-380°C corresponded to the decomposition of the residual organic component. However, the sample also consisted of about 6 wt.% of organic alkyl residue. From this result, the optimal calcination temperature for preparing TiO₂ thin-film photocatalyst was about 480°C.

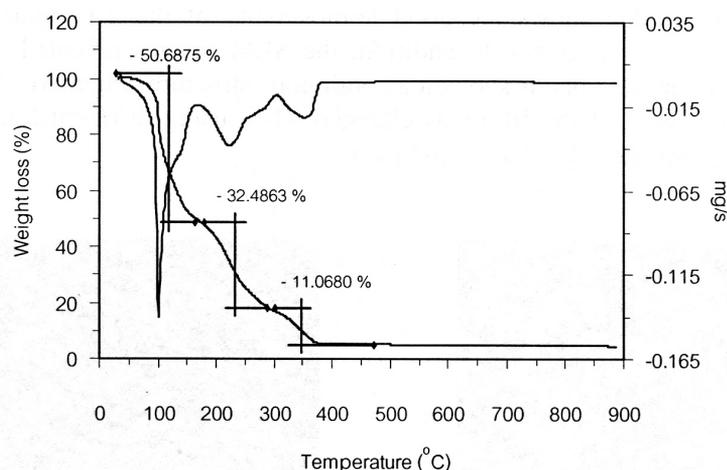


Figure 1. TGA profiles of the as-synthesized TiO_2 gel dried at 200°C for 1 day.

The immobilized TiO_2 film was subjected to calcine at 480°C for 1 h and repeating the dip-coating and sintering process for 20 times. The XRD patterns were recorded as shown in Figure 2. It was obvious from the XRD patterns that the TiO_2 thin-film obtained from two kinds of ligand showed 200% anatase phase. The peak was indicated at 2θ equals to 25.3 degrees. Sharp and narrow-intensity peaks of all samples indicated that the anatase phase contained crystalline component. Note that; the TiO_2 particles dispersing on the glass plate are very small crystallite size.

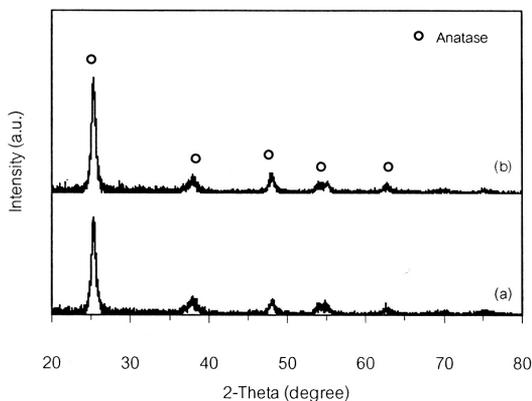


Figure 2. XRD patterns of the TiO_2 thin-film obtained from using different kind of ligands; (a) 2, 4-pentanedione, (b) diethanolamine.

The well-defined crystallinity and particle size of TiO_2 was confirmed by the good correlation with DFM analysis as shown in Figure 3. The image presents a surface composing the small TiO_2 particles with the same average size about 11 nm for the sample obtained from Figure 3(a) and 3(b). It was also important to

note that the roughness values also evaluated from this image which is equal to 4.29 nm and 4.74 nm for the film contains 2, 4-pentanedione and diethanolamine, respectively. The lower roughness value shows the good homogeneity of the TiO₂ particles on the surface (Bernardi et al., 2001). In addition, the SEM images revealed that the film immobilized at various ligands showed a continuous structure (Figure 4). It was found out that the thickness of the film was changed when using different ligands (Figure 4(a) shows 952 nm and 4(b) shows 1.62 μm).

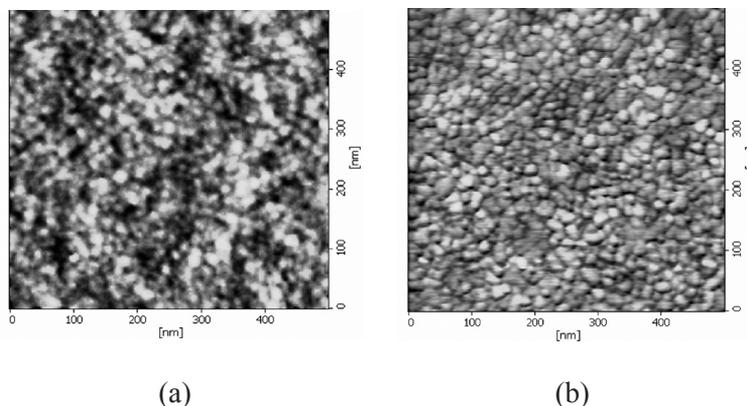


Figure 3. DFM surface morphology of thin-film TiO₂ photocatalysts obtained from using different kind of ligands; (a) 2, 4-pentanedione, (b) diethanolamine.

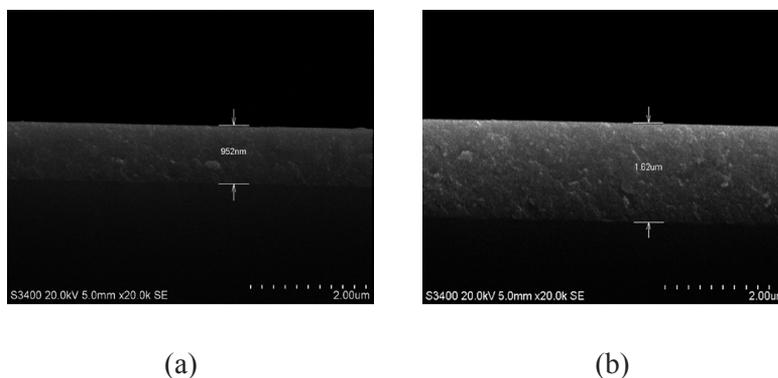


Figure 4. SEM images of TiO₂ thin-film photocatalyst obtained from using different kind of ligands; (a) 2, 4-pentanedione, (b) diethanolamine.

Determination of bactericidal activity of TiO₂ thin-film photocatalysts

Bactericidal activity of TiO₂ thin-film photocatalysts with different using ligand were investigated under UV light for 24 h. It was demonstrated that the coated glass plate reveal higher antimicrobial activity than uncoated glass plate (Figure 5). It was found that the TiO₂ thin-film using 2,4-pentandione as a ligand showed better activity than diethanolamine.

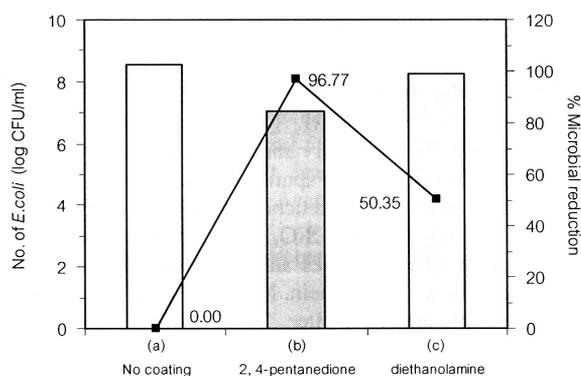


Figure 5. Bactericidal activity of thin-film TiO₂ photocatalyst obtained from using different kind of ligands; (a) 2, 4-pentanedione, (b) diethanolamine.

CONCLUSION

A homogeneous and transparent thin-films photocatalyst were successfully prepared by using the dip-coating process with the thermal decomposition of titanium alkoxide complex. This method was found to synthesize the single anatase phase and having well-defined crystallinity. The texture and the thickness of film could be formulated by using different type of ligand. A photocatalytic activity testing shows that the thin-film had strong antimicrobial effect against *E. coli*.

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