



A novel solution for cathodic deposition of porous TiO₂ films

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ABSTRACT

The redox reaction between TiCl₃ and NaNO₃ to form Ti(IV) and NO₂⁻ prior to deposition in a specially designed TiCl₃ + NaNO₃ solution is the key step effectively promoting the cathodic deposition of porous TiO₂ films. The continuous reduction of NO₂⁻ to N₂ and NH₃ generates extensive OH⁻, enhancing the deposition rate of TiO₂. The linear sweep voltammetric (LSV) and electrochemical quartz crystal microbalance (EQCM) studies reveal the electrocatalytic effect of oxy-hydroxyl-titanium already deposited onto the substrate for the NO₂⁻ and N₂ reduction. The porous and crystalline structures of as-deposited and annealed TiO₂ films are examined by field-emission scanning electron microscopic (FE-SEM), transmission electron microscopic (TEM) and selected area electron diffraction (SAED) analyses.

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1. Introduction

Titanium dioxide, also known as titania, is widely recognized as an important electrode material in semiconductor photo-electrochemistry. Among the three main crystalline phases: anatase, rutile, and brookite TiO₂, the anatase form (A-TiO₂) is the most popular photo-electrode because the lowest unoccupied molecular orbital of Ru-based dyes such as N719 is very close to the conduction band of A-TiO₂ [1,2]. In addition, A-TiO₂ generally shows relatively high reactivity and chemical stability under ultraviolet light excitation for water and air purifications, photocatalysts, gas sensors, electrochromic devices, and so on [3–5], further emphasizing its practical importance.

Several techniques were proposed for fabricating TiO₂, such as sol-gel, chemical vapor deposition, hydrothermal, electrospinning, anodizing, and electrodeposition [5–8]. Among these methods, electrodeposition of TiO₂ becomes attractive because electrochemical deposition displays the advantages of thickness and morphology control, by varying the electroplating parameters; relatively uniform deposits on complex shapes; and low cost of instruments [9]. Although both anodic and cathodic depositions have been employed to prepare TiO₂ films [10–20], there are few studies discussing the deposition mechanism.

This study shows the preliminary results on developing a newly designed solution containing TiCl₃ and NaNO₃ for cathodic deposition of porous TiO₂ films. The mechanism of this deposition process

is systematically investigated to allow facile control of the deposition of TiO₂ for future applications.

2. Experimental

Titania particulates are cathodically deposited onto graphite substrates from a simple deposition bath containing 0.47 M HCl, 25 mM TiCl₃ and 75 mM NaNO₃ in a three-compartment cell. The pretreatment procedure of graphite substrates completely followed our previous work [21]. An Ag/AgCl electrode (Argenthal) was used as the reference and a piece of platinum gauze was employed as the counter electrode. The open-circuit potential of this solution is about 0.63 V and the range for potentiodynamic deposition is between 0.63 V and –1.2 V at a scan rate of 50 mV s⁻¹ for 20 cycles. The electrodes were cleaned in an ultrasonic DI water bath and dried under a cool air flow. After cleaning and drying, some electrodes were annealed in air at 400 °C for 1 h.

The morphologies were examined by a FE-SEM (Hitachi S-4700I). The EQCM study was performed by an electrochemical analyzer, CHI 4051A (CH Instrument) in a one-compartment cell. The microstructure and SAED patterns of as-deposited and annealed TiO₂ deposits were observed through a TEM (FEI E.O Tecnai F20 G2). The depth profiles of Ti and O were measured by an X-ray photoelectron spectrometer (XPS, ULVAC-PHI Quantera SXM), which employed Al monochromator ($h\nu = 1486.69$ eV) irradiation as the photosource.

3. Results and discussion

Fig. 1 shows the redox reaction between TiCl₃ and NO₃⁻ during preparation of the deposition solution. Nitrates, acting as the

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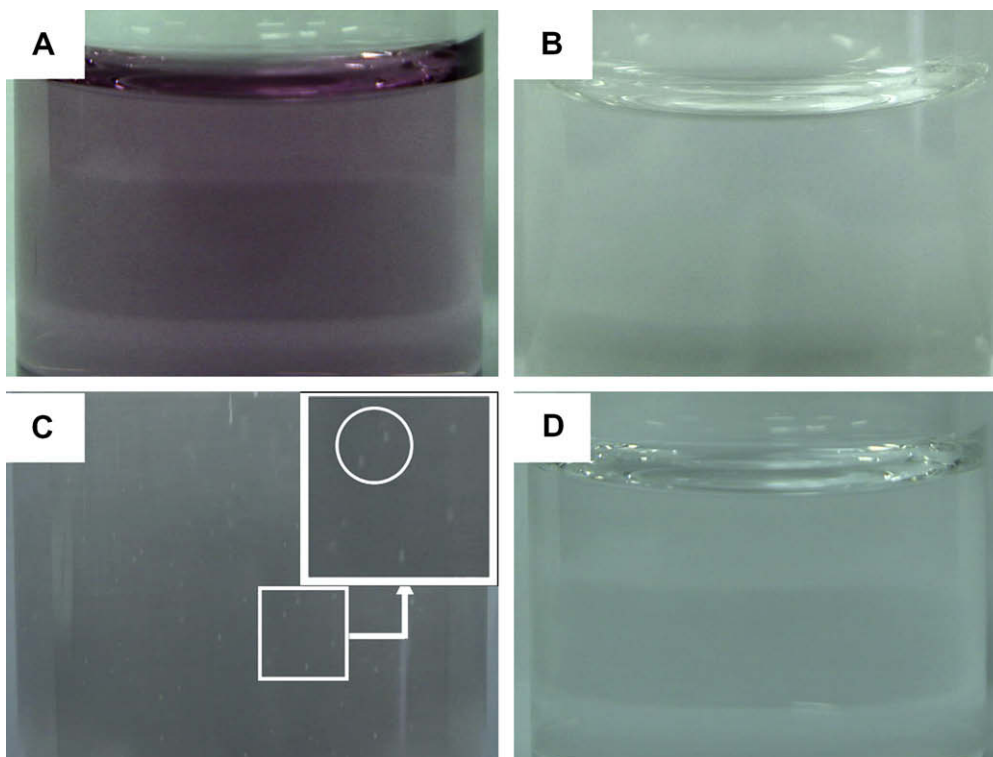


Fig. 1. Photographs of (A) TiCl₃, (B) NaNO₃, and a mixture of 25 mM TiCl₃ and 75 mM NaNO₃ at (C) 10 and (D) 40 s.

oxidizers, were reduced to NO₂ (see bubbles in Fig. 1C) when the transparent NaNO₃ solution (Fig. 1B) was added into the purple TiCl₃ solution (Fig. 1A). Since NO₂ molecules are soluble in aqueous media, they automatically convert into NO₃⁻ and NO₂⁻. This statement is supported by the observation that bubbles gradually disappear within 30–40 s and the purple TiCl₃ solution standing for the existence of Ti³⁺ became colorless transparent, representing the formation of TiO²⁺.



Curves 1–4 in Fig. 2 showing the *i*-*E* responses measured in various electrolytes are used to clarify the mechanism. On curves 1 (0.47 M HCl) and 2 (0.47 M HCl + 75 mM NaNO₃), reduction

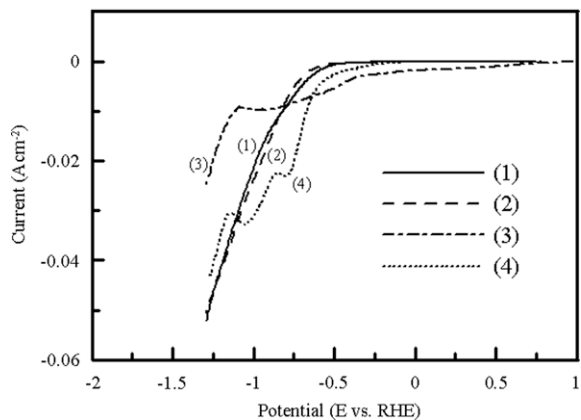


Fig. 2. LSV curves measured at 5 mV s⁻¹ from 1.0 V to -1.3 V in a solution containing (1) 0.47 M HCl, (2) 0.47 M HCl + 75 mM NaNO₃, (3) 0.47 M HCl + 75 mM NaNO₂ and (4) 0.47 M HCl + 25 mM TiCl₃ + 75 mM NaNO₃.

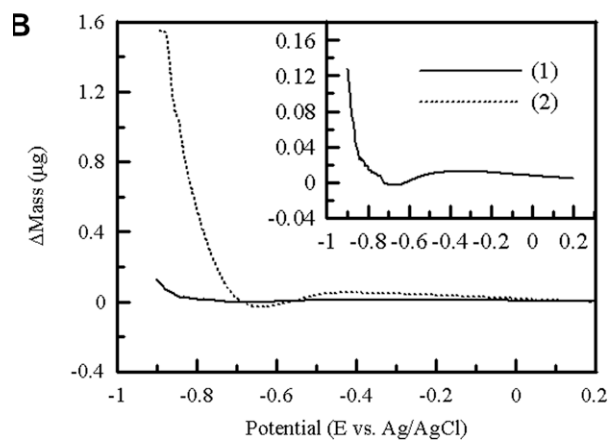
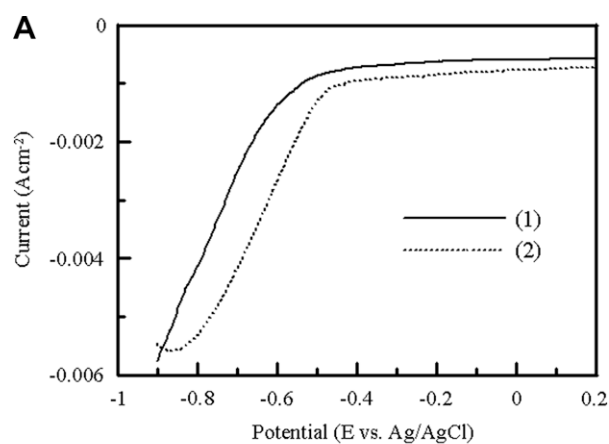


Fig. 3. (A) LSV and (B) EQCM curves measured at 5 mV s⁻¹ from 0.2 V to -0.9 V in a solution containing 0.47 M HCl + 25 mM TiCl₃ + 75 mM NaNO₃ for the (1) first and (2) second scans. Inset in (B) is the first scan.

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