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Dye Adsorption Characteristics of Anatase TiO_2 Film Prepared in an Aqueous Solution

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ABSTRACT

Anatase TiO_2 film was deposited on SnO_2: F substrate in aqueous solution. The film had an assembly of acicular TiO_2 nanocrystals on the surface. The crystals grew along the *c*-axis, i.e. perpendicular to the substrate. Dye adsorption increased with film thickness. Intensity of photoluminescence originating from the dye adsorbed on the nanostructured film after annealing was 3 times higher than that of thicker particulate film constructed of TiO_2 nanoparticles (P25). Additionally, dye adsorption property of the film without annealing was two times higher than the film with annealing. Consequently, the as-deposited film had high dye adsorption property which is about 6 times higher that that of thicker particulate film constructed of TiO_2 nanoparticles (P25). Assemblies of acicular crystals on the surface increased the surface area and amount of dye adsorption. The film may be useful for biomolecule sensors and dye-sensitized solar cells.
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1. Introduction

TiO_2 film having high dye adsorption characteristics is of interest for biomolecule sensors[1] and dye-sensitized solar cells[2,3]. Transparent conductive substrate such as FTO (Fluorine doped Tin Oxide) or ITO (Indium Tin Oxide) is covered by porous TiO_2 film for these applications. Dye adsorption characteristics directly affect the sensitivity and efficiency of devices. High surface area and nano/micro relief structure are required for adsorbing large amounts of dye. Especially, we are developing environmental molecular sensors[1]. Adsorption property of ssDNA-Cy5(cy5-DP53-t: Cy5-GCGGCAT-GAACCTGAGGCCCATCCT, dye labeling DNA) is very important for the sensor. The sensors require high adsorption property of ssDNA-Cy5.

TiO_2 film has been fabricated using various techniques such as TiO_2 nanoparticle sintering (P-25), sol-gel[4], magnetron sputtering[5], chemical vapor deposition[6], etc. However, the dye adsorption characteristics need to be improved if the TiO_2 film is to be used for sensors and solar cells. Additionally, the substrate in these processes was annealed at high temperature for a long time in order to crystallize anatase TiO_2. This decreased the electrical conductivity of the transparent electrodes.

On the other hand, methods based on an aqueous solution have attracted considerable attention as an environment-friendly synthesis process[7–17]. The morphology of oxide crystals has been successfully controlled during the solution processesfor fabricating unique nano/micro structures[18–21]. Controllability of crystal morphology is one of the advantages of the solution processes.

In this study, we realized morphological control of TiO_2 crystals in aqueous solution and produced TiO_2 film having assemblies of acicular TiO_2 crystals on the surface. Crystals grew along the *c*-axis, making them perpendicular to the substrate. The amount of dye adsorption increased with the increase of film thickness. The 760-nm-thick film achieved dye adsorption that was 3 times larger than that of 1000-nm-thick particulate film constructed of TiO_2 nanoparticles (P25).

2. Experimental

2.1. Surface modification of FTO substrate

Glass substrate coated with F-doped SnO_2 transparent conductive film (FTO, SnO_2: F, Asahi Glass Co., Ltd., 9.3-9.7 Ω/ , $26\times50\times1.1$ mm) (Fig. 1-(1)) was subjected to air-blowing to remove dust and was exposed to ultraviolet light (low-pressure mercury lamp PL16-110, air flow, 100 V, 200 W, SEN Lights Co., 14 mW/cm^2 for 184.9 nm at a distance of 10 mm from the lamp, 18 mW/cm^2 for 253.7 nm at a distance of 10 mm from the lamp) for 10 min (Fig. 1-(2)). The initial FTO substrate showed a water contact angle of 96°. The UV-irradiated surfaces were, however, wetted completely (contact angle 0–1°). Various functional groups such as octadecyl or phenyl groups are known to be modified to OH groups by UV irradiation using low-pressure mercury lamps[22,23]. These suggest that a small amount of adsorbed molecules on the FTO substrate was completely removed by UV irradiation. Original FTO surface covered by hydrophilic OH groups was exposed after irradiation. Consequently, the FTO substrate was modified to super-hydrophilic surface (Fig. 1-(2)). TiO_2 crystallization is sensitive to the substrate surface and OH groups were reported to accelerate crystallization of TiO_2 in the solution[24–28]. Super-hydrophilic OH surface was thus utilized to accelerate TiO_2 deposition

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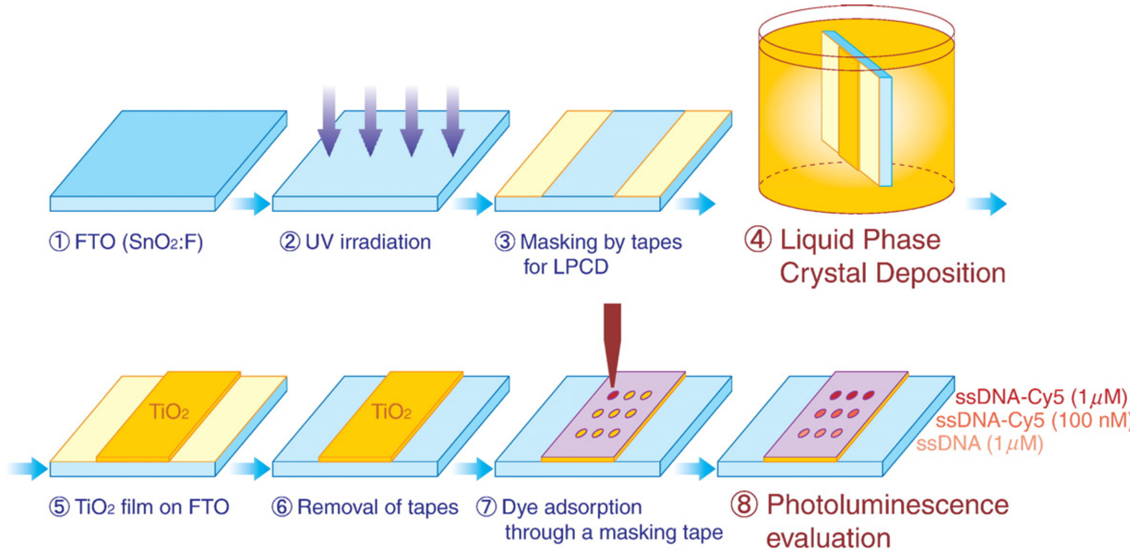

Fig. 1. Conceptual process for fabrication of anatase TiO_2 thin film and evaluation of dye adsorption characteristics.

in our study. Both ends (26×14 mm) of the glass substrate were masked using Scotch tape (CM-18, 3 M) to prevent deposition[29] (Fig. 1-(3)).

2.2. Liquid phase crystal deposition (LPCD) of TiO_2 film

Ammonium hexafluorotitanate ($[NH_4]_2TiF_6$) (Morita Chemical Industries Co., Ltd., FW: 197.95, purity 96.0%) and boric acid (H_3BO_3) (Kishida Chemical Co., Ltd., FW: 61.83, purity 99.5%) were used as received. Ammonium hexafluorotitanate (2.0096 g) and boric acid (1.86422 g) were separately dissolved in deionized water (100 mL) at 50 °C[11]. Boric acid solution (concentration 0.15 M) was added to ammonium hexafluorotitanate solution (concentration 0.05 M). FTO substrate was immersed vertically in the middle of the solution (Fig. 1-(4)) immediately after mixing of two solutions. The solution was kept at 50 °C for 48 h. Substrate was removed from the solution after 2, 5, 25 and 48 h (Fig. 1-(5)). The film was rinsed with distilled water and annealed at 500 °C for 30 min in air after removal of the Scotch tape (Fig. 1-(6)). Dye adsorption properties of them were evaluated. TiO_2 films were annealed because of comparison with TiO_2 films consisted of nanoparticles (TiO_2 P25, Degussa). Additionally, dye adsorption property of the film immersed for 5 h was evaluated without annealing.

2.3. Morphology and crystal phase characterization

TiO_2 film morphology was observed by field emission scanning electron microscope (FE-SEM; JSM-6335F, JEOL Ltd.) and transmission electron microscope (TEM; H-9000UHR, 300 kV, Hitachi). Crystal phase was evaluated by X-ray diffractometer (XRD; RINT-2100 V, Rigaku) with CuKα radiation (40 kV, 30 mA). Diffraction patterns were evaluated using data from the ICSD (Inorganic Crystal Structure Database) (FIZ Karlsruhe, Germany and NIST, USA) and FindIt.

2.4. Dye adsorption characteristics of TiO_2 film

Polyvinyl chloride tape (PVC, CH_2-$CHCl)_n$, 26×22 mm, 100-μm thickness) was perforated with 9 (3 holes×3 rows) holes 25 mm in diameter using a flatbed cutting plotter (CG-60ST; Mimaki Engineering Co., Ltd.). The TiO_2 film was covered with PVC tape (Fig. 1-(7)).

ssDNA-Cy5 (cy5-DP53-t: Cy5-GCGGCATGAACCTGAGGCCCATCCT, dye labeling DNA) or ssDNA (lambda-gt10: TTGAGCAAGTTCAGCCTGGTTAAG) was dissolved in water. ssDNA-Cy5 solution (1 μM), ssDNA-Cy5 solution (100 nM) and ssDNA solution (1 μM) were dropped with pipettes onto the 3 holes in the upper, middle and bottom row, respectively, in the PVC tape (Fig. 1-(7))[1]. The film was dried at 95 °C for 10 min in air. The film was then rinsed 3 times in sodium dodecyl sulfate (SDS, $NaC_{12}H_{25}SO_4$) for 15 min each time and rinsed 3 times in ultrapure water. SDS was used for cleaning of the substrates. Strongly-connected dyes were remained on the substrates and they contributed to photoluminescence property. It was then boiled in water for 2 min, immersed in dehydrated ethanol at 4 °C for 1 min and dried by strong air flow.

Photoluminescence image and intensity were evaluated by Typhoon Trio scanner (GE Healthcare UK Ltd.) using excitation light of 633 nm (He/Ne laser) (Fig. 1-(8)).

Particulate film 1000 nm thick was formed using TiO_2 nanoparticles (TiO_2 P25, Degussa) and was sintered at 500 °C for 30 min in air. Photoluminescence intensity of the particulate film and bare FTO substrate was evaluated after adsorption of 100 nM ssDNA-Cy5 for comparison.

3. Results and Discussion

3.1. Deposition of anatase TiO_2

Deposition of anatase TiO_2 proceeds by the following mechanisms [11] (Fig. 1-(4)):

$$TiF_6^{2-} + 2H_2O \rightleftharpoons TiO_2 + 4H^+ + 6F^- \ldots \quad (a)$$

$$BO_3^{3-} + 4F^- + 6H^+ \longrightarrow BF_3^- + 3H_2O \ldots \quad (b)$$

Equation (a) is described in detail by the following two equations:

$$TiF_6^{2-} \xrightarrow{nOH^-} TiF_{6-n}(OH)_n^{2-} + nF^- \xrightarrow{(6-n)OH^-} Ti(OH)_6^{2-} + 6F^- \ldots \quad (c)$$

$$Ti(OH)_6^{2-} \longrightarrow TiO_2 + 2H_2O + 2OH^- \ldots \quad (d)$$

Fluorinated titanium complex ions gradually change into titanium hydroxide complex ions in the aqueous solution as shown in Eq. (c).

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