Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2014, Article ID 637532, 7 pages
http://dx.doi.org/10.1155/2014/637532

Research Article

Photocatalytic Activity of Hierarchically Structured TiO_2 Films Synthesized by Chemical Vapor Deposition

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Received 28 January 2014; Accepted 7 February 2014; Published 10 March 2014

Academic Editor: Kangle Lv

Hierarchically structured TiO_2 photocatalyst films were synthesized using low-pressure metal-organic chemical vapor deposition (LPMOCVD) method to examine their photocatalytic activity. The thickness of the TiO_2 films increased proportionally with increasing deposition time. The TiO_2 film synthesized at 773 K showed a hierarchical structure composed of vertically grown laminar (112)-oriented anatase crystals. With increasing deposition time, the grain became larger and the morphology became sharper. In the initial CVD stage, small particular crystals were formed, above which sequential growth of layers of columnars with increasing size took place, forming hierarchical structure. The hierarchically structured TiO_2 film exhibited much higher photocatalytic activity than unhierarchically structured TiO_2 film. The photocatalytic activity increased with increasing film thickness.

1. Introduction

Photocatalysis is a process in which a semiconducting material absorbs light energy more than or equal to its band gap, thereby generating holes and electrons, which can further generate free radicals on surface [1, 2]. The resulting free radicals are very efficient oxidizers of organic matter [3, 4]. TiO_2 has been considered to be an effective photocatalyst due to its large surface area [5, 6]. Recently, many efforts have been concentrated on maximizing the catalytic performance of TiO_2-based photocatalysts [7–10]. It has been proved that highly crystalline TiO_2 materials have higher photocatalytic activities than their amorphous counterparts because of a higher rate of photogeneration of electron-hole pairs. Furthermore, a high surface area is also one of the critical factors in maximizing the amount of redox reaction sites available on the catalyst surface [11].

Hierarchical structured materials provide photocatalyst with large surface area in wide applications including catalysis [12]. Such hierarchical structure can promote chemical reactions occurring on surface more effectively [13, 14]. Therefore, the high reaction activity can be achieved with hierarchical structured TiO_2 photoatalyst films. A variety of synthesis techniques, including sol-gel methods [15] and chemical vapor deposition (CVD) growth [16], have been used to form hierarchically structured TiO_2. Among these, CVD is considered a promising method to prepare high-quality thin films over large surface area with a well-controlled composition and low defect density [5, 11].

In this paper, we prepared anatase crystal structure TiO_2 photocatalyst films with different morphologies using CVD and determined the effects of film morphology on photocatalytic activity. We also investigated the change in TiO_2 film morphology during the growth by CVD process.

2. Experimental Procedure

2.1. Preparation of LPMOCVD-Grown TiO_2 Photocatalyst Films. For the analysis of the crystal structure, TiO_2

photocatalyst films were grown on silicon substrate, and also on alumina balls, using a LPMOCVD apparatus, with titanium tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$, TTIP) as a reagent. Details of the apparatus have been described in our previous paper [11]. The LPMOCVD conditions used for the preparation of TiO_2 films were as follows: total flow rate of gas fed to the reactor of 1500 sccm, oxygen concentration at the reactor inlet of 50 mol%, operating pressure of 1 torr, and deposition temperature of 673 K and 773 K. The morphology of the films grown on the Si substrate was evaluated using a field emission-scanning electron microscope (FESEM, Hitachi, S-4700). The crystal structure was characterized by X-ray diffraction (Max Science, MPX3).

2.2. Evaluation of Photocatalytic Activity. The photocatalytic activities of the TiO_2 films were evaluated by the photocatalytic decomposition of an aqueous solution of bromothymol blue (BTB) in a recirculation type annular tube photoreactor. Details of the photoreactor have been described in our previous paper [11]. The photocatalyst balls were placed in the annular space of the reactor. A UV-A lamp (Philips, TL4W/05, with the UV output power of 0.2 W which is most intensive at 365 nm) was used as a light source. The decomposition rate was evaluated as a function of the irradiation time from the change in the BTB concentration at the reactor outlet. The concentration of BTB was measured by the absorbance at $\lambda = 420$ nm, using a spectrophotometer (UV-1601, Shimadzu). The initial BTB concentration was about 3.0×10^{-5} mol/liter, with 500 cm^3 of solution circulated in the reactor at a flow rate of 200 cm^3/min. Specific surface area of TiO_2 films is very small so that it was measured by a BET adsorption apparatus with differential tensimeter of a symmetrical design (Belsorp-18plus, BEL Japan, Inc.) at liquid nitrogen temperature by adsorbing krypton gas (99.995%) to the film. Films with different temperatures grown on 1 gram of the small glass beads were pretreated by heating the samples up to 383 K for two hours in flowing helium gas (99.9999%) under vacuum.

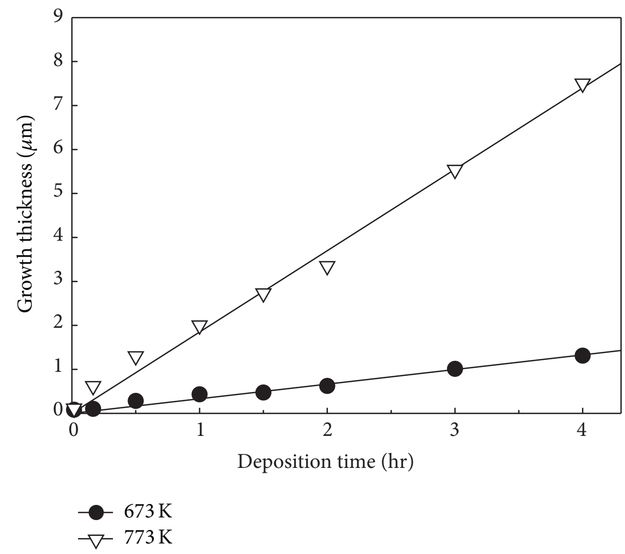


Figure 1: Thickness of TiO_2 films as a function of deposition times.

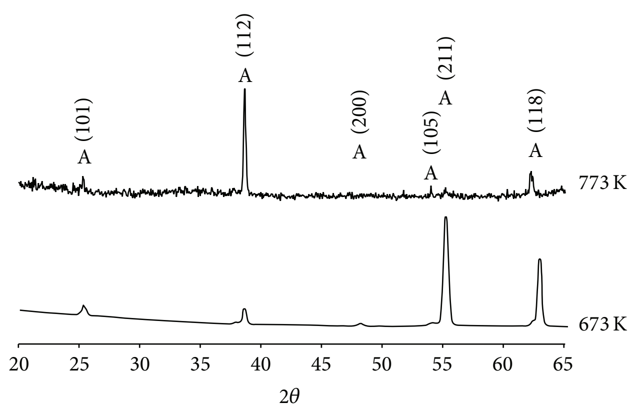


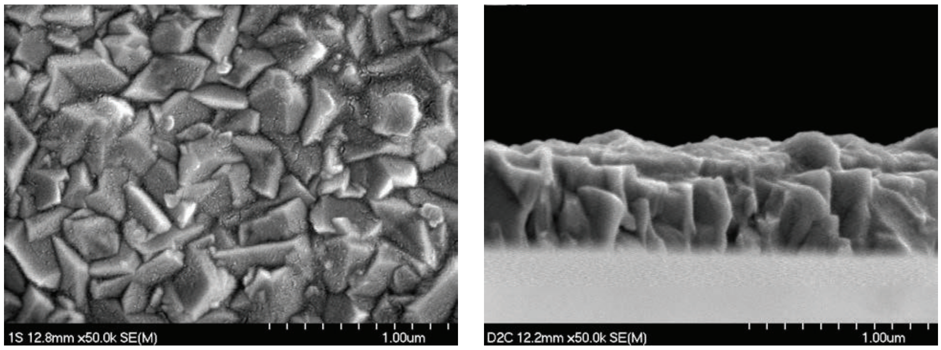
Figure 2: X-ray diffraction of anatase TiO_2 films prepared by CVD method under different deposition temperatures.

3. Results and Discussion

3.1. Preparation of TiO_2 Films by CVD. TiO_2 films with different morphologies were synthesized to examine the effects of the film morphology on photocatalytic activity. The morphology of crystal structure of TiO_2 films synthesized by CVD varies depending on CVD reaction temperature. A previous study reported that TiO_2 film with hierarchical structure could be obtained when the CVD process temperature was high [5]. Therefore, we synthesized TiO_2 films at two different temperatures: 773 K to obtain hierarchical structure and 673 K to obtain nonhierarchical structure. Figure 1 compares the time evolution of TiO_2 film thickness observed at two CVD temperatures. The film thickness was proportional to the deposition time at both temperatures. The film thickness obtained at 773 K was 5.5 times higher than that obtained at 673 K.

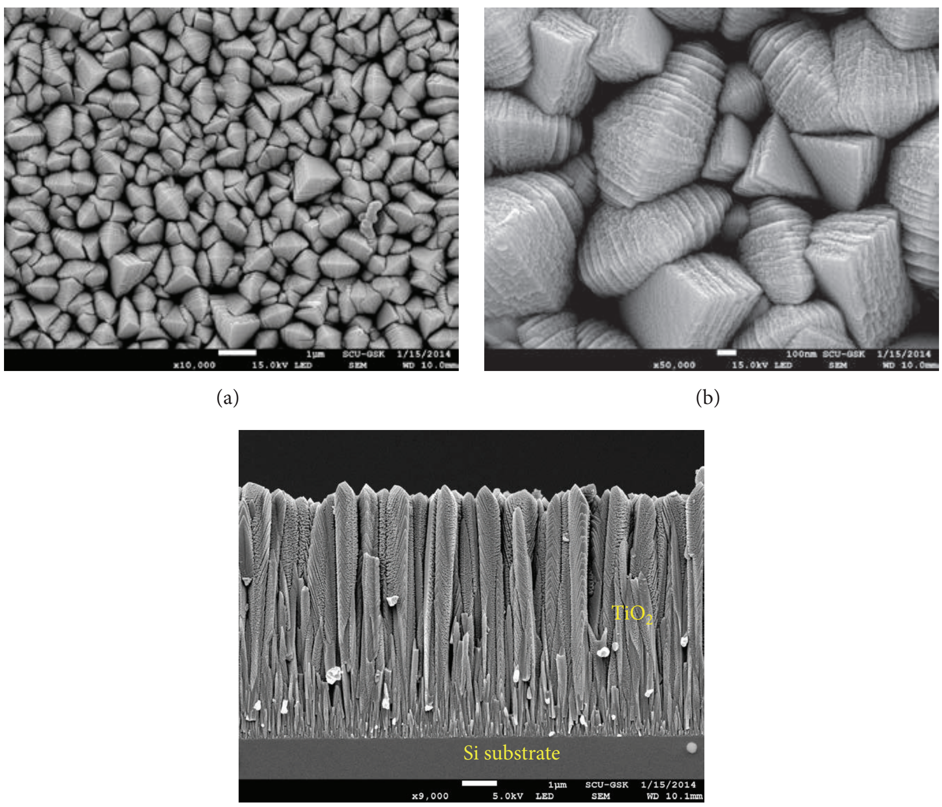
One method that can be used to increase the film growth rate at a given CVD temperature is to increase the TTIP dose rate by reducing CVD operating pressure or increasing source evaporator temperature. The supply of excessive quantity of TTIP, however, may lead to the generation of airborne TiO_2 particles by gas-phase reaction among reactive species with high concentration. The concurrent deposition of these TiO_2 aerosol particles reduces the film density, and, hence, the photocatalytic activity of the film. Therefore, in this study, caution was given so that the TTIP concentration was suppressed to prohibit the generation of aerosol particles.

TiO_2 has three crystal phases: brookite, anatase, and rutile; the latter two crystal phases have been widely adopted in photocatalysis, solar cells, and self-cleaning. A previous study reported that TiO_2 film was formed with amorphous structure below 577 K, with anatase crystal structure between 673 K and 823 K, with anatase-rutile combined crystal structure between 873 K and 1023 K, and with rutile crystal structure at and above 1073 K [11]. In this study, TiO_2 films were synthesized at 673 K and 773 K to obtain anatase crystal phase. Figure 2 shows the X-ray diffraction patterns



(a) (b)

Figure 3: Surface and cross-sectional morphology of TiO_2 films prepared by the CVD methods. Deposition time: 2 hours; deposition temperature: 673 K.



(a) (b)

(c)

Figure 4: Surface and cross-sectional morphology of TiO_2 films prepared by the CVD methods. Deposition time: 4 hours; deposition temperature: 773 K.

of the TiO_2 films grown at the two deposition temperatures. Although TiO_2 films with anatase crystal structure were synthesized at both temperatures, the film grown at 773 K was (112)-oriented, whereas the one grown at 673 K was (211)- and (118)-oriented.

Figure 3 shows the FESEM images of a TiO_2 film prepared at 673 K using the CVD method: surface morphology (a) and cross-section morphology (b). Grains deposited irregularly with the size of 200~300 nm were observed. The surface and cross-section morphology of the film grown at 673 K revealed that the film structure was not amorphous but crystalline. However, the crystalline structure was not hierarchical.

Figure 4 shows the FESEM images of the TiO_2 film prepared at 773 K: low-resolution surface morphology (a), high-resolution surface morphology (b), and cross-section morphology (c). In the low-resolution surface image (a), 0.5~1.0 μm sized grains deposited irregularly were observed. The high-resolution surface image (b) reveals that each

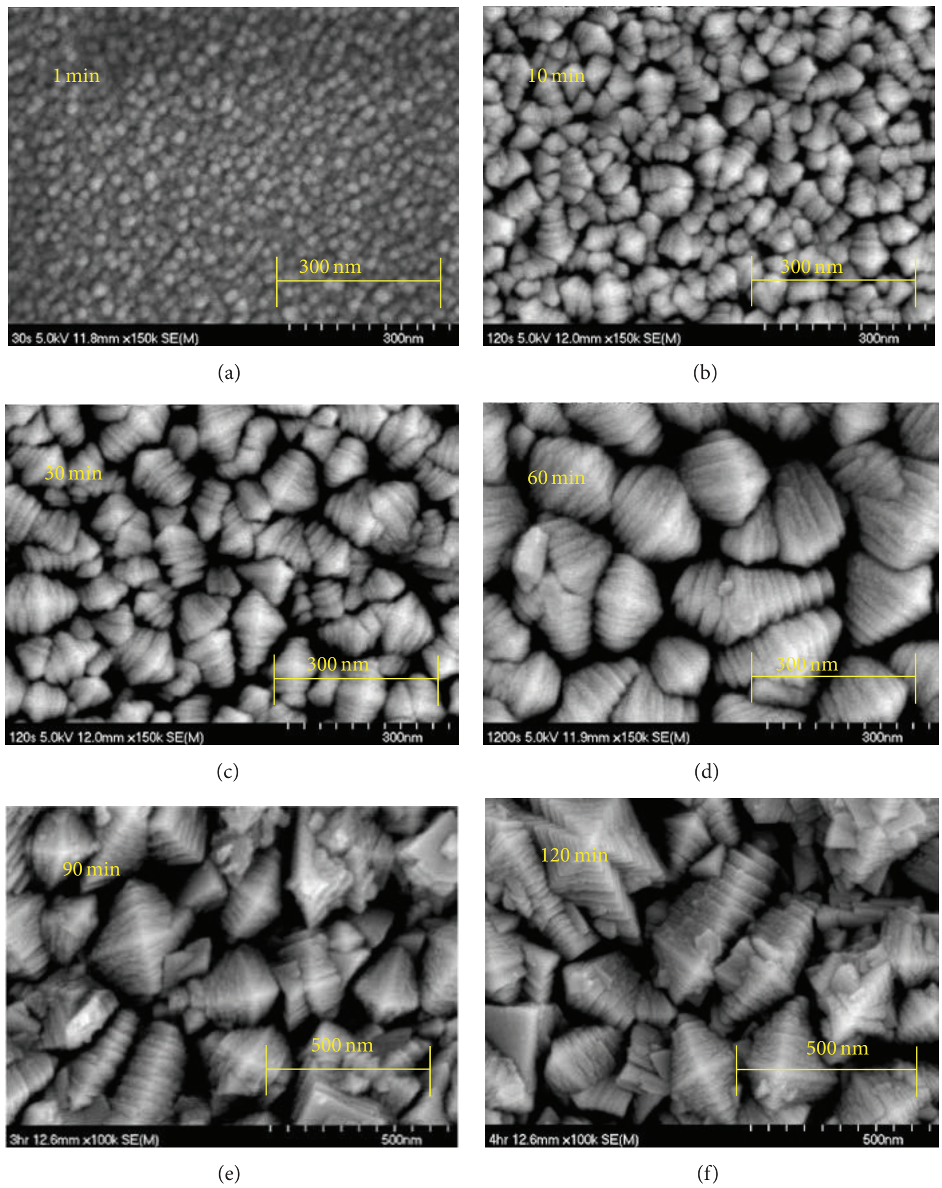


FIGURE 5: Surface morphology of TiO_2 films grown by CVD at different deposition times.

grain is composed of sheet-like (laminar) crystals. Generally, this laminar crystal structure is observed in vermiculite. The cross-section morphology (c) shows that the TiO_2 film with laminar crystal structure has grown vertically from substrate. The columnar crystals of the film found near substrate were small, whereas larger columnar crystals were observed at distant locations from the substrate. This layered structure with different crystal sizes is called hierarchical structure. Figure 4(c) shows that the structure of the TiO_2 film synthesized at 773 K is hierarchical with the columnar crystal size increasing along the *c*-axis.

Figure 5 shows the FESEM images of the surface of TiO_2 films prepared with different deposition times. Flat surface composed of tiny particles was observed when the deposition time was 1 min. TiO_2 grains with laminar structure were observed when the deposition time was 10 min or longer. The grain size increased with increasing deposition time. The grain morphology also became sharper with increasing deposition time. In a previous study [5], the BET analysis showed that the grain size and specific surface area increased rapidly in the early TiO_2 film growth phase of CVD process, whereas the grain size and surface area increasing rates became lower after two hours, which is in good agreement with the hierarchical structure with increasing columnar crystal size observed in Figure 4.

3.2. Mechanism of Hierarchical Growth of TiO_2 Film. As shown in Figures 4 and 5, small particular crystals were observed in the initial growth stage (in the bottom part of film), while larger columnar crystals were observed above these particles. A mechanism for the growth of hierarchically structured TiO_2 film by CVD is suggested in Figure 6. In

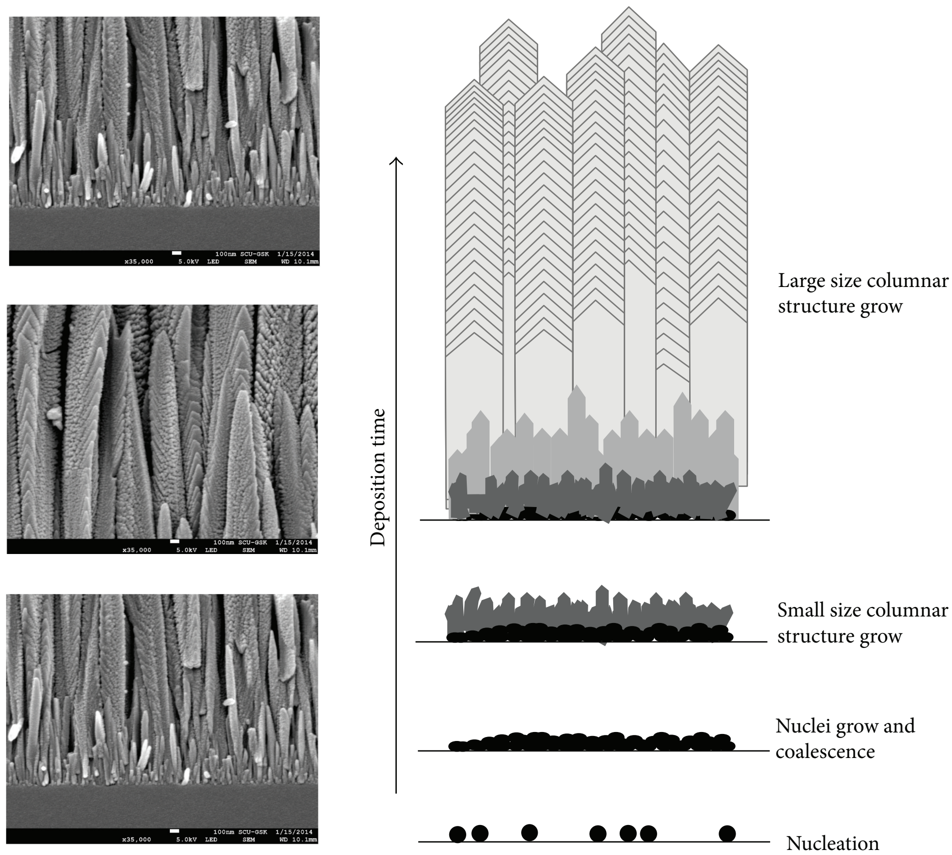


Figure 6: Proposed growth mechanism for the hierarchically structured TiO_2 films by CVD.

the initial stage, small particular crystals are formed on the substrate via TiO_2 nucleation, nuclei growth, and coalescence. Then, small-sized columnar grows on these particles, followed by sequential growth of larger and larger columnaris constructing hierarchical structure. After the deposition time of two hours (after the TiO_2 film grew thicker than 3 μm), the TiO_2 crystal width remained almost uniform (about 0.5~0.7 μm). These changes may correspond to Kolmogorov's "geometrical selection" of crystals [17]. In conclusion, TiO_2 film with hierarchical anatase crystal structure is synthesized by CVD at 773 K until a certain deposition time (or up to a certain crystal thickness), beyond which the crystal width remains unchanged.

3.3. Evaluation of Photocatalytic Reaction Activity. The TiO_2 films synthesized in this study were used for the photocatalytic decomposition of BTB. Figure 7 shows the BTB concentration decay as a function of the irradiation time. The decomposition of BTB via the photocatalytic reaction in the presence of TiO_2 photocatalyst could be approximated with a pseudo-first-order reaction model:

$$\frac{C}{C_0} = \exp(-kt), \tag{1}$$

where C is the BTB concentration at time t, C_0 the initial concentration, and k the overall rate constant.

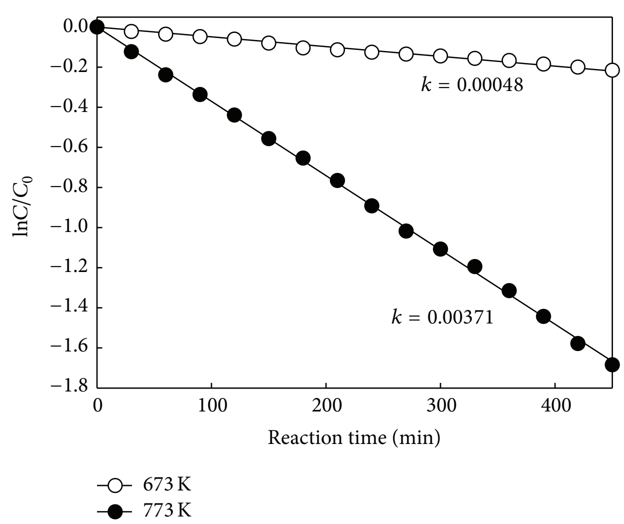


Figure 7: Photocatalytic decomposition of BTB on the CVD grown TiO_2 film with different deposition temperatures.

The hierarchically structured TiO_2 photocatalyst grown at 773 K showed much higher catalytic activity than the unhierarchically structured TiO_2 photocatalyst grown at 673 K. This result can be attributed to the larger surface area of the hierarchically structured TiO_2 photocatalyst. BET analysis showed that the specific surface area of hierarchically

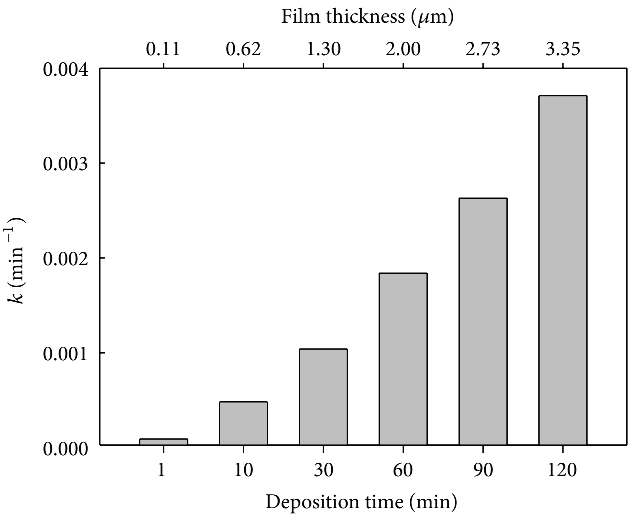


Figure 8: Effect of hierarchically structured TiO_2 film thickness on the apparent first-order rate constant.

structured TiO_2 photocatalyst was 0.1373 m^2/g, whereas that of unhierarchically structured TiO_2 film was 0.0615 m^2/g.

Figure 8 compares the BTB decomposition rate constants obtained with the hierarchically structured TiO_2 photocatalysts prepared at 773 K with different deposition times (with different thicknesses). The overall rate constant, k, was determined from the slopes of the lines in Figure 7 using linear regression analysis. The rate constant k increased with increasing deposition time. This can be attributed to the increase in the surface area of the photocatalyst film with increasing film thickness. A previous study [5] also reported that the decomposition rate of methylene blue increased with increasing TiO_2 film deposition time, which was attributed to the increase in the surface area of TiO_2 film. The slowdown of the increase in film surface area after the deposition time of two hours (after the TiO_2 film grew thicker than 3 μm), leading to the slowdown of the decomposition of methylene blue, was also reported in that study. The results of the present study also showed that the photocatalytic activity of the hierarchically structured TiO_2 photocatalyst film synthesized using CVD method increased with increasing deposition time (with increasing film thickness) due to increasing specific surface area.

4. Conclusions

The conclusions obtained in this study with the hierarchically structured TiO_2 photocatalyst films synthesized using the CVD method are as follows.

(1) TiO_2 film thickness increased proportionally with deposition time.

(2) The TiO_2 film synthesized at 773 K showed (112)-oriented anatase crystal structure.

(3) In the TiO_2 film synthesized at 773 K, laminar crystal TiO_2 grew vertically from the substrate forming a hierarchical structure.

(4) With increasing deposition time, the grain size increased and the morphology became sharper.

(5) In the initial stage of CVD, small particular crystals are formed, above which sequential growth of columnaris with increasing size takes place leading to a hierarchical structure. After the deposition time of two hours, or after TiO_2 film grew thicker than 3 μm, the width of TiO_2 crystalline columnar remains uniform.

(6) The photocatalytic activity of the hierarchically structured TiO_2 film grown at 773 K was much higher than that of unhierarchically structured TiO_2 film. The photocatalytic activity increased with increasing film thickness.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2013R1A1A2A10004797).

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