Surface Chemistry of Super-Hydrophilic SiO₂-Doped TiO₂ Photo-Catalysts for Self-Cleaning Glass

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The self-cleaning of glass surface can be enhanced by coating the photoinduced super-hydrophilic nanoporous thin film based on TiO₂ photocatalysts *via* sol-gel process. In this article, a new method has been introduced to enhance the photocatalytic activity of TiO₂ thin film, directly coated on the glass, developed by doping SiO₂. The effects of post-annealing and the SiO₂ content in TiO₂ 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 SiO₂ doped TiO₂ film is super-hydrophilic with water contact angle less than 1°, this favours greatly the self-cleaning purpose of the glass surface.

Key Words: Sol-gel, Spin-coating, SiO₂ doped TiO₂, 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 TiO₂ started with Honda-Fujishima effect at the beginning of the 1970s¹. When TiO₂ 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 TiO₂ surface²⁻⁴. When exposed under UV light irradiation, TiO₂ 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 SiO₂ addition in TiO₂ films enables to increase in-time persistence of the photo-induced super-hydrophilicity⁵⁻¹¹.

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 SiO₂, were deposited on glass substrates. The solution contains TiO₂ and SiO₂ precursor sols, resided at 25 °C for 4 h. Fig. 1 shows the flow chart of TiO₂ and SiO₂ precursor sols preparation. The TiO₂ and SiO₂ sols were prepared by reacting metal alkoxide with a mixture of critical amount of water and/or acid in diluted alcohol medium. Afterword, the SiO₂/TiO₂ mixed with the ratio of 1:10 for 2 h in order to prepare the final solution for coating.

The SiO₂-TiO₂ 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. Afterward, each film was pre-baked at 80 °C for 20 min and then followed by post baked at 200–700 °C 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 SiO₂ doped TiO₂ sol preparation

Surface hydrophilicity of the films was quantified from measurements of the water contact 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 SiO₂ 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 TiO₂ films, prepared at the temperature varying from 200 to 700 °C. 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 TiO₂ films with anatase (a naturally occurring crystalline form of titanium dioxide) preferred orientation (101) increase when annealing temperature increased. The pure TiO₂ films formed of anatase phase show a very high efficiency photocatalytic activity due to their large internal surface¹⁴. Both the optical properties and the photocatalytic activity of TiO₂ coatings strongly depend on the crystalline phase, the crystallite size and the porosity of the coatings^{15,16}. Moreover, the TiO₂ films formed of rutile preferred orientation (101) when the sample annealed at a temperature more than 600 °C.

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 °C and UV-light illuminates for 20 min, which is illustrated by contact angle close to 5°. Then, contact angle increases after annealed more than 600 °C, 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

TiO₂ films in order to study wettability behaviours under different annealing temperature.

Fig. 2. X-ray diffraction patterns of pure TiO₂ films after annealed at different temperature

Fig. 3. Evolution of the water contact of pure TiO₂ films after annealed at different temperature

Fig. 4 illustrates the wet ability behaviour of SiO₂/TiO₂ composite films with the different SiO₂/TiO₂ mixing ratio at 200 °C. The contact angle of water on the SiO₂/TiO₂ composite films after UV irradiation for 0 to 20 min was determined. The behaviour of a pure TiO₂ film is also presented as a reference data. The contact angle of the film, which consists of only TiO₂, is about 7° after 20 min of irradiation. Wettability studies show that a suitable control of the TiO₂/SiO₂ 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 SiO₂/TiO₂ = 5 mol % shows a natural super-hydrophilic character with a contact angle of 0.8°.

Fig. 4. Evolution of the water contact angle with UV light illuminates for pure TiO₂ and SiO₂ doped TiO₂ composite films

The morphology of SiO₂-TiO₂ composite films were characterized by FESEM. Fig. 5a-5d shows SEM images of a pure TiO₂ films, in addition, 1 mol, 5 mol and 10 mol % SiO₂ doped TiO₂ composite films, respectively. The image of a pure TiO₂ 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 % SiO₂ doped TiO₂ composite films with the increase in roughness of the surface.

Fig. 5. SEM images of the SiO₂-doped TiO₂ films with different SiO₂ doping ratio as shown in figure and the films annealed at 500 °C for 1 h

Fig. 6a shows the spectra of the SiO₂ doped TiO₂ composite films prepared by varying SiO₂/TiO₂ ratio. The chemical states of titanium, silicon, carbon and oxygen on the surface of the SiO₂ doped TiO₂ 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 SiO₂ doped TiO₂ composite films were at 100, 285, 458.8 and 529.9 eV, respectively. From Fig. 6b, the results indicate that the as-deposited TiO₂ film with SiO₂/TiO₂ ratio on the surface was about 1.92. According to these results, the contents of silicon and titanium in the films were dependent on SiO₂/TiO₂ ratio, but the content of oxygen was independent on SiO₂/TiO₂ ratio. It was found that the Si content increase from 2.3 % to 7.7 % with the increase of the SiO₂/TiO₂ ratio from 0.01 to 0.1. The titanium content decreases from 30.7 % to 25.7 % when SiO₂/TiO₂ ratio increases from 0.01 to 0.1. The result indicates the Si atom replace the Ti atom in the SiO₂ doped TiO₂ composite films. According to the preceding statements, the XPS data confirms the composition of the SiO₂ doped TiO₂ films.

Fig. 6. (a) XPS spectra and (b) corresponding atomic ratio of SiO₂-doped TiO₂ films prepared by different SiO₂/TiO₂ 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 (SiO₂/TiO₂ = 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

SiO₂ doped TiO₂ composite films have been deposited by using spin coating of SiO₂-TiO₂ mixed solution. Our study focused the dependence on photocatalytic activity of composite films with different SiO₂/TiO₂ 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 SiO₂/TiO₂ = 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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