Effect of Fabrication Process on the Hydrophilic Properties of Porous TiO₂ Thin Films for Self-Cleaning Application

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Abstract: Self-cleaning effect of nano-TiO₂ films have been intensively studied and widely applied in practice. In this report, nano TiO₂ materials were prepared from Titanium (IV) Tetraisopropoxide (TTIP) C₁₂H₂₈O₄Ti, by sol-gel method and the thin films TiO₂ were fabricated by spin coating from TiO₂ sol on silicon wafer. The porosity and surface morphology TiO₂ thin films has been adjusted by using polyethylene glycol (PEG) at different concentration from 0% to 50%. The prepared nano TiO₂ films were mainly characterized by powder X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), specific surface area (BET Method) and water contact angle (WCA) measurement. Effects of the addition of PEG on the wetting performance of the resulting films were investigated. The results show that the prepared films display super-hydrophilic property when exposed to ultraviolet light and the optimal concentration of PEG was 40%. Moreover, the obtained films also exhibit considerable durability in the super-hydrophilicity when stored in the dark, which is very useful for self-cleaning application in practice.

Key words: Titanium dioxide (TiO₂), water contact angle (WCA), polyethylene glycol (PEG), porosity, hydrophilic.

1. Introduction

Titanium dioxide TiO₂ is one of the most promising photocatalysts with several advantages such as high efficiency, chemical stability, non-toxicity, and inexpensive cost. This oxide has been intensively investigated for its attractive applications in the photocatalytic degradation of toxic organic substances [1]. Moreover, in the past years, the self-cleaning actions of TiO₂ related to its photoreaction activity have been also published. It has been known that there are two types of photochemical reaction proceeding on a TiO₂ surface when irradiated with ultraviolet light. The first one includes the photo-induced redox reaction of adsorbed substances, and the other is the photo-induced hydrophilic property of TiO₂ itself. The development of self-cleaning materials with variable wetting ability become an active research sector in material science due to their wide applications in

various fields ranging from indoor to exterior such as in fabrics [2], furnishing materials [3], window glasses [4], construction materials, roof tiles [5, 6], car mirrors [7], and solar panels [8]. The surface of these materials can easily be cleaned by a stream of natural water such as rainfall, and therefore the routine maintenance cost can be significantly reduced.

A lot of publications has been reported on self-cleaning action of TiO₂ over the past years that mainly develop a TiO₂ thin film structure in order to improve the recycling purpose and especially to obtain a super-hydrophilic surface with water contact angle (WCA) value usually below 5°. Under UV light, there is a linear relationship between the WCA reciprocal and the irradiation time. However, the hydrophilicity of TiO₂ film surfaces tends to reconvert to its initial state when stored under dark conditions. From a viewpoint of practical application, the durable super-hydrophilicity of TiO₂ film surface is one of the most important factors. In fact, the low surface area of TiO₂ thin film structure results in a lower

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photocatalytic activity. In order to overcome this disadvantage, several studies have been reported that TiO₂ thin film containing porous structure can be fabricated during the preparation procedures by introducing polymers, organic templates [9, 10]. Among the templates, polyethylene glycol (PEG) is a traditional pore-forming one, which is commonly used for the preparation of porous thin films. TiO₂ films with a porous structure are interesting because of the high surface/volume ratio, which enhances the photo-catalytic performance. However, it has been well known that the wettability of solid surfaces is mainly governed by both chemical composition and geometric microstructure. In this study, the porous TiO₂ thin films have been fabricated by the sol-gel method using PEG-2000 as the template agent. Different concentrations of PEG were used and several film thickness were tested in order to modify the surface morphology, porous and hydrophilic properties of the films. The effect of pH of water on the hydrophilicity was also studied and it was found that contact angle was clearly dependent on the pH.

2. Experimental

The titania sols were obtained by sol-gel method. The precursor solutions were prepared from Titanium (IV) Tetraisopropoxide (TTIP) C₁₂H₂₈O₄Ti, water as solvent and nitric acid as catalyst. To obtain micro-nanostructured surfaces, different amounts of polyethyleneglycol-PEG (0, 10, 20, 30, 40 and 50 wt.%) were added to the mother solution and getting 6 different samples, which were named A0, A1, A2, A3, A4 and A5 respectively. The porous TiO₂ thin films on Silicon wafers were prepared by spin coating from TiO₂ sols at 2,000 rpm, they were then heated during an annealing process in air at temperatures of 500°C for 1 hour with a heating rate of 3 °C/min. The micro-structural morphology of TiO₂ thin films was observed by using field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi). The crystalline phase of titanium dioxide was identified by

powder X-ray diffraction (XRD). The porosity of TiO₂ films was examined through specific surface area measurement of Brunauer-Emmett-Teller (BET) method. The wettability of the films and their retention of hydrophilic property in the dark were studied by contact angle measurement.

3. Results and Discussion

Fig. 1 shows the XRD patterns of TiO₂ samples containing PEG from 0 to 50 wt.% (A0-A5). The characteristic peaks appear mainly in anatase phase. The rutile phase, an unwanted structure in photocatalysis applications, remains the minority and can be seen only at the samples with lower PEG concentration. The anatase to rutile transformation is an irreversible process of metastable phase to stable phase and commonly taken place at high temperature. It is noticable that the rutile phase decreased with the increase of PEG concentration from samples A0 to A5. Therefore, the introduction of PEG could result in the anatase-rutile transformation being inhibited.

Surface morphology of the thin films of samples A0-A5 (0-50% PEG, respectively) was investigated by scanning electron microscopy (SEM) and showed in Fig. 2. The difference in size of porous structure of the film surface can be clearly distinguished for all samples. Obviously, the pores created on the TiO₂ thin films tend to increase in their size and depth with the increase of PEG content from 0 to 40%, but the pore size has been significantly reduced when the PEG concentration increasing up to 50%. This observation is consistent with the measured results of specific surface area BET, which are shown in the Table 1.

Fig. 3 reflects the time-dependant change in the WCA on TiO₂ films irradiated with UV light and stored in the dark. Prior to the WCA measurement, the films are not exposed to UV irradiation and they exhibit hydrophilic with the WCA value around 35°. It was found that, the WCA curves under UV-irradiation and recovering in the dark are asymmetrical, recovery time is a few days while irradiation time needs only a

Fig. 1 X-ray diffraction patterns of the samples A0-A5 corresponding to 0-50 wt.% PEG concentration.

Fig. 2 SEM pictures of the samples from A0 to A5 (0, 10, 20, 30 and 50% PEG).

Table 1 Specific surface area BET of the samples A0-A5 (0-50% PEG).

Sample	Specific surface area (m ² /g)
A0 - 0% PEG	41.5
A1 - 10% PEG	47.1
A2 - 20% PEG	63.2
A3 - 30% PEG	68.5
A4 - 40% PEG	86.7
A5 - 50% PEG	54.3

Fig. 3 Dependence of contact angle on UV irradiation time and the recovery in the dark.

Fig. 4 Dependence of WCA values on the percentage of PEG.

few hundred minutes. Thus, the super-hydrophilic properties of the materials can be retained long after turning off the UV light. Under UV-irradiation the contact angle decrease rapidly at intervals of the first 60 seconds and tend to saturation after 120 seconds exposure with WCA of about 10° and showing super-hydrophilic properties. The content of PEG in samples had a clear effect on the hydrophilic properties of the film. It can be seen that the larger PEG content in TiO₂ film, the lower WCA value

obtained. Generally speaking, the increase in the PEG concentration is favorable to improve wettability. Fig. 4 shows that the contact angle decreased as a percentage of PEG in solution increased from 0 to 40% and reached the lowest value at 40% PEG. However, the WCA value starts to rise when the PEG concentration reached 50%. By comparison with the results of specific surface area measurement (BET) and surface morphology study (SEM), it can be concluded that the hydrophilic properties of the film

are optimal at the PEG content of 40%. This observation can be explained as follows: During the preparation, PEG was introduced in TiO₂ solution, thin film was coated and thermally treated then at high temperature to evaporate the PEG and create pores in the film. Therefore, the present of PEG will normally make the film highly porous and increase internal surface area, that also enable more water molecules absorbed and increase the number of free OH groups on the film surface. These OH groups will create hydrogen bonds with water so that water can easily spread itself on the film surface and thus decrease WCA values. However, the porosity of the film can be only optimal at a certain PEG concentration. At a high content of PEG greater than the optimal concentration, the porosity of the film will be deteriorated due to phase separation of TiO₂ and PEG, they will be unevenly distributed in solution as well in film, the aggregation of TiO₂ particles into islands will take place and the total internal surface area will decrease.

4. Conclusions

The super-hydrophilic TiO₂ films have been prepared by sol-gel method and *via* spin coating processes. The wettability of the films and their retention of hydrophilic property in the dark were studied by contact angle measurement. The porosity and surface morphology TiO₂ thin films has been modified by using PEG at different concentration from 0 to 50%. The content of PEG had a clear effect on the hydrophilic properties of the film. The contact angle decreased as a percentage of PEG in solution increased from 0 to 40% and reached the lowest value at 40% PEG. The PEG/TiO₂ films also exhibit considerable durability in the super-hydrophilicity when stored in the dark. This work will promote the practical applications of nano-sized TiO₂ coatings in

self-cleaning.

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