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Surface Chemistry of Super-Hydrophilic SiO_2-Doped TiO_2 Photo-Catalysts for Self-Cleaning Glass

SHUI-YANG LIEN[1,*], ASHEESH NAUTIYAL[2], JIA-HE JHU[1], JEN-KEN HSU[1] and SHUO JEN LEE[2]

[1]Department of Materials Science and Engineering, Ming Dao University, Chunghua 52345, Taiwan
[2]Department of Mechanical Engineering, Yuan Ze University, Zhongli, Taiwan

*Corresponding author: Fax: +886 4 8871020; Tel: +886 4 8876660 ext.8411; E-mail: syl@mdu.edu.tw; devo.mech@hotmail.com

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The self-cleaning of glass surface can be enhanced by coating the photoinduced super-hydrophilic nanoporous thin film based on TiO_2 photocatalysts *via* sol-gel process. In this article, a new method has been introduced to enhance the photocatalytic activity of TiO_2 thin film, directly coated on the glass, developed by doping SiO_2. The effects of post-annealing and the SiO_2 content in TiO_2 film on the photocatalytic activity were investigated. The microstructure and hydrophilic properties of the film were studied by using differential X-ray diffraction, field-emission scanning electron microscope. After illuminated by ultraviolet light, the SiO_2 doped TiO_2 film is super-hydrophilic with water contact angle less than 1º, this favours greatly the self-cleaning purpose of the glass surface.

Key Words: Sol-gel, Spin-coating, SiO_2 doped TiO_2, Self-cleaning glass.

INTRODUCTION

Self-cleaning glass is a specific nature of glass with a surface which maintains itself free of dirt and grime. Self-cleaning coatings are advancing recently, numerous techniques are known for the patterning of hydrophobic surfaces. The transparent coating is applied to hot glass during the forming process to form a strong, long-lasting bond, which creates the coating a connected part of the outer glass surface. Self cleaning glass uses a transparent coating of titanium dioxide applied during the manufacturing process.

Research on the semiconductor photocatalyst represented by TiO_2 started with Honda-Fujishima effect at the beginning of the 1970s[1]. When TiO_2 is irradiated with ultraviolet light, the active oxygen is generated on the surface of the film due to the photo-redox reaction. These photo-generated chemical species have the ability to decompose the organic contaminants adsorbed on the TiO_2 surface[2-4]. When exposed under UV light irradiation, TiO_2 reacts with the oxygen and water molecules present in the atmosphere to produce free radicals leading to oxidative species. These species could degrade organic material causing stains adsorbed on the surface into volatile molecules. Both technologies cover products designated by the general term of self-cleaning. Grease, dirt and other staining materials can easily be attached to the glass. Firstly, the UV rays react with coating to and break down organic dirt, which reduces the adherence of inorganic dirt. When rainwater hits the glass, the water droplets spread out on sheet, the dirt particles on the surface are picked up by water and washed off from the glass. Compared with conventional glass, the strong organic dirt and particles are not easy to be removed by water. In previous works, it has been observed that SiO_2 addition in TiO_2 films enables to increase in-time persistence of the photo-induced super-hydrophilicity[5-11].

Despite the commercialization of a hydrophilic self-cleaning glass for a number of products, the field needs much investigation into the fundamental mechanisms of self-cleaning glass and characterizations of new coatings. By these technologies, glasses reside cleaner for longer time, thus reducing the maintenance costs. The self cleaning glass technique can be applied to both solar glass as well as blue tinted glass to keep the area cool, ideal for conservatories and out houses.

EXPERIMENTAL

In this study, silica-titanium composite films having mol % of 1 to 10 of SiO_2, were deposited on glass substrates. The solution contains TiO_2 and SiO_2 precursor sols, resided at 25 ºC for 4 h. Fig. 1 shows the flow chart of TiO_2 and SiO_2 precursor sols preparation. The TiO_2 and SiO_2 sols were prepared by reacting metal alkoxide with a mixture of critical amount of water and/or acid in diluted alcohol medium. Afterword, the SiO_2/TiO_2 mixed with the ratio of 1:10 for 2 h in order to prepare the final solution for coating.

The SiO_2-TiO_2 coatings on glass substrates were done by spin-coating, the best parameter obtained for spin coating is 2000-6000 rpm for 30 sec. The desired film thickness can be tuned by the spin coating speed. Afterword, each film was pre-baked at 80 ºC for 20 min and then followed by post baked at 200-700 ºC for 1 h in atmosphere. The detail sol-gel processes are also discussed in our previous reports[12,13].

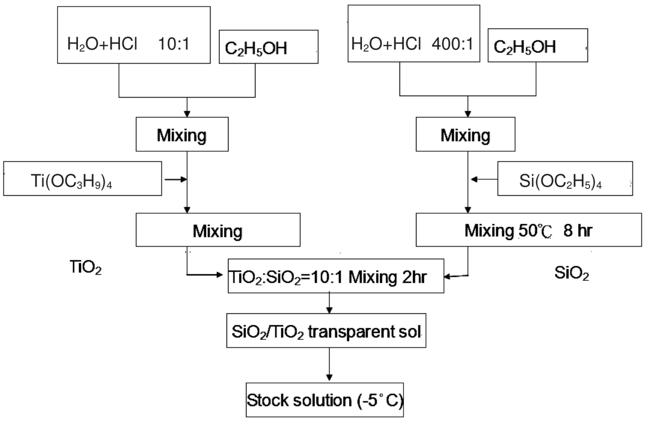

Fig. 1. Systematic flow chart of SiO_2 doped TiO_2 sol preparation

Surface hydrophilicity of the films was quantified from measurements of the water contant angle. The contact angles for water were measured by using contact angle analyzer on the random spots of film's surface. The crystallography of the films was determined by using XRD technique. The aim of compositional and chemical states used X-ray photoelectron spectroscopy to study properties of surface variation by various SiO_2 doping concentration. The surface microstructure of the films was examined using FESEM.

RESULTS AND DISCUSSION

Fig. 2 shows the glancing incidence XRD patterns of the pure TiO_2 films, prepared at the temperature varying from 200 to 700 ºC. These XRD patterns are given in the figure along with the peaks reported in the literature for anatase and rutile structures. By XRD analysis, we can observe that the pure TiO_2 films with anatase (a naturally occurring crystalline form of titanium dioxide) preferred orientation (101) increase when annealing temperature increased. The pure TiO_2 films formed of anatase phase show a very high efficiency photocatalytic activity due to their large internal surface[14]. Both the optical properties and the photocatalytic activity of TiO_2 coatings strongly depend on the crystalline phase, the crystallite size and the porosity of the coatings[15,16]. Moreover, the TiO_2 films formed of rutile preferred orientation (101) when the sample annealed at a temperature more than 600 ºC.

Fig. 3 shows the contact angle as a function of post-annealing temperature and UV light illuminates time. The result indicates that a hydrophilic character immediately after annealed at 500 ºC and UV-light illuminates for 20 min, which is illustrated by contact angle close to 5º. Then, contact angle increases after annealed more than 600 ºC, which is explained by rutile phase formation. Surface hydrophilicity of the films was quantified from measurements of the water contact angle. Assuming that the geometry of the drop is a spherical shape, the contact angle can be estimated by directly from the diameter of the contact circle, the diameter measured by an optical-microscope. This measurement was first performed on pure TiO_2 films in order to study wettability behaviours under different annealing temperature.

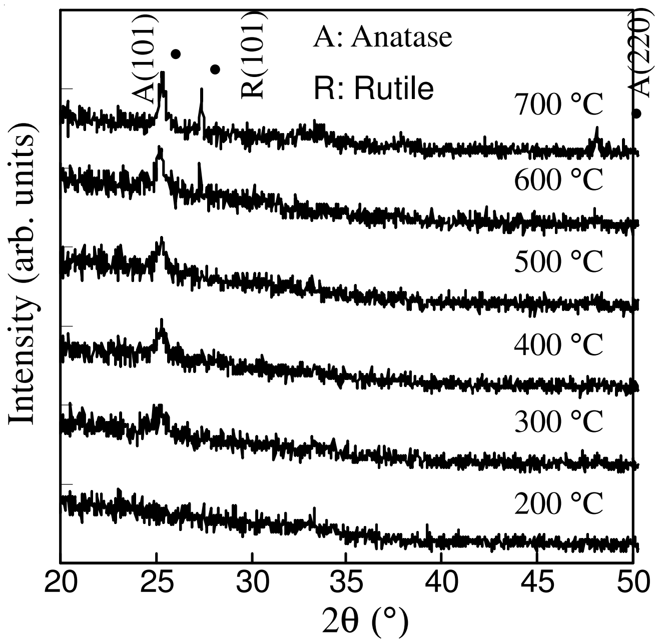

Fig. 2. X-ray diffraction patterns of pure TiO_2 films after annealed at different temperature

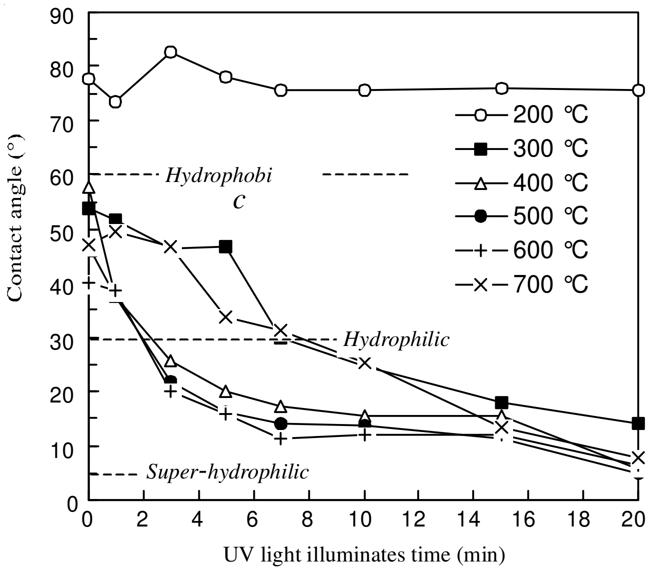

Fig. 3. Evolution of the water contact of pure TiO_2 films after annealed at different temperature

Fig. 4 illustrates the wet ability behaviour of SiO_2/TiO_2 composite films with the different SiO_2/TiO_2 mixing ratio at 200 ºC. The contact angle of water on the SiO_2/TiO_2 composite films after UV irradiation for 0 to 20 min was determined. The behaviour of a pure TiO_2 film is also presented as a reference data. The contact angle of the film, which consists of only TiO_2, is about 7º after 20 min of irradiation. Wettability studies show that a suitable control of the TiO_2/SiO_2 mixed rate can enhances persistence of the natural super-hydrophilicity in composite films. The process of hydrophobic to hydrophilic conversion is fast, the water contact angle quickly decreases with time of UV irradiation. The composite films with $SiO_2/TiO_2 = 5$ mol % shows a natural super-hydrophilic character with a contact angle of 0.8º.

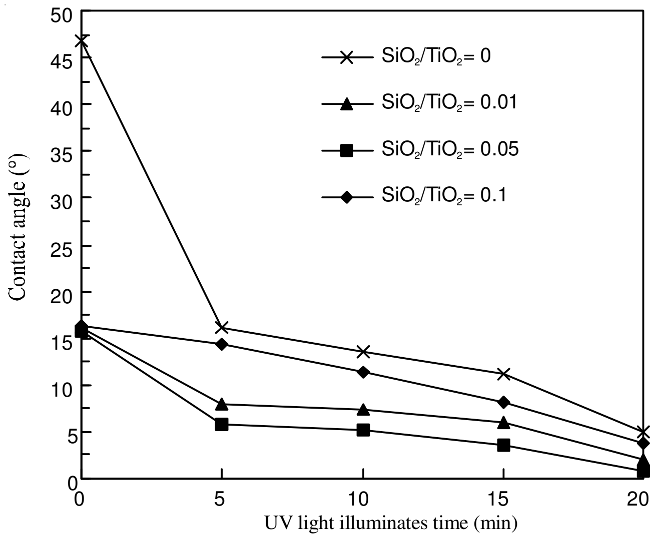

Fig. 4. Evolution of the water contact angle with UV light illuminates for pure TiO_2 and SiO_2 doped TiO_2 composite films

The morphology of SiO_2-TiO_2 composite films were characterized by FESEM. Fig. 5a-5d shows SEM images of a pure TiO_2 films, in addition, 1 mol, 5 mol and 10 mol % SiO_2 doped TiO_2 composite films, respectively. The image of a pure TiO_2 film indicates fairly homogeneous grain boundaries (Fig. 5a). In contrast, SEM images (Fig. 5b-5d) show that the composite films exhibit a sponge-like morphology with rather large cavities, which indicates an important surface porosity of these films. It shows that the enhancement of the in surface porosity from 1 mol % to 10 mol % SiO_2 doped TiO_2 composite films with the increase in roughness of the surface.

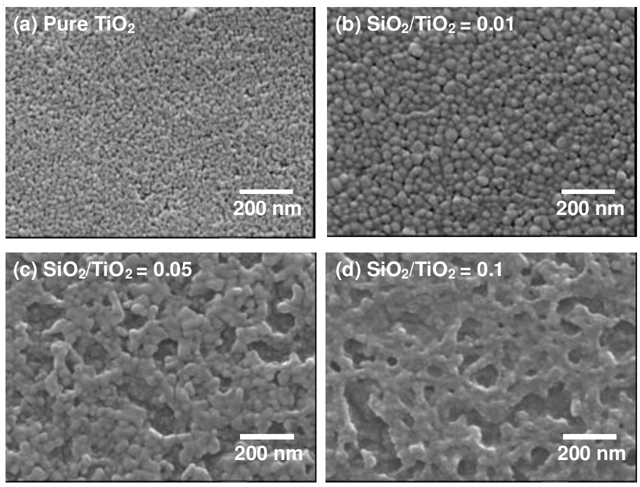

Fig. 5. SEM images of the SiO_2-doped TiO_2 films with different SiO_2 doping ratio as shown in figure and the films annealed at 500 ºC for 1 h

Fig. 6a shows the spectra of the SiO_2 doped TiO_2 composite films prepared by varying SiO_2/TiO_2 ratio. The chemical states of titanium, silicon, carbon and oxygen on the surface of the SiO_2 doped TiO_2 composite films were studied by XPS measurements. From the high resolution of XPS spectra, the silicon, carbon, titanium and oxygen peak obtained on natural surface of SiO_2 doped TiO_2 composite films were at 100, 285, 458.8 and 529.9 eV, respectively. From Fig. 6b, the results indicate that the as-deposited TiO_2 film with SiO_2/TiO_2 ratio on the surface was about 1.92. According to these results, the contents of silicon and titanium in the films were dependent on SiO_2/TiO_2 ratio, but the content of oxygen was independent on SiO_2/TiO_2 ratio. It was found that the Si content increase from 2.3 % to 7.7 % with the increase of the SiO_2/TiO_2 ratio from 0.01 to 0.1. The titanium content decreases from 30.7 % to 25.7 % when SiO_2/TiO_2 ratio increases from 0.01 to 0.1. The result indicates the Si atom replace the Ti atom in the SiO_2 doped TiO_2 composite films. According to the preceding statements, the XPS data confirms the composition of the SiO_2 doped TiO_2 films.

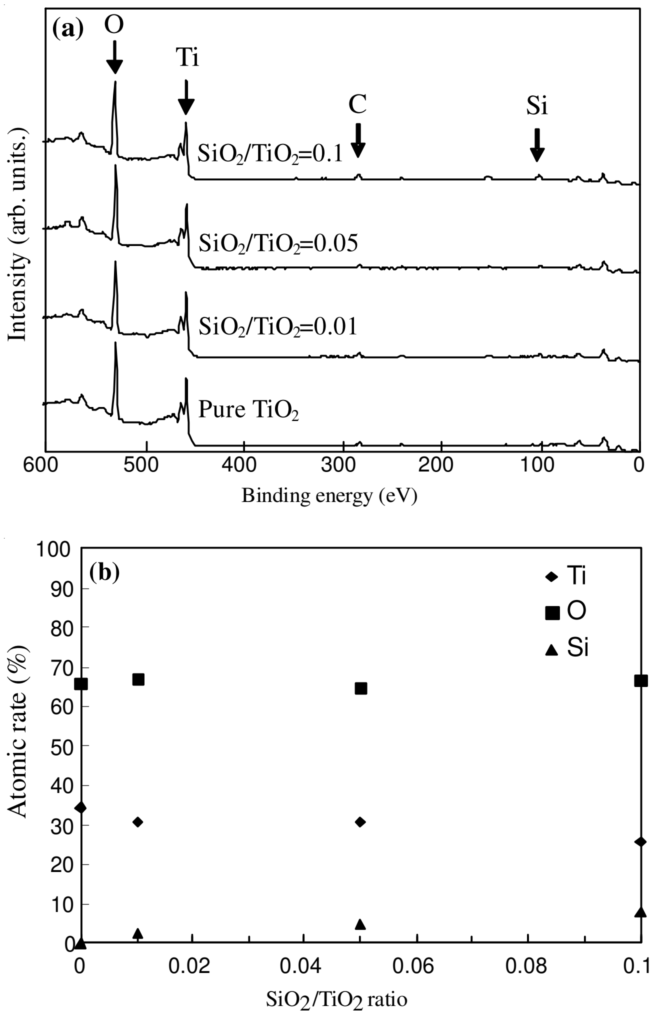

Fig. 6. (a) XPS spectra and (b) corresponding atomic ratio of SiO_2-doped TiO_2 films prepared by different SiO_2/TiO_2 ratio

In order to define appropriate tests for the self-cleaning properties of nano-structured surface, the project is based on two main objectives. We used self-cleaning glasses (SiO_2/TiO_2 = 5 mol %) compared to standard float glasses (conning 7059). Fig. 7 shows the photo illustrates the sheeting effect of self-cleaning glass (right) compared to conventional glass (left). There are set of figures that can show the self cleaning effects in clear and rainy day. We used simple methods to evaluate the self-cleaning performance of these glass surfaces. Firstly, the samples exposed outdoor for 1 h and then sprayed water, the water effectively rinse away dust and dirt. The self-cleaning glass with hydrophilic property makes water droplets spread out, or sheet, across the surface of the glass. The self-cleaning glass has super-hydrophilic properties make windows easier to clean.

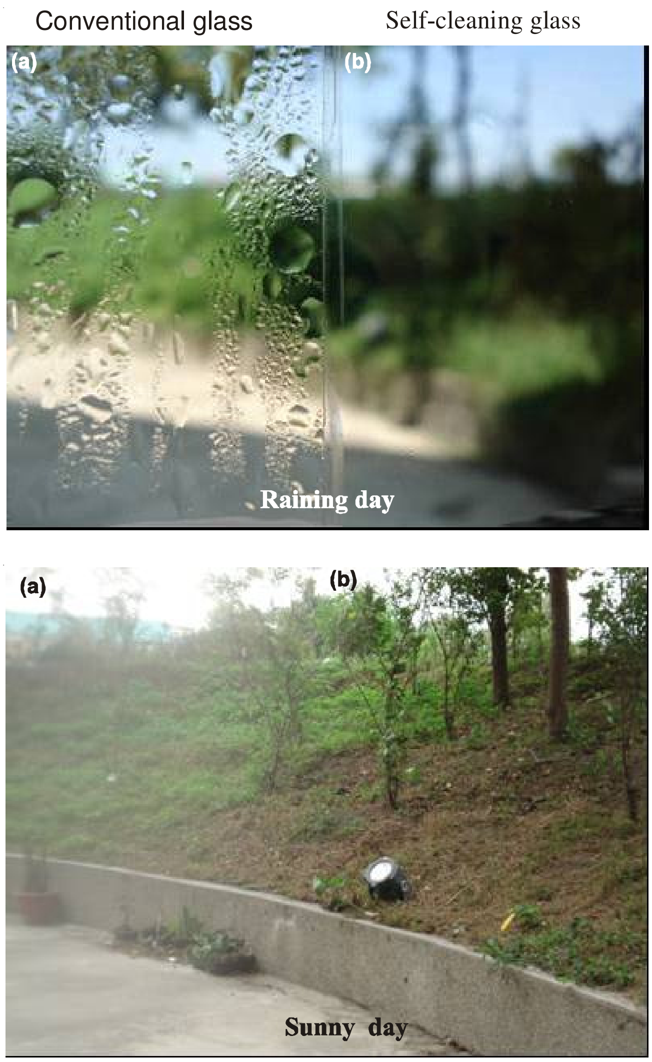

Fig. 7. Image shows the photo illustrates the sheeting effect of self-cleaning glass (right) compared to conventional glass (left) in clear and rainy day

Conclusion

SiO_2 doped TiO_2 composite films have been deposited by using spin coating of SiO_2-TiO_2 mixed solution. Our study focused the dependence on photocatalytic activity of composite films with different SiO_2/TiO_2 ratio. The chemical and structural properties of these films have been investigated by XRD and FESEM characterizations in relation to their hydrophilic properties. Water contact angle measurements show that the composite films with SiO_2/TiO_2 = 5 mol % shows a natural super-hydrophilic character with a contact angle of 0.8 degree. The outdoor test shows the self-cleaning glass has super-hydrophilic properties to make windows easier to clean.

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