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Short communication

# Preparation of anatase phase titanium dioxide film by non-aqueous electrodeposition

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ABSTRACT

The electrodeposition–annealing route to fabricating thin film of the promising photocatalyst material anatase-titanium dioxide (anatase-$TiO_2$) has been studied. The sample was deposited with a solution of N,N-dimethylformamide containing titanium compound by controlled-potential technique. SEM image showed the annealed sample at 600 °C for 1 h under air provided a continuous film with a thickness of ca. 350 nm. In this sample, X-ray photoelectron spectrum corresponding to the Ti 2p peak assigned to a chemical bond of $TiO_2$ and X-ray diffraction peaks assigned to the anatase phase were observed, respectively. Electrochemical oxidation in sodium sulfate solution on this annealed film was enhanced in the presence of UV light radiation. These results confirm the successful synthesis of photocatalytic anatase-$TiO_2$ film by the electrodeposition and annealing process.
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## 1. Introduction

Titanium dioxide ($TiO_2$) is known as an attractive material for application as photocatalyst [1,2,3,4], including cathode material for dye sensitized solar cells and antibacterial agents. There are many reports concerning titanium crystal structures and their reactivity [5,6]. Anatase $TiO_2$ also has a superior reactivity of the organic reagents because it produces hydroxyl radical by light absorption, which makes it attractive for several applications for photocatalyst [1,4]. As for the fabrication process, the synthesis of anatase-$TiO_2$ films by sol–gel [7], sputtering [8], and chemical coprecipitation [9] was reported. In addition to these methods, electrodeposition technique has been actively researched since the late 1990s [10,11] owing to its potential to deliver high-performance and cost-effective films. Two methods have been reported for the electrodeposition of $TiO_2$ in an aqueous solution. One involves the utilization of $H^+$ generated during the anodic process [10,12,13] and the other employs $OH^-$ generation at the cathode [11,14,15]. Electrodeposition of titanium complex from an ionic liquid [16,17], a high-temperature molten salt [18], N,N-dimethylformamide (DMF) containing $TiCl_4$ [19] and DMF bath using $TiCl_4$ and hydrogen peroxide ($H_2O_2$) [20]. However, $TiCl_4$ and $H_2O_2$ are unstable and dangerous to handle. Therefore, we have focused on the synthesis of a new titanium compound to be used in the fabrication of titanium or titanium oxide films. In this study, we demonstrated the fabrication of a titanium complex film by electrodeposition from a newly synthesized titanium compound in N,N-dimethylformamide (DMF) and studied photosensitized electrolytic oxidation on the annealed film.

## 2. Material and methods

### 2.1. Synthesis of titanium compound

Titanium compound for use in the electrodeposition process was synthesized by precipitation technique from a mixture of 50 mL propylenecarbonate and 5 mL titaniumtetrachloride for 24 h, followed by removal of the supernatant solution. A white powder was collected by natural drying and was confirmed to be orthotitanic acid n-hydrate, $Ti(OH)_4 \cdot nH_2O$ (hereafter Ti compound) through nuclear magnetic resonance (NMR) spectroscopy, ultraviolet–visible (UV–vis) spectroscopy, and composition analysis by inductively coupled plasma (ICP) spectrometry.

### 2.2. Preparation of electroplating solution

The synthesized powder and tetrabutylammoniumchloride were used as the Ti compound and supporting electrolyte, respectively. A

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**Table 1**
Chemical composition of non-aqueous electrodeposition bath for titanium complex plating.

| Ingredient | Chemical reagents | Quantity or concentration |
|---|---|---|
| Organic solvent | N,N-dimethylformamide (DMF) | 58 mL |
| | EtOH | 2 mL |
| Ti compound | Orthotitanic acid n-hydrate, $Ti(OH)_4 \cdot nH_2O$ | 0.05 mol $dm^{-3}$ |
| Supporting electrolyte | Tetrabutylammonium chloride (TBAC) | 0.1 mol $dm^{-3}$ |

mixture of DMF and ethanol was used as the organic solvent. The mixing of the Ti compound, supporting electrolyte, and organic solvent was handled in a dry-room (dew point < −50 °C, temperature: 20 °C). The bath composition is listed in Table 1.

### 2.3. Preparation of substrate

The preparation of the working electrode was conducted in the following steps: A micro slide glass (S1127, Matsunami Co., Ltd.) was cut to a size of 10 mm × 30 mm by a dicing saw (DAD 321, Disco Co., Ltd.). After a titanium adhesion layer with 20 nm thickness was sputtered on the slide glass, a platinum layer with 100 nm thickness was coated by a sputtering system (SPF430H, Anelva Co., Ltd.). Titanium plate (purity >99.5%) (Nilaco, Co., Ltd.) was used as the counter electrode and the reference electrode. Each of these electrodes was pretreated by electrolytic degreasing in the solution (EETOREX #12, EEJA Ltd.) and surface activation with 10% $H_2SO_4$ before electrochemical measurements.

### 2.4. Electrodeposition and annealing

The films were deposited with controlled-potential at −1.8 V (vs. Ti-reference), for 1 min with a potentiostat (VSP-300, BioLogic). This operation was conducted in an argon glove box ($O_2$ < 10 ppm, dew point < −25 °C, MDB-1B-NRA, MIWA MFG Co., Ltd.). The annealing of the electrodeposited samples was carried out at 600 °C for 1 h under air with a muffle furnace (KDF S-70, DENKEN-HIGHDENTAL Co., Ltd.). The heating rate of the furnace was set at 10 °C $min^{-1}$.

### 2.5. Characterization of film

The surface morphology of the deposited sample was observed by a field-emission scanning electron microscope (FE-SEM) (S4800, Hitachi, Ltd.), and the thickness was measured from a cross sectional SEM image (S4500, Hitachi, Ltd.). The chemical composition and crystal structure were investigated by X-ray photoelectron spectroscopy (XPS) (PHI-5000 Versa ProbeII, ULVAC-PHI Inc.) and X-ray diffraction (XRD) with Cu-Kα radiation (RINT-Ultima III, Rigaku Corp.), respectively. The

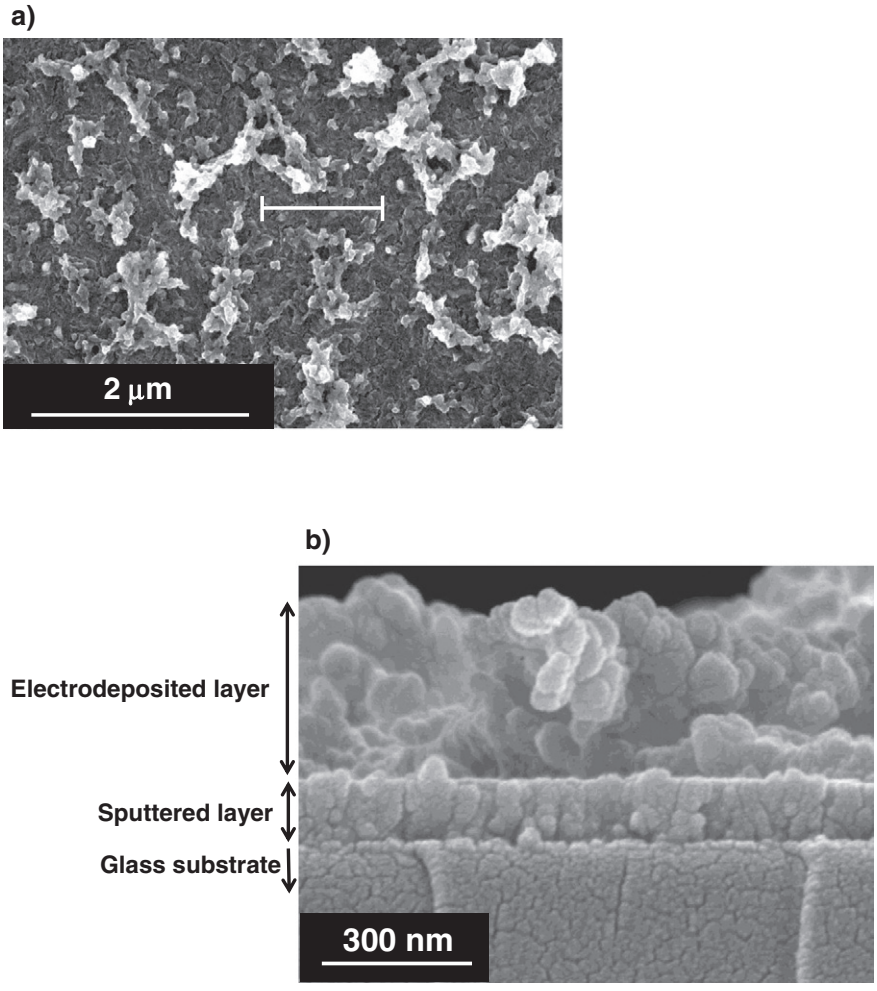


**Fig. 1.** FE-SEM images of the annealed sample. (a) Plan view, (b) cross-sectional view of the area of the H-shaped line in (a).The electrodeposition was operated at an electrode potential of −1.8 V vs. Ti for 1 min.

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