

# Control of porous structure in TiO<sub>2</sub> thin films using nano replica prepared by layer-by-layer self-assembly process

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A new fabrication method of anatase TiO<sub>2</sub> thin films deposit on the polymer thin films formed by layer-by-layer self-assembly process is suggested. Scanning electron microscopic observation of the resultant films reveals that using the systematically controlled nano structure of the layer-by-layer self-assembly thin films as the replica forms porous TiO<sub>2</sub> thin films. After removing the polymer thin films through calcination, nanoscale porous TiO<sub>2</sub> films with both layered and pillar-like structure are successfully fabricated. Furthermore, it was found that the thickness of the TiO<sub>2</sub> thin films can be systematically controlled in nano scale.

Key words: layer-by-layer, replica, TiO<sub>2</sub>, layered, pillar-like

## 1. INTRODUCTION

Crystalline titanium dioxide (TiO<sub>2</sub>), anatase, is well-known material for its photocatalyst and various applications such as gas sensors, electrochromic display devices and photoelectrodes in wet-type photocells [1,2] are reported. The highly porous structure and the high surface area of TiO<sub>2</sub> anatase films are considerably important for the photocatalytic applications. The coating method of a crystalline powder with organic binders [3] and other fabrication techniques, such as sputtering, spray pyrolysis and sol-gel process [4] are proposed, however, both the minute controlling of the structure and the construction of the large area, uniform coating of the TiO<sub>2</sub> films are not always very easy for using these methods.

In recent years, new direct deposition techniques using supersaturated chemical solutions have been developed for preparation of metal-oxide films, such as SiO<sub>2</sub>, TiO<sub>2</sub>[5], SnO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>. In particular, thin films consisting of well crystallized anatase particles are easily obtained from titanium tetrafluoride (TiF<sub>4</sub>) solutions, even at temperatures below 60°C[5]. Using this technique, coating of anatase films on various matrices with complex shapes was achieved through heterogeneous nucleation [6]. However, in this method, because of the direct adsorption from the TiF<sub>4</sub> solutions, substrates were required to fulfill the porousness

for photocatalytic properties. Therefore, the control of the porousness is the essential problem to achieve higher performance catalysts.

On the other hand, recently, there are many reports on the fabrication method for organic films. Among them, the layer-by-layer selfassembly process of polyelectrolytes reported in 1992 [7,8] is very promising because of its simplicity and the capability of application for wide range of materials, which can be used in this technique. Just by the alternate dipping of the negatively charged substrate to poly-anion and poly-cation solutions sequentially, the organic multilayer thin film can be formed on the substrate. In the case of the using weak polyelectrolytes, the surface nano structure is changed by adjusting the solution pH [9,10]. Furthermore, it was reported that microporous thin films can be readily fabricated from layer-by-layer self-assembled multilayers [11].

In this paper, we report the new fabrication method of anatase TiO<sub>2</sub> thin films deposit on the polymer thin films formed by layer-by-layer self-assembly process. Using the systematically controlled nano structure of the layer-by-layer self-assembly thin films as the replica forms porous TiO<sub>2</sub> films. After removing the polymer thin films through calcination, nanoscale porous TiO<sub>2</sub> film with both layered and pillar-like structure are successfully

fabricated.

## 2. EXPERIMENTAL METHODS

### 2.1. Preparation of layer-by-layer selfassembly thin films

Poly(acrylic acid) (PAA) (Mw=90,000) was obtained from Polysciences as a 25% aqueous solution. Poly(allylamine hydrochloride) (PAH) (Mw=70,000) was purchased from Aldrich Chemical. The polyelectrolytes were used without any further purification. Both polyelectrolytes were dissolved into 18.3MΩ pure water, concentration of 10<sup>-2</sup>M solutions were prepared. The silicon substrates were etched by KOH solution, the surface of the substrate was charged negatively. Solution pH, which PAA was pH 3.5 and PAH was pH 7.5, was adjusted with either HCl or NaOH

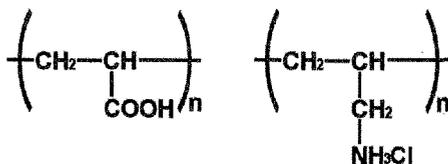


Fig.1 Chemical structures of PAA and PAH

Silicon substrates were immersed in PAH solution for 5 min followed by rinsing in three successive baths of pure water for 1min. The substrates were then immersed into the oppositely charged PAA solution for 5 min and subjected to the same rinsing procedure. After the deposition, the selfassembled multilayer films were dried at 70°C, for 1h in vacuum. The multilayer thin films were immersed into pH2.5 diluted HCl solution for 2min followed by rinsing in pure water for 20sec, and then dried at 70°C, for 1h in vacuum.

The surface morphology of the fabricated multilayer thin films was observed using an atomic force microscope (AFM, nanoscope IIIa, Digital Instruments).

### 2.2. Preparation of anatase TiO<sub>2</sub> thin films

TiO<sub>2</sub> anatase was adsorbed onto the microporous structure of fabricated multilayer thin films. Details of the fabrication method of TiO<sub>2</sub> thin films are reported in the previous[5,6]. Precursor solutions were prepared by dissolving 0.248g TiF<sub>4</sub> (Aldrich) in 50ml pure water containing NH<sub>4</sub>OH. Precursor solutions pH was adjusted at the value between 1.8 to 2.2 by adding the aqueous NH<sub>4</sub>OH. The fabricated multilayer thin films on the silicon substrate were immersed into the precursor solution, which were maintained at 60°C for 4h. Then the substrate was removed from the precursor solution, rinsed with pure water in supersonic bath for 10min. The polymer thin films were removed by calcination at 650°C for 1h in air.

The morphology of fabricated anatase TiO<sub>2</sub> thin films was investigated using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700).

## 3. RESULTS AND DISCUSSION

### 3.1. Surface morphology of layer-by-layer selfassembly thin films

PAA/PAH multilayer thin films deposited under the conditions of pH3.5 for the PAA solution and pH 7.5 for the PAH solution were prepared in this study. As shown in Fig.2, AFM observation reveals that the 3.5/7.5 film surface has texture-like pattern. The RMS and surface area were 10nm and 103 μm<sup>2</sup>, respectively. A remarkably rough surface was constructed at this pH conditions.

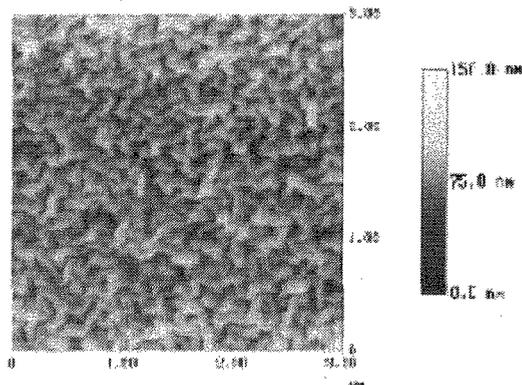


Fig.2 AFM image of PAA(pH3.5)/PAH(pH7.5) film surface (10bilayers)

The surface nano-structure of the 3.5/7.5 film can be altered dramatically to a microporous structure when only exposed to the diluted HCl solution (pH≤2.5). Fig.3 depicts the AFM image of the transformed surface nano-structure of the 3.5/7.5 film, after immersion in the diluted HCl solution. A highly interconnected porous microstructure was obtained, with pore length scale in the range 150-600nm.

Furthermore, it has been observed that the porous nano-structure will undergo a secondary rearrangement when immersed in pure water (pH≈5.5-6.5). The AFM images of the 3.5/7.5 film after immersion in the diluted HCl and pure water is shown in Fig.4 (a) and (b). The RMS and surface area obtained from the image shown in Fig.4 (a) were 100nm and 155 μm<sup>2</sup>, respectively. As shown in Fig.4(a) and (b), exposure to pure water for a few second the porous microstructure, leading to the high surface area and porous nano-structure with more discrete rounded pores of both 50-400nm in diameters and penetrated to the substrate surface.

We consider that the efficiency of photocatalytic property of the TiO<sub>2</sub> will be improved by using such high surface area and systematically controlled porous nano-structure as replica for TiO<sub>2</sub> films.

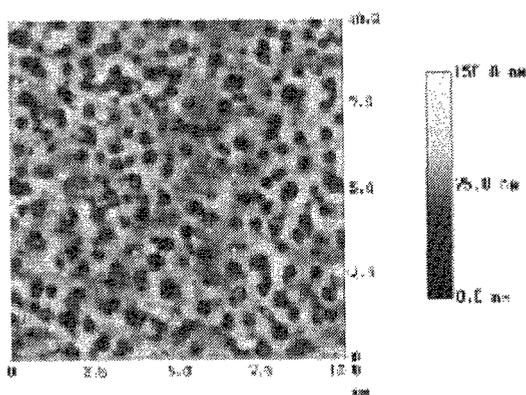


Fig.3 AFM image of PAA(pH3.5)/PAH(pH7.5) film surface after immersion in pH2.5 diluted HCl

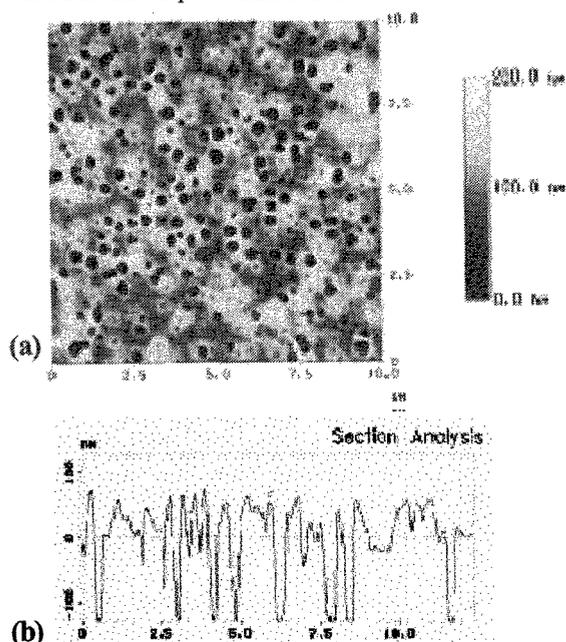


Fig.4 AFM image of (a) the surface structure (b) the sectional analysis of PAA(pH3.5)/PAH(pH7.5) film after immersion in pH2.5 HCl followed by rinsing in pure water (film thickness $\approx$  200nm)

### 3.2. Morphology of anatase TiO<sub>2</sub> thin films

100 bilayers of the layer-by-layer selfassembly thin film was prepared by the fabrication condition described above. The AFM and SEM observation revealed that the high surface area, porous nano-structure were maintained. Fig.5 depicts the surface structure of TiO<sub>2</sub> thin film deposited on the polymer thin film after immersion in the diluted HCl, pure water and then calcinated. As shown in Fig.5, the surface structure of TiO<sub>2</sub> thin film is evidently traced the high surface area and systematically controlled porous nano-structure of the layer-by-layer selfassembly thin film. Additionally, by the SEM observation, we ascertained that the high surface area, porous nano-structure of the surface in TiO<sub>2</sub> thin film

is maintained through calcination. Furthermore, TiO<sub>2</sub> nano particles with approximately 50nm in diameters grow on the surface of the layer-by-layer selfassembly thin film.

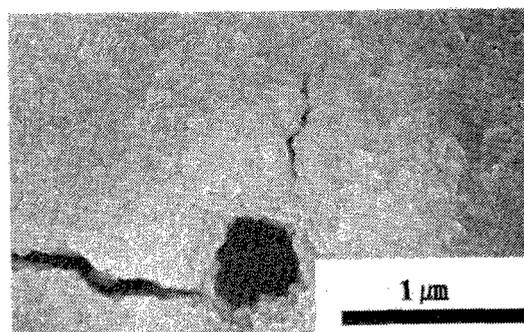


Fig.5 SEM image of the surface structure of TiO<sub>2</sub> thin film deposited on the polymer thin film after immersion in pH2.5 HCl followed by rinsing in pure water

Fig.6 is the SEM image of the surface structure of TiO<sub>2</sub> nano particles directly deposited on the Si substrate. By comparison of the two images shown in Fig.5 and Fig.6, it was found that the former has the higher surface area, highly porous body systematically controlled in submicron order.

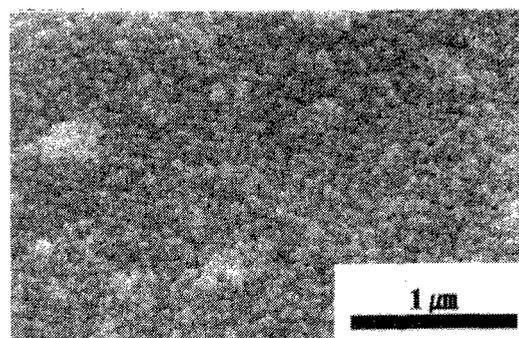


Fig.6 SEM image of the surface structure of TiO<sub>2</sub> thin films deposited on the Si substrate

Furthermore, it has been observed that the TiO<sub>2</sub> thin film deposited on the high surface area, porous nano-structure of the polymer thin film has the peculiar pillar-like structure with 50-400nm in diameters, penetrated to the substrate surface inside of the TiO<sub>2</sub> thin film. The cross-sectional SEM image of the TiO<sub>2</sub> thin film after calcination is shown in Fig.7 (a). Deciding from the results that the TiO<sub>2</sub> nano particles even grow inside of pores formed on the polymer thin film, the diameters of the pillar-like structure correspond to the pore size (50-400nm) formed on the polymer thin film and the discrete rounded pores penetrate to the substrate surface, the pillar-like structure is caused by the gradually deposition of TiO<sub>2</sub> nano particles out of the bottom of pores

formed on the polymer thin film.

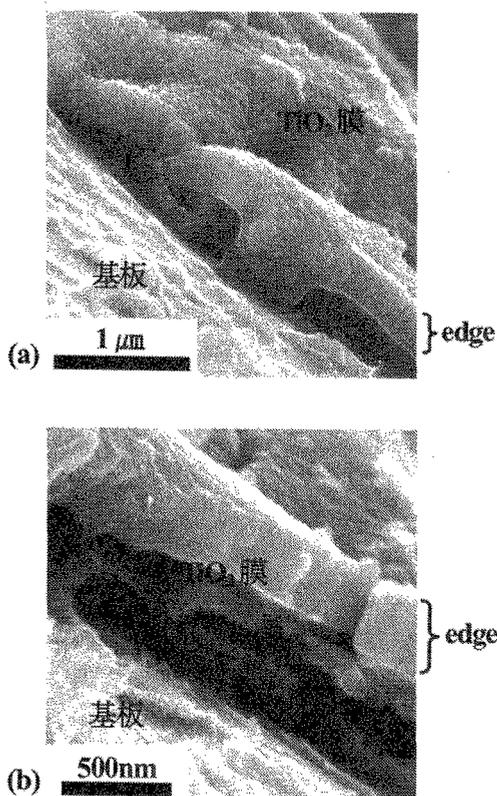


Fig.7 The cross-sectional SEM images of the TiO<sub>2</sub> thin films deposited on the polymer thin films after immersion in pH2.5 HCl followed by rinsing in pure water

Additionally, layered structure of TiO<sub>2</sub> was constructed inside the TiO<sub>2</sub> thin film. The cross-sectional SEM image are shown in Fig.8 (b). It was found that the TiO<sub>2</sub> nano particles grow not only on the surface of the polymer thin film, but also inside of the film. We considered that the layered structure was formed by the crystallization of TiO<sub>2</sub> nano particles inside of the polymer thin film caused by the penetration of the TiF<sub>4</sub> solution into the polymer thin film, because of the facts that the surface characteristic and morphology of the polymer thin film are hydrophilic and highly porous. Therefore, the penetrated TiO<sub>2</sub> nano particles formed the layered structure.

It was found that the total thickness of the TiO<sub>2</sub> thin film almost corresponds to the thickness of the layer-by-layer selfassembled film. Therefore, we conclude that the thickness of the TiO<sub>2</sub> thin film can be systematically controlled in nano scale, by the control of both the thickness of the layer-by-layer selfassembled film and the immersion time of TiF<sub>4</sub> solution.

#### 4. CONCLUSION

A new fabrication method of the controlling the nano-structure of anatase TiO<sub>2</sub> thin film was suggested by using the high surface area, porous nano-structure of the layer-by-layer selfassembled film with nano pores of 50-400nm in diameter, penetrated to the substrate surface. The nano-structure and thickness of the TiO<sub>2</sub> thin film were systematically controlled. Furthermore, we consider that the resulting structures of porous TiO<sub>2</sub> are 2-3 times the surface area of TiO<sub>2</sub> film directly deposited on the substrate. Consequently, by using this new replication method, we successfully carried out the structure control in nano-scale and the construction of high surface area.

#### ACKNOWLEDGEMENT

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