

Preparation of a transparent hydrophilic TiO₂ thin film photocatalyst

Hye-Yeon Chun^a, Sam-Sik Park^a, Sang-Hee You^a, Gi-Hyeon Kang^a, Won-Tae Bae^a, Kwang-Wook Kim^b, Jong-Ee Park^c, Abdullah Öztürk^c and Dong-Woo Shin^{a,*}

^aDivision of Advanced Materials Science and Engineering, Engineering Research Institute, Gyeongsang National University, Jinju, Gyeongnam 660-701 Korea

^bKorea Atomic Energy Research Institute, 150 Dukjin, Yusong, Taejeon, 305-600, Korea

^cMiddle East Technical University, Metallurgical and Materials Engineering Department, Ankara 06531, Turkey

A great deal of attention has been drawn to the coating of transparent photocatalytic TiO₂ onto outdoor building materials, such as glass, tile and stone, for utilizing the self-cleaning effect originating from the hydrophilic behavior of the coated layer under ultraviolet irradiation. Two key technologies should be developed for the successful commercialization of a hydrophilic photocatalyst, i.e., superior activity of the TiO₂ sol, and a transparent and strong adhesive coating. A photocatalytic TiO₂ sol showing a high degree of hydrophilicity was prepared by a sol-gel technique using titanium (IV) isopropoxide as a starting materials. The concentration of TiO₂ was controlled by varying the amount of water and ethanol. The sol was coated on the glass substrate by either a spray or dip coating technique. The characteristics of the coated layer were evaluated in terms of wetting angle, transparency and adhesion strength under the conditions of ultraviolet irradiation. The wettability of a water drop for the wetting angle, UV-visible spectrometer for transparency and pencil hardness for adhesive strength were employed for the evaluations. The coated TiO₂ layer using 1.54 wt% TiO₂ sol showed more than 95% transparency, less than 10° of wetting angle and an adhesive strength of 7H. As a result of this study, photocatalytic TiO₂ coated stone for the application of outdoor building materials has been successfully commercialized.

Key words: Photocatalytic TiO₂ sol, Hydrophilicity, Coating, Transparency.

Introduction

Depletion of fossil fuel energy resources together with environmental contamination has long been a crucial global issue depending on the degree of industrialization. Research on photocatalysts showed the decomposition of organic contaminant using clean solar energy without yielding any harmful by-products [1, 2]. In particular, photocatalytic TiO₂ exhibited higher activities in oxidation and reduction processes and stability to chemical reactions in comparison with SiO₂, ZnO, WO₃, CdS while maintaining a relatively low cost [3, 4]. Although the slurry of photocatalytic TiO₂ particles was extensively studied earlier, the problems of recycling power and blocking of stimulus light due to dispersed particles caused the development of techniques for fixing the photocatalyst on the substrate. Furthermore, a transparent coating layer of photocatalytic TiO₂ on the substrate was required to have same color and texture after coating as the support had originally revealed. Coating of an adhesive and transparent photocatalytic TiO₂ layer could be achieved by combining the preparation of a transparent sol with a proper concentration of nano-crystalline TiO₂ and relevant coating technology. The coated thin TiO₂ layer would show the self-cleaning effect due to the hydrophilicity

which reduces the wetting angle of water to less than 10° under the conditions of ultraviolet irradiation. Water with a low wetting angle can penetrate between the contaminant and substrate, and cleans the surface from rainfall [5]. This self-cleaning effect of the transparent photocatalytic layer could be extensively applied to various lamps, anti-fogging mirrors, window glass and car bodies etc [3].

Photocatalytic TiO₂ samples were conventionally fabricated by one of several methods. i.e., precipitation, hydrothermal and sol-gel. The hydrothermal technique was used for a powder form of TiO₂ and required complex equipment and had the disadvantage of discontinuous processing, whereas the precipitation technique allowed relatively easy fabrication but resulted in an inhomogeneous composition and agglomerations [6, 7]. On the other hand, the sol-gel process can produce a high purity and homogeneous sol at low temperature using simple equipment for a coating layer [8].

An aim of this study was to establish the techniques of (a) forming a transparent TiO₂ sol using a conventional sol-gel method and (b) coating this sol on to a glass substrate for the self-cleaning effect.

Experimental

Synthesis of TiO₂ sol

Amongst the metallic compounds such as metal alkoxides, carboxylate and metal inorganic complexes, the metal

*Corresponding author:
Tel : +82-55-751-5332
Fax: +82-55-755-6755
E-mail: dwshin@gsnu.ac.kr

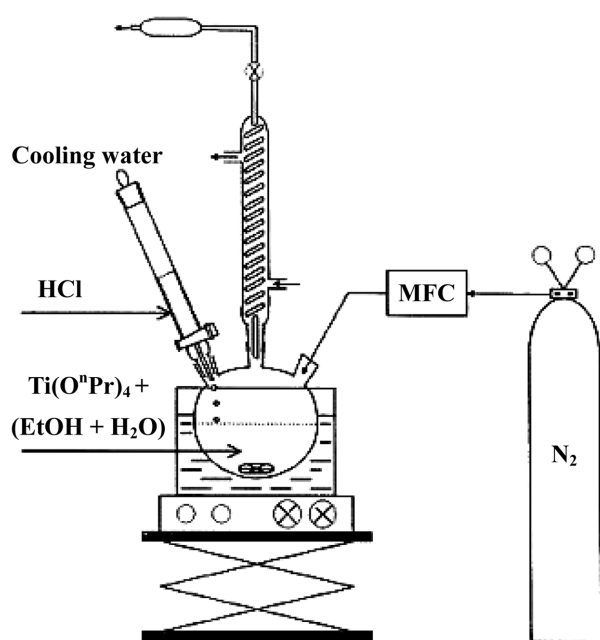


Fig. 1. Experimental set-up for preparation of TiO_2 sol via sol-gel process using titanium (IV) isopropoxide as the raw starting material. The sol was heat-treated for 2 hours yielding anatase crystallites.

alkoxide precursor, titanium isopropoxide (TTIP; 98% Junsei Chemical Co., LTD., Japan, $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$), was selected due to its higher reactivity. Although TTIP exhibited the advantage of forming crystalline TiO_2 at a relatively low temperature, but a high reactivity caused fast hydrolysis with even a little moisture in the air. Thus, the hydrolysis was performed in a N_2 atmosphere. A schematic of the experimental set-up is presented in Fig. 1. Distilled water in the range of 30 to 100 M was added to the precursor for hydration while adding HCl with a pH of 1 to generate the electrostatic attractive force which resulted in a stable and homogeneous solution by preventing sedimentation and agglomeration due to the fast hydration and subsequent condensation process [9]. The mixture of precursor, water and acid was stirred for 2 hours at 80°C in order to reduce the reaction time required for the formation of the sol, and the temperature for generating the anatase type crystalline TiO_2 . The mixture was heated for 30 minutes to evaporate the acid, then ethanol was added as a solvent which would contribute to the rapid drying after coating and transparency of the coated layer. The processing of the TiO_2 sol is shown in Fig. 2, and the concentrations of TiO_2 in various sols are summarized in Table 1.

Coating of TiO_2 thin film

Conventional soda lime glass (25×75 mm) slides were prepared as substrates after ultrasonic cleaning for 30 minutes to remove any contaminant on the surface. Dip and spray coating were performed as shown in Fig. 3. The equipment for dip coating (KEE-PAE Trading Co., Model KPD-101) was used for dipping the glass sample in to the sol with a speed of 300 mm/minutes and holding time of 30 seconds in the sol and then pulled out with the same speed. Spray

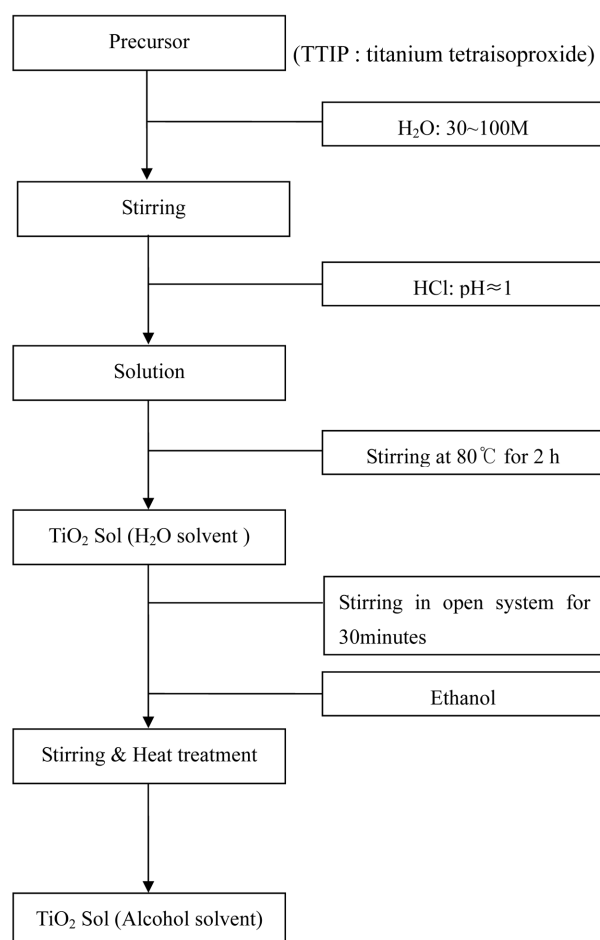


Fig. 2. Flow chart for manufacturing the coating solution using titanium (IV) isopropoxide.

coating was also performed using the equipment shown in Fig. 3. The sol was sprayed through the nozzle with an air pressure of 288 MPa. The moving speed of spray nozzle above the glass sample and the amount of sol while spraying were controlled automatically by a computer. Coating was carried out only one time, and dried for 2 hours at ambient temperature prior to subsequent drying for 1 hour at 60°C .

Characterization of TiO_2 sol and TiO_2 thin films

DSC/TG (TA, Model SDT Q600) and XRD (RIGADU Model D/Max-3c) techniques were used to analyze the crystallization behaviour of the TiO_2 sol and the type of crystalline phase formed, respectively. The precursor

Table 1. Concentration of TiO_2 sol depending on H_2O . One mole of TTIP, 100 mole of ethyl alcohol and HCl for $\text{pH} \approx 1$ were fixed except mole number of H_2O .

H_2O	$\text{TiO}_2(\%)$
120M	1.54
60M	2.43
30M	4.4

*TTIP : titanium tetraisopropoxide

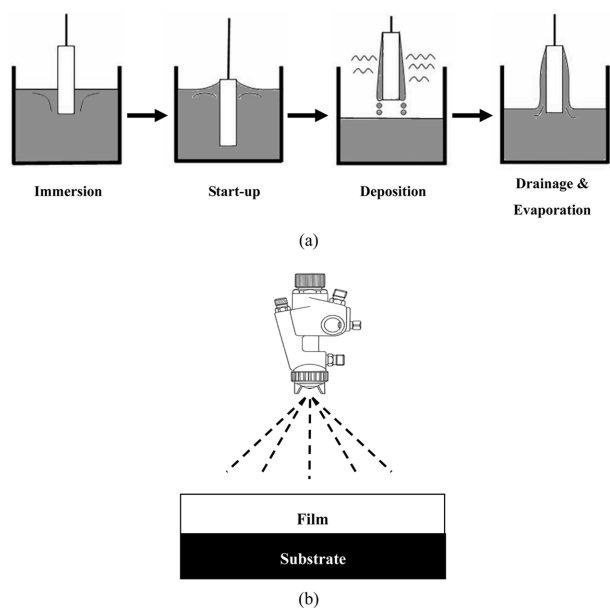


Fig. 3. A schematic of coating methods (a) dip coating, (b) spray coating.

was reacted with water, and then the slurry was dried below 70 °C to obtain precursor powder. The TiO₂ sol was also dried at room temperature before subsequent drying below 70 °C to obtain the powder. Both powders were used for the analysis. The hydrophilicity of the coated layer was evaluated by measuring the wetting angle of a water drop using the equipment (SEO, Model SEO 300A, Korea) while irradiating with the ultraviolet light generated by a lamp of 25W UV-A.. In addition, the transparency of the coated layer was measured by a UV-visible spectrophotometer (SCINCO Co., Model s-3100). The thickness and surface morphology of the coated layer depending on the coating method were examined by FE-SEM (Jeol Co., Model JSM-6400).

Results and Discussion

Characteristics of photocatalytic TiO₂ sol

The occurrence of anatase crystallites was examined using DSC/TG together with XRD analysis for the powder

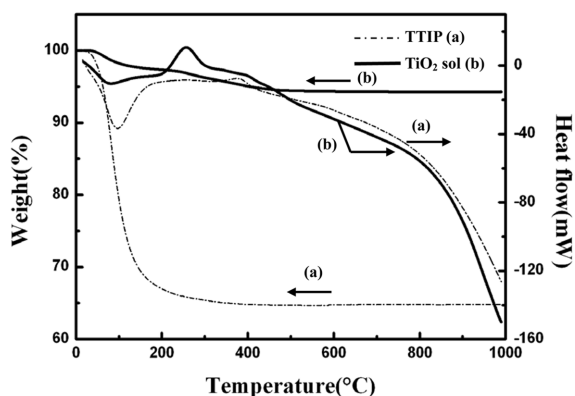


Fig. 4. DSC/TG curves of the (a) precursor, (b) TiO₂ sol.

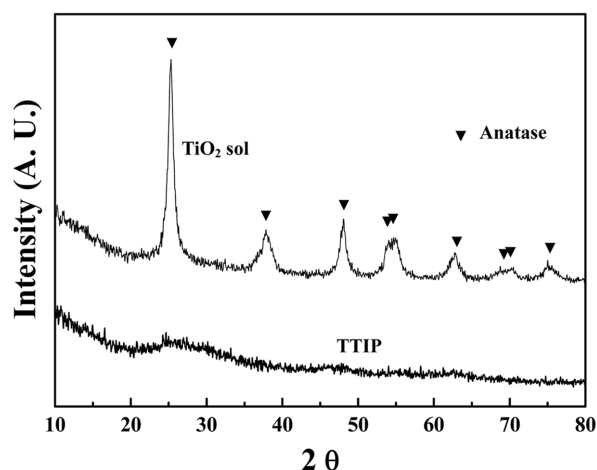


Fig. 5. X-ray diffraction patterns of the (a) TiO₂ sol, (b) precursor.

prepared from the sol fabricated by stirring at 80 °C for 2 hours showing Fig. 4. For the TTIP precursor, a weight loss at around 100 °C due to the evaporation of water was observed in the TGA curve, and an endothermic peak due to water evaporation at around 100 °C and exothermic peak at around 400 °C in the DSC curve which would be attributed to the crystallization are observed as shown in Fig. 4(a). A weight loss at around 100 °C for the powder obtained from the sol and the exothermic peak due to the ignition of C-H organics are observed in Fig. 4(b). However, the exothermic peak presumed to originate from crystallization was not observed at around 400 °C. The powder obtained from the sol which was reacted at 80 °C exhibited the anatase crystalline structure as shown in Fig. 5. This implies that the sol prepared at 80 °C contains anatase crystallites although the TTIP precursor needs to be heat treated at a temperature as high as 400 °C for crystallization. Thus coating at room temperature using the sol can show photocatalytic activity without further

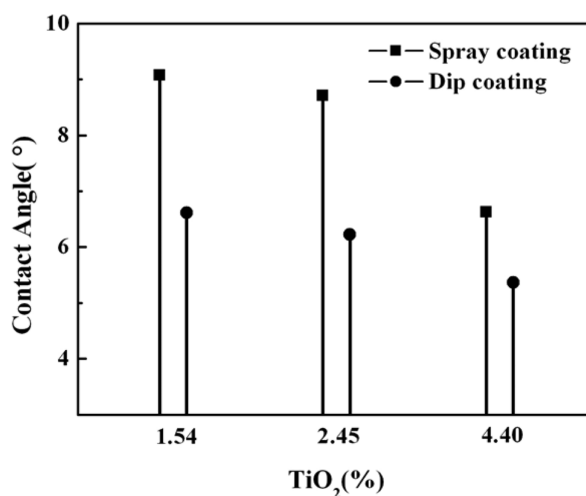


Fig. 6. Variation of contact angles depending on coating method and TiO₂ concentration. The spray coated layer showed thinner 2 μm thickness compared to 4 μm of dip coated layer, and high contact angle.

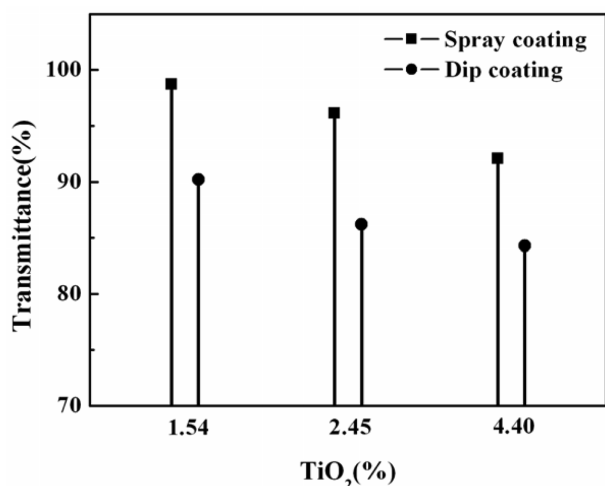


Fig. 7. Variation of transmittance 380-770 nm depending on the coating method and the TiO₂ concentration spray coated layer of 2 μm thickness showed better transmittance.

heat treatment at a higher temperature after coating. This can certainly widen the applicability of the sol to various substrate materials.

Characteristics of coated layer

The hydrophilicity of the coated layer was evaluated by measuring the wetting angle of a water drop on the surface. The contact angles both left and right hand sides of a water drop were averaged. Various contact angles depending on the coating method, i.e., spray or dip coating, and the concentration of TiO₂ in the sol were compared as shown in Fig 6. A wetting angle below 10° was observed irrespective of the coating method, however the angle on the surface of the dip coated layer exhibited a smaller angle that on the spray coated layer. Also the angle decreased with an increase in the TiO₂ concentration.

Many attempts of coating using commercially available photocatalytic TiO₂ solutions have consistently produced opaque layers, and could not reveal the original color of the substrate. Thus, a transparent coating layer formed at room temperature should be developed for the wider applications of photocatalytic TiO₂. The transparency of visible light depending on the coating method and TiO₂ concentration was measured using a UV-visible spectrophotometer and showing Fig.7. The dip coated layer showed about 10% lower transparency in comparison

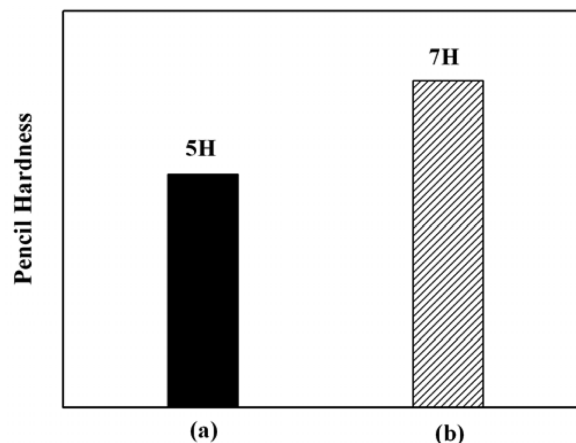


Fig. 9. Adhesion strength of TiO₂ thin film tested by a pencil hardness tester: (a) spray coating, (b) dip coating, dip coated layer showed stronger adhesion.

with the spray coated one, which is attributed to the thickness of layer. However, both coating techniques yielded a transparency of higher than 85%.

The thickness of the coated layer depending on the coating method was examined by SEM and showing Fig. 8. About 4 μm coated layer was formed by dip coating whereas about 2 μm thickness was observed in the spray coated layer. Accordingly, the lower transparency of the dip coated sample could be explained by the thicker coating layer. The surface morphology of the spray coated sample Fig. 8(c) showed closely packed spherical TiO₂ particles several tens of nm in size.

The adhesion between the coating layer and substrate was measured by a pencil hardness tester. The dip coated layer showed 7H pencil hardness which is significantly higher than the 4H of the commercially available TiO₂ solution coated by the same dip coating technique.

Conclusions

1. A photocatalytic TiO₂ sol containing anatase crystallites was fabricated through a conventional sol-gel process using a titanium isopropoxide precursor.
2. A coating with a 1.54% sol TiO₂ on the soda lime glass by a spray coating technique showed a high hydrophilicity ($\sim 7^\circ$ wetting angle) and better than 95% transparency for visible light.

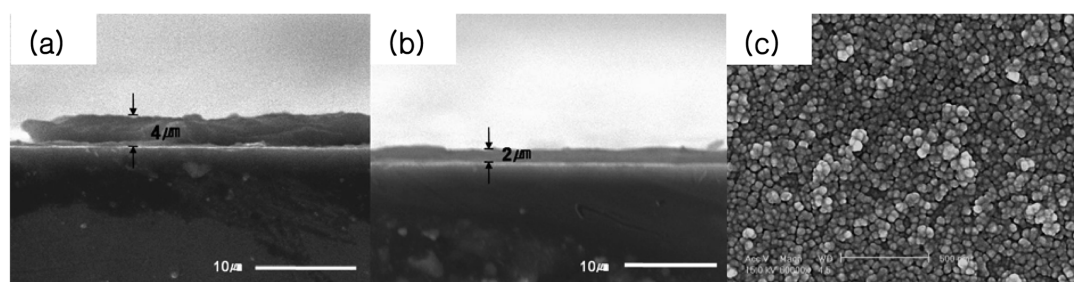


Fig. 8. SEM micrographs showing side view of (a) dip coated layer (b) spray coated layer and top view of (c) spray coated layer.

3. The dip coating technique caused a thicker layer in comparison with the spray coated layer for the same sol, consequently, led to less transparency and a stronger adhesion to substrate.
4. The process of fabricating a TiO₂ sol resulting in a transparent (90% of visible light transmittance), high hydrophilicity (wetting angle of 7 °) and strong adhesion (7H) layer when coated by a dip coated technique was established by this study.

Acknowledgement

The authors acknowledge the support from Engineering Research Institute of Gyeongsang National University.

References

1. D.Y. Shin, S.M. Han and K.N. Kim, J. Kor. Ceram. Soc. 38[12] (2001) 1092-1103.
2. Roberta L. Ziolli and Wilson F. Jardim, J. Photochem. Photobiol. A: Chem. 147 (2002) 205-212.
3. N. Negishi, T. Iyoda, K. Hashimoto and A. Fujishima, Chem. Lett. 24[9] (1995) 841-842.
4. H.D. Jang, and S.K. Kim, Perspectives of Industrial Chemistry 3[6] (2000) 41-47.
5. Harunori Murakami, Ceramics Japan 30[8] (1995).
6. S.K. Ellis and E.P. Mc Namara Jr., Am. Ceram. Soc. Bull. 68(1989) 988-991.
7. Q. Chen, Y. Qian, Z. Chen, G. Zhou and Y. Zhang, Mat. Lett. 22(1995) 77-80.
8. X.Z. Ding, Z.Z. Qi and Y.Z. He, J. Mat. Sci. Lett. 14(1995) 21-22.
9. Brian L. Bischoff and Marc A. Anderson, Chem. Mat. 7(1995) 1772-1778.