

Self Assembly of Honeycomb TiO₂ Coatings by Tea-Leaf Extracts as the Dispersoids

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ABSTRACT

Photo catalytic TiO₂ coatings with well defined honeycomb structure were successfully self-assembled on glass substrates by a simple “dip and burn sol-gel method”. The crux of this new method is that the starting material for the sol-gel coating (the water solution of ammonium titanium citrate) was “doped” with “tea-leaf extracts”. Tea-leaf extracts were completely dissolved in the water solution of ammonium titanium citrate and nucleate uniformly during the drying procedure of the coating precursor formation. This uniformly dispersed nucleation of the “tea-leaf extracts (tannin, catechin, etc.)” were extracted during calcinations and leaving honeycomb-cell like nano-structure in the TiO₂ coatings. Self-assembled cells were uniformly distributed in the TiO₂ coatings and the diameter of the cells was in the range of 200 - 1000 nm. Fine honeycomb structures were clearly observed with microscopic observations.

Keywords: TiO₂, Coatings, Photo-Catalysis

1. Introduction

Growth process for the porous photo-catalytic Titanium-dioxide (TiO₂) thin films has attracted significant attention since it is essential for the dye-sensitized solar cells. The porosity of the coatings enlarges the effective surface area of the coatings and enhances the photo-catalytic efficiency of the TiO₂ thin films. Coating process capable of providing large-area Sol-gel processes with additives in the coating solutions have been reported to be successful for obtaining porous TiO₂ thin films with enhanced photo-catalytic efficiencies [1-4]. These additives play the principal role in the microstructure of the self-assembled porous TiO₂ coatings. Survey studies for better additives have been intensely performed since the additives vaporize during the annealing process and the materials properties of the additives dominate the microstructure of the porous films. The ideal morphology of the porous TiO₂ coatings is nano-sized honeycomb structure. In this study for the formation of the well-defined honeycomb structure in the coatings, a new additive for the honeycomb TiO₂ films “tea leaf extracts” is successfully combined with the water soluble ammonium titanium citrate.

2. Experimental

In this study, a simple “dip and burn sol-gel method” was

applied as the coating process for TiO₂ thin films. The water solution of ammonium titanium citrate (NH₄)₄[Ti₂(C₆H₄O₇)₂]-4H₂O was adopted as the starting material for sol-gel coating. The Ti concentration in the solution was 2 wt% (*i.e.* 2% of the weight of the solution correspond to Ti). The reference samples (Sample Ref.) were fabricated as follows: Quartz glass (0.5 mm) plates were dipped into this 2 wt% water solution of ammonium titanium citrate and dried in the ambient for 1 - 2 hours to form coating precursors on the glass plates. Afterwards, these samples were sintered at 450°C for 5 hours in the air for crystallization of TiO₂.

In order to obtain TiO₂ coatings with the porous (honeycomb) structure, “red-tea leaves” (0.6 g) were added in the above water solution of ammonium titanium citrate (10 cc) and extracted for 24 - 72 hours at room temperature. As a result, the yellowish color of the water solution of ammonium titanium citrate turned into red-brownish color which is familiar to us as the color of the strong red tea. The coating, drying and sintering procedure was identical to those for the sample Ref. Six grams of Sugar was also applied as additives into the in the above water solution of ammonium titanium citrate (10 cm³) and stirred until complete dissolution. The details of the preparation conditions for three kinds of samples (Ref, Tea, and Sug) are summarized in **Table 1**.

Table 1. The details of the preparation conditions for three kinds of samples Ref, Tea, and Sug.

	Starting material	additive	Coat.	Sint.
Ref	2 wt% 10 cm ³ (NH ₄) ₄ [Ti ₂ (C ₆ H ₄ O ₇) ₂].4H ₂ O	none	Dip Dry burn	450°C 5h
Tea	do.	red tea leafs (0.06 g/cm ³)	do.	do.
Sug	do.	sugar (0.6 g/cm ³)	do.	do.

The crystalline structure of the films was investigated by x-ray diffraction method with Cu K α line (RIGAKU RINT 1500). Digital Optical microscope (KEYENCE VHX) with the magnification up to 5000 \times was applied for the observation of the surface morphology of the TiO₂ films. The thickness of the films was investigated by the optical thickness measurement system (FILMETRICS F-20). The photo-catalytic activity of the films was investigated by the photo-catalytic decomposition of isopropanol (CH₃CH(OH)CH₃) under ultraviolet irradiation. The TiO₂ sample for evaluation was placed in an airtight quartz vessel. The initial atmosphere of this vessel was controlled carbon dioxide (CO₂) free by gas substitution. Isopropanol (CH₃CH(OH)CH₃) with the concentration of 60 - 70 ppm was introduced into this CO₂ free quartz vessel with the TiO₂ sample inside and succeeded by UV irradiation by black-light (wavelength: 300 - 400 nm, intensity: 0.27 mW/cm², time: 30 hours). The change of the composition of the gas inside the vessel during UV irradiation was periodically monitored by gas sampling and checking by gas chromatography.

3. Results and Discussion

The crystalline structure of the three kinds of samples, Ref, Tea and Sug showed broad halo pattern with faint diffractions assigned to TiO₂ rutile or anatase structures. The thickness of the films (Ref, Tea, Sug) were 100 nm, 80 nm, 100 nm, respectively. **Figures 1(a)** and **(b)** show the optical micrographs of the samples Tea (a) and Sug (b) respectively. Well-defined honeycomb structures with the cell diameter of 200 - 1000 nm were clearly observed in **Figure 1(a)**. However, sample Sug (**Figure 1(b)**) showed flat surface with no particular structures identical to that of the sample Ref (not shown). The above described decrease in the film thickness in the sample Tea by 20% compared with those of the samples Ref and Sug is related to the successful porous structure formation in the sample Tea.

Well defined honeycomb structure seems to be the fruit of the additive (red tea leaf extracts) which is completely soluble to the coating solution (water solution of ammonium titanium citrate) and shows uniform nucleation in the coating precursor followed by vaporization during calcinations. The coating solutions used in this

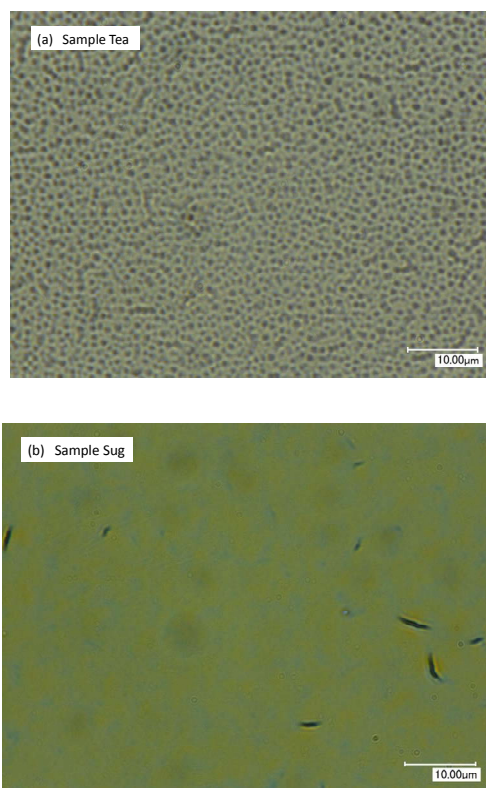


Figure 1. The optical micrographs of the samples (a) Tea and (b) Sug, respectively. Well-defined honeycomb structures with the cell diameter of 200 – 1000 nm were clearly observed.

study (water solution of ammonium titanium citrate added with red tea extracts or sugar) are very stable and showed no precipitation or separation. The additives such as acryl beads, which are not soluble to the coating solution is not for the honeycomb structure but for the films with random pores. For the purpose of obtaining TiO₂ films with uniform honeycomb structure, the completely soluble additives (red tea extracts, sugar, etc.) seem to have the advantage1.

The photocatalytic activities of the samples Ref, Tea and Sug were evaluated by photo-catalytic decomposition of isopropanol (CH₃CH(OH)CH₃) under ultraviolet irradiation and the results are shown in **Figure 2**. The initial concentration of isopropanol (60 - 70 ppm) gradually decreased according to the ultraviolet irradiation in all samples (Ref, Tea, and Sug) (**Figure 2(a)**). Accordingly, the concentration of acetone (CH₃COCH₃) and CO₂ gradually increased with the ultraviolet irradiation (**Figures 2(b)** and **(c)**).

Figure 3 shows the change of the concentration of the isopropanol, acetone, and CO₂ with ultraviolet irradiation up to 30 hours on the sample Sug. First period up to 8

hours, the concentration of isopropanol consistently decreased and reached around zero value, while the concentration of acetone consistently increased and showed a maximum value (~60 ppm) at 8 hours. The second period (8~30 hours) the concentration of acetone gradually decreased and reached zero value around 24 hours, while the concentration of CO₂ showed consistent increase throughout (8 - 24 hours) and saturate. These results are consistent with the fact that photo catalytic decomposition of isopropanol to CO₂ takes place via acetone [5-7].

Effective surface area is the one of the major factor for dominating photo catalytic activity of the photo catalytic coatings. The larger the surface area is, the more active the photo catalytic activity becomes. The sample Tea showed well-defined honeycomb structure with the cell diameter of 200 - 1000 nm while the samples Ref and Sug showed flat surface with no particular structures (**Figure 1**). However, the photo catalytic activities of the samples of Tea and Ref were very close and no clear advantage in the photo catalytic activity was found in sample Tea. This paradox can be explained by the dimensions of the honeycomb cell and the film thickness.

Generally, honeycomb structured films possess larger effective surface area compared with that of the films with flat surfaces since the surface area inside the honeycomb cells acts as extra surface area. However, we have to take the relation of the film thickness and the cell diameter of the honeycomb structure into account. **Figure 4** shows the schematic drawing of the sample "Tea", which possesses well defined honeycomb structure with the cell diameter between 200 - 1000 nm and the thickness of 80 nm as described above. The point is that the cell diameter is larger than the film thickness as schematically illustrated in **Figure 4**.

There do exist the gain of the effective surface area with the honeycomb structure, however this gain is rather small because of the shallowness of the cells. Moreover, at the bottom of the shallow and wide honeycomb cells, not the surface of the photo catalytic film but the surface of the raw glass is exposed. Accordingly, the decrease in the surface coverage takes place in the honeycomb film compared with that of the films with flat surfaces which is a direct decrease in the effective surface area. The gain in the effective surface area originate from the inside area of the honeycomb cells is counterbalanced by the loss in the surface area caused by the surface coverage of the film itself forced by the shallow and wide dimensions of the cells. Hence the photo catalytic activities of the samples of Tea (honeycomb) and Ref (flat) were almost identical according to the photo decomposition of isopropanol (**Figure 2**).

Another paradox observed in **Figure 2** is that the sample Sug grown by sugar as additive showed higher photo

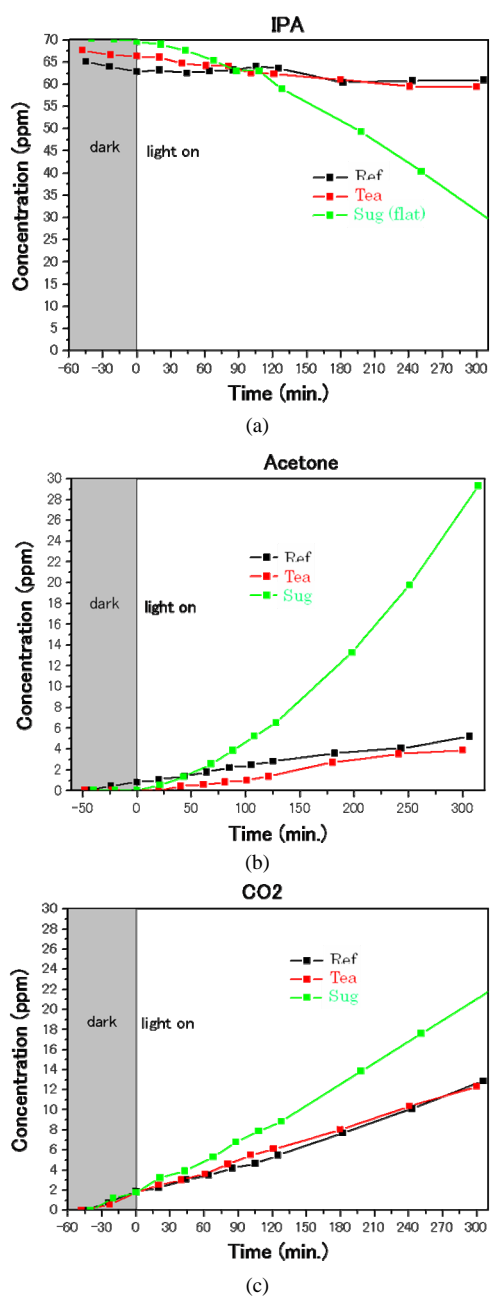


Figure 2 The photocatalytic activities of the samples Ref, Tea, and Sug evaluated by photo-catalytic decomposition of isopropanol ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$) under ultraviolet irradiation.

catalytic activity than those of the samples Ref and Tea. The reproducibility of this superiority of the samples Sug (checked by several samples grown under same conditions shown in **Table 1**) was quite good and cannot be accidental. The samples Sug showed flat surface similar to that of the samples Ref by optical microscopy. One possibility is that the samples Sug possess nano pores which are invisible by optical microscopy; however

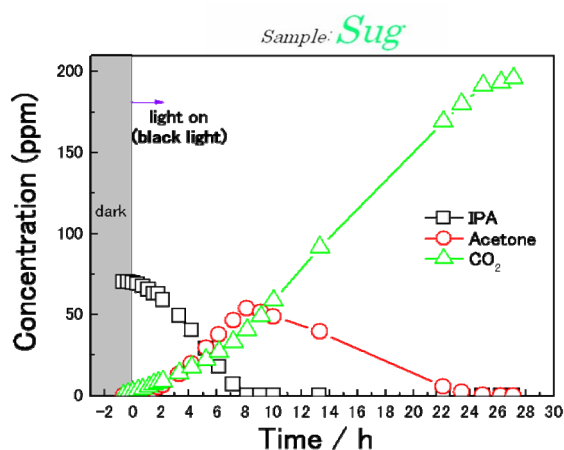


Figure 3. The change of the concentration of the isopropanol, acetone and CO₂ with ultraviolet irradiation up to 30 hours on the sample Sug.

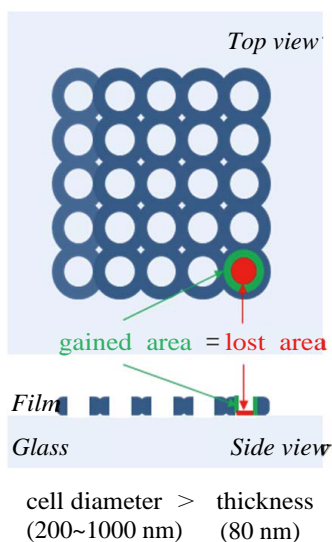


Figure 4. The schematic drawing of the sample Tea, which possesses well defined honeycomb structure with the cell diameter between 200 – 1000 nm and the thickness of 80 nm.

scanning electron microscopy could not provide evidences for the nano pores so far. Another interesting

possibility is that the surface of the sample Sug was chemically improved by sugar additives during film growth processes, resulting in surfaces with higher photo catalytic activity.

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