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TiO_2 thin films prepared from aqueous solution and their sterilizing capability

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A liquid phase deposition method (LPD) has been devised for the deposition of TiO_2 thin films on glass at a low temperature. The substrates were immersed in a diluted homogeneous aqueous solution which was prepared by mixing equal volumes of ammonium hexauorotitanate and boric acid solution. The TiO_2 thin films obtained were well-adhered, homogenous and colored by interference of reflected light. XRD indicated TiO_2 thin films showed a high degree of crystallinity and the crystal phase observed was anatase. SEM experiments showed that the films are formed by small crystallites having linear dimensions under 50 nm. Their thickness was in the range of 100~300 nm. The sterilizing experiment of *S. aureus* and *E. coli* showed that TiO_2 thin films have excellent sterilizing activity. The optimum conditions of the films were with heat treatment at 400°C where their sterilizing percentage reached over 99% after 24h.

Key words: TiO_2 thin films, deposition process, sterilizing capability.

Introduction

Several reports on TiO_2 thin films obtained by many methods have recently appeared due to the importance of these films in different applications. TiO_2 thin films find extensive application in several fields such as photo-catalysis [1], dye-sensitized solar cells [2-3], anti-reflectance coatings [3, 4] photo-oxidation of water [5], electro-chromic devices [6] and other uses [7].

TiO_2 thin films have been prepared by a number of deposition techniques, such as sputtering, spray pyrolysis [8], sol-gel processing [9] and chemical vapor deposition (CVD) [10, 11]. These methods usually require the cost-competitive techniques and expensive devices in those application areas for film deposition. Thus, TiO_2 thin films on glass and ceramics were not easily achieved using these techniques. However, a successful deposition process can be achieved by a liquid phase deposition method (LPD) [12] in a soft-solution at a low temperature. This gives a quality improvement, lower costs and environmental-friendly processing. Deki et al. [13] did not report catalysis of TiO_2 films obtained by LPD method.

However, in our work, anatase TiO_2 thin films having excellent crystallinity were directly obtained on glass by heat treatment using aqueous solutions of ammonium hexauorotitanate and boric acid as starting materials. Here, we report the microstructure of the TiO_2 thin films and influence of the deposition conditions upon the growth rate from a viewpoint of hydration of the titanium precursor in the solution. In addition, the photo-catalytic properties of the deposited anatase TiO_2 thin films are also discussed for applications in sterilizing experiments.

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Experiments

The precursor aqueous solution was freshly prepared by mixing 200 ml ammonium hexauorotitanate (IV) solution ($[Ti]=3.4\times10^{-2}$ M) and 200 ml boric acid (1.02×10^{-1}M) solution. Glass was cut into pieces of $20\times20\times2$ mm^3 in size and washed ultrasonically with diluted nitric acid, ethanol and deionized water for 1h. The washing cycle was repeated three times. The as-cleaned specimens were immersed into the precursor aqueous solution and maintained at a constant temperature of 25-30°C for 24-96 h. Then, the specimens were rinsed with deionized water and heated at various temperatures for 1h (Fig. 1).

The crystal phase of the as-prepared TiO_2 thin films was identified using an X-ray diffractometer (XRD, Cu Ka, Rigaku, Japan, λ=0.1541 nm). Data were collected from 20° to 70° 2θ at a scan rate of 1° $minute^{-1}$. Thickness measurements were performed using a scanning electron microscope (SEM, JEOL JSM-6300, Japan) equipped with an energy-dispersive X-ray analyzer, after the surfaces were coated with gold film.

S. aureus ATCC6538 and *E. coli* O157 were used as the experimental bacteria in this experiment. The bacteria was diluted to a concentration from 10^1 to 10^6 cfu/ml. 0.5 ml bacteria solution was used to inoculate and spread onto the surface of the 50 mm×50 mm glass sample, a blank sample was used as a positive control. The surface of the sample was covered by an anti-staling film. The humidity was kept above 90%. The sample was scattered in a 36°C ± 1°C thermostat

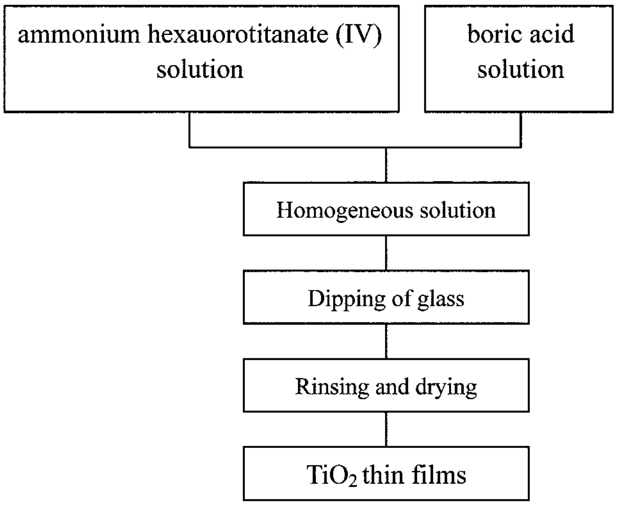

Fig. 1. Schematic of the preparation technique.

illumination container. Samples were taken out of the container after 12h and 24h. The bacterial solution was brushed onto the sterilizing sample and the film plate using 9.5 ml normal salt solution. An 0.1 sample is used to calculate the cfu. The formula to calculate sterilizing rate is:

$$\text{Sterilizing rate (\%)} = \frac{C_0 - C_1}{C_0} \times 100\% \qquad (1)$$

Where: C_0 the lank cfu
C_1 the sample cfu

Results and Discussion

Deposition conditions and film properties

The deposition conditions for the preparation of anatase films were examined using borosilicate glass plates as a substrate. The molar ratio of ammonium hexauorotitanate (IV) solution and boric acid was 1:3, when the concentration of ammonium hexauorotitanate (IV) solution was 0.1 mol/l, the deposited films were opaque and easily peeled off in a heating treatment. At a concentration of ammonium hexauorotitanate (IV) solution below 0.01 mol/l, neither precipitation nor film formation was observed. Selecting 0.34 mol/l, the films were uniform and even, light transmittance may reach 97%.

Powder X-ray diffraction patterns (Fig. 2) indicated that the deposited films only consisted of anatase particles with high crystallinity after different heat treatments. The crystallite size increased with the heat treatment temperature. At the same time, in the light of the Scherrer equation:

$$D = K\lambda/(\beta\cos\theta) \qquad (2)$$

K=0.89, λ=0.1541 nm, θ is the half-diffraction angle, β is the half-peak width, D is the diameter of crystalline particle. The diameter of the particles in the films gradually increased with the heat treatment temperature. The estimated average crystal sizes are 10.2 nm, 17.6 nm, 28.4 nm and 36.0 nm in samples processed, respectively, at 300, 400, 500 and 600°C.

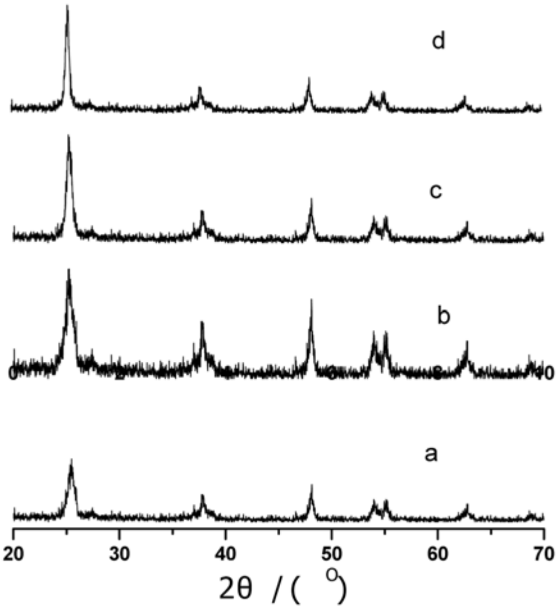

Fig. 2. Powder X-ray diffraction patterns of deposited TiO_2 at different heat treatment temperatures. a: 300°C; b: 400°C; c: 500°C; d: 600°C

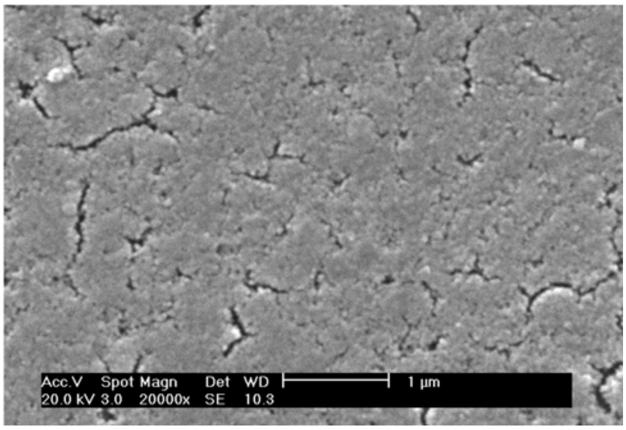

Fig. 3. SEM micrograph of TiO_2 thin film after heat treatment at 400°C.

A SEM image (Fig. 3) revealed that the deposited films consisted of fine particles with a diameter of several tens of nanometre. The diameter of the particles in the films gradually increased with the deposition time. The transparency of the deposited films decreased as the diameter increased because of scattering of light. As shown in Fig. 4, the thickness of the deposited films increased with the deposition time. However, films thicker than 200 nm easily peeled off after heat treatment. On the other hand, because of their different thicknesses, films showed reflection-interference colors including yellow, pink and green.

Table 1. Test results of sterilizing capability of TiO_2 thin films

	Sample	G300		G400		G500		G600	
	Time (h)	12	24	12	24	12	24	12	24
S. aureus	Sterilizing percentage (%)	72.64	85.73	88.46	98.71	84.55	90.47	83.66	89.62
	Positive comparison ($\times 10^4$)	5.0	4.7	5.0	4.7	5.0	4.7	5.0	4.7
E. coli	Sterilizing percentage (%)	81.23	83.44	94.68	99.47	92.66	98.32	93.57	97.46
	Positive comparison ($\times 10^4$)	5.0	4.7	5.0	4.7	5.0	4.7	5.0	4.7

Note ≤ ½no bacterium can live through negative comparison

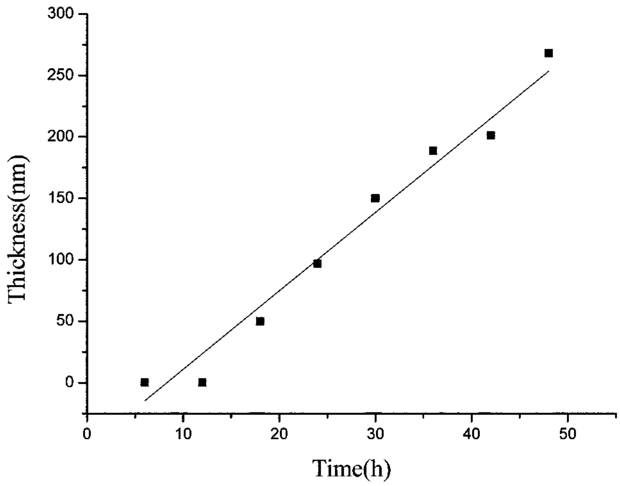

Fig. 4. The thicknesses of the deposited films as a function of the reaction time.

The sterilizing capability and mechanism

The tests of the sterilizing capability are shown in Table 1 (G300 represents the thin film sample after the heat treatment at 300). The TiO_2 thin films have a strong sterilizing capability. The sterilizing rate increases with the increase of the illumination time. At 12h, the G400 sterilizing rate of *S. aureus* and *E. coli* is about 15.8% and 13.5% higher than those of the G300, respectively, however, the sterilizing rate of the G500 and G600 showed an obvious decrease. At 24h, the sterilizing rate of the G400 which reaches the optimum condition compared to other sample is about 99%.

The increase of heat treatment causes two effects of the photocatalytic property. The first effect is, with the increase of the crystallinity, a decrease of combination rate of the photogenerated electron-cavity; the other effect is, with an increasing of the particle size and a rapid decrease of the specific surface area this causes the decrease of the absorption capacity of the reagent and activated centers of the reaction. The influence of the second effect is obviously higher than that of the first effect, so the sterilizing rates of the G500 and G600 are lower than that of the G400. The increase of the heat treatment temperature is disadvantageous to the photo-catalytic property.

It is the photo-catalytic property of the TiO_2 thin films that makes it have a sterilizing capability. Under the illumination of the Ultraviolet light from natural light, the TiO_2 thin films can spontaneously decompose positive-negative, electron e^- and cavity h^+, which can form the electron-cavity, the cavities oxidize the OH^- and H_2O which are absorbed on the surfaces of the TiO_2 thin films to ·OH, ·OH using the oxidizing activity and can quickly decompose the organisms. When *S. aureus* and *E. coli* were illuminated in the absence of TiO_2 thin films, with the decomposition of the cell wall and the cell membrane of the bacteria, the leakage of intracellular molecules will result in a change in the cell viability. These results imply that TiO_2 thin film photo-catalysts have excellent sterilizing activity.

Conclusions

From our above studies, it has been found that transparent TiO_2 thin films were obtained on glass by a liquid phase deposition method (LPD) using ammonium hexauorotitanate as precursor. The TiO_2 thin films obtained adhered well, were homogenous and colored by interference of reflected light. XRD and SEM experiments indicated TiO_2 thin films have the anatase crystal structure with crystallite dimensions under 50 nm and thicknesses in the range of 100~300 nm. When *S. aureus* and *E. coli* are illuminated in the presence of TiO_2 thin films, in natural light, the films display excellent sterilizing activity.

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