Cathodic Electrodeposition of TiO_2 Thin Films for Dye-Sensitized Photoelectrochemical Applications

Subbian Karuppuchamy, Dinesh P. Amalnerkar, Koichi Yamaguchi, Tsukasa Yoshida, Takashi Sugiura, and Hideki Minoura*
Environmental and Renewable Energy Systems (ERES) Division, Graduate School of Engineering,
Gifu University, 1-1 Yanagido, Gifu 501-1193

(Received October 27, 2000; CL-000988)

A convenient – and quick to realize – approach for cathodic electrodeposition of TiO_2 films is suggested. Scanning electron microscopic examination of the resultant films reveals the formation of mesoporous TiO_2. Since dye-sensitized photoelectrochemical investigations on cathodically electrodeposited TiO_2 films are hitherto unreported, we performed such investigations by sensitizing our mesoporous TiO_2 films with *cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)bis(thiocyanato)ruthenium(II). The preliminary studies exhibit incident photon-to-current conversion efficiency (IPCE) above 35% in the first attempt.

We are witnessing resurgence of wide band-gap semiconductor–photoelectrochemistry [especially pertaining to TiO_2 and ZnO] after Grätzel and coworkers[1] announced a highly efficient solar cell based on the remarkably efficient photo-induced charge separation at the dye-sensitized porous nanocrystalline TiO_2 electrodes. Although 'nano' colloidal coating of such semiconductors is the most popular method adopted in producing dye-sensitized solar cells,[2–4] the other methods like electrophoretic deposition,[5] sputter deposition,[6,7] electrochemical deposition,[8–14] etc. were also exploited for this purpose. Electrochemical deposition of wide band gap semiconductor films is of specific interest to us[10–14] in view of its inherent advantages such as (i) simplicity and economy, (ii) rigid control on film thickness, uniformity and deposition rate, and (iii) possibility of deposition on substrates of complex shape. It may be further noted that there are ample reports dealing with cathodic electrodeposition of ZnO for usage in dye-sensitized photoelectrochemical cells.[9–14] The electrodeposited ZnO thin films have been recently reported to exhibit a superior performance than the colloid-processed TiO_2 films when used in solid-state dye-sensitized solar cells in combination with p-CuSCN hole transporting layer.[9] However, cathodic electrodeposition of TiO_2 from aqueous solutions is rarely reported in the literature. In an only report available, Natarajan and Nogami[15] have described preparation of nanocrystalline TiO_2 thin films by two-stage process comprising of (i) cathodic electrodeposition of titanium oxyhydroxide gel film from an aqueous solution containing a Ti precursor, and (ii) subsequent heat-treatment of the resultant gel film to realize the formation of TiO_2 film. However, it is opined that preparation of Ti precursor [$TiOSO_4$] solution adopted by Natarajan and Nogami[15] is rather tedious and time-consuming. In order to simplify this process and, in turn, to reduce the preparation "downtime", we thought it would be interesting to directly use commercially available titanium(IV) oxide sulfate [$TiOSO_4$] as a requisite precursor. Indeed, we could succeed in such an attempt, which undoubtedly has certain processing advantages. Besides, dye-sensitized photoelectrochemical investigations on cathodically electrodeposited TiO_2 films have not been reported to the best of our knowledge. In this letter, (i) we propose a convenient approach for relatively quick realization of cathodic electrodeposition of TiO_2, and (ii) report, in our most preliminary studies, IPCE value of 37.3% for the resultant TiO_2 electrodes sensitized with *cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)bis(thiocyanato)ruthenium(II) to be denoted as N3 dye.

By and large, we have followed the preparation conditions reported by Natarajan and Nogami[15] for cathodic electrodeposition of TiO_2 films with the exception of directly using the commercially available hydrated salt of $TiOSO_4$ as starting material [obtained from Nacalai tesque Co. Ltd] instead of synthesizing the same by using Ti powder. A conventional three-electrode single compartment cell was used with an ITO coated glass as a working electrode, a Pt foil as a counter electrode and an SCE as a reference electrode. The deposition bath consisted of an aqueous solution of $TiOSO_4$, H_2O_2, HNO_3 and supporting salt KNO_3 each in concentration range as indicated by Natarajan and Nogami.[15] Cathodic electrodeposition was carried out in the potential range between –0.9 to –1.2 V (vs SCE) which led to the formation of $TiO(OH)_2 \cdot xH_2O$ gel film on the ITO electrode. Subsequently, this gel was subjected to heat-treatment at 400 °C for 1 h in air to obtain TiO_2 thin film. The resultant films were characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM).

The as-deposited film was found to be X-ray amorphous. Figure 1 shows a typical XRD pattern of cathodically electrodeposited and heat-treated sample. It confirms the formation of anatase TiO_2. The average crystallite size is found to be about 25 nm as estimated from Scherrer's method by using XRD data. Figure 2 presents a typical SEM photomicrograph of the TiO_2 thin film. It reveals morphological homogeneity with the grain size falling mostly in the submicron range. Careful examina-

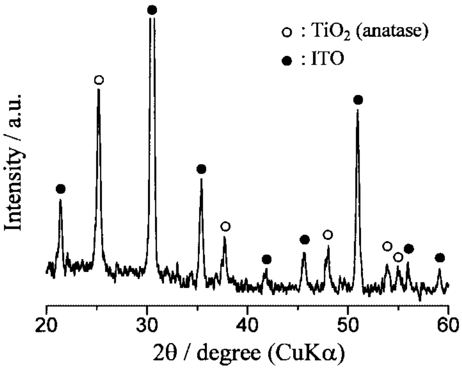

Figure 1. Typical X-ray diffractogram of TiO_2 thin film cathodically electrodeposited at –1.1 V (vs SCE) from an aqueous solution containing 0.02 M $TiOSO_4$, 0.03 M H_2O_2, and 0.01 M HNO_3, and subsequently heat-treated at 400 °C for 1 h.

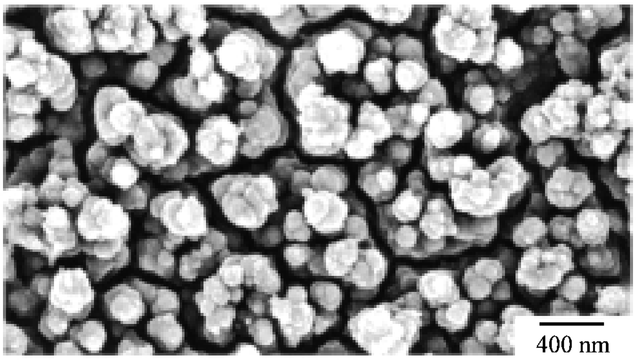

Figure 2. SEM photograph of the TiO_2 film same as that in Figure 1.

tion of SEM picture clearly evinces that each grain is made up with an aggregation of very small (nano-meter size) crystallites. The estimated crystallite size of 25 nm also supports this observation. The aggregates also tend to indicate cauliflower type of morphological features. This film has more open structure and higher crystallinity compared to that made by Natarajan and Nogami.[15] A film thickness of 1.2 μm was measured after the heat treatment.

For dye-sensitized photoelectrochemical investigations on our electrodeposited TiO_2 thin films, we preferred to use N3 dye in view of its known effective performance.[2] Sample films of TiO_2 were, thus, immersed in an ethanolic solution of N3 dye [concentration of ca. 0.5 mM] for 12 h at room temperature. The photoelectrochemical investigations were performed on such N3 dye modified TiO_2 electrodes in a three-electrode setup. Visible light illumination [> 420 nm, 20 mW cm^{-2}] of the dye-modified TiO_2 electrode at +70 mV (vs SCE) in ethylene carbonate/acetonitrile [v/v = 1/4] containing I^-/I_3^- redox electrolyte generated anodic photocurrent of ca. 1.7 mA/cm^2. The photocurrent action spectrum recorded is presented in Figure 3 along with pertinent absorption spectra of the bare and dye-modified TiO_2 electrodes. Close agreement between action and absorption spectra of the dye-modified film is clearly noticed. The maximum IPCE value of 37.3% is achieved at the absorption maximum of the loaded N3 dye (ca. 520 nm). The insufficient efficiency of the present material could be partly due to the low amount of dye in the film. The loaded dye in the present case was indeed much lower (5.25×10^{-9} mol/cm^2) than the optimum value (exceeding 1×10^{-7} mol/cm^2),[2] which is attributable to the low surface area of our films. When the fraction of incident photons absorbed by the dye is calculated from the difference in absorbance at 520 nm between the bare TiO_2 film (curve c) and the dye-modified one (curve b), the absorbed photon-to-current conversion efficiency (APCE)[16] was estimated to be ca. 62%, showing rather high efficiency of separation and collection of charge in the present material. Further investigations to improve the photoelectrochemical performance of the electrodeposited TiO_2 are under way in the directions such as (i) optimization of the electrolyte composition including the choice of the iodide salt, additives and solvent, (ii) enhancement of the dye loading by modifying the adsorption method including the surface treatment of TiO_2 and by increasing surface area of the TiO_2 film which, in turn, can be controlled by deposition potential and/or heat-treatment details, and (iii) improvement in the overall electrical conductivity of the TiO_2 film by fine-tuning the deposition conditions and heat treatment as well as by chemical doping of TiO_2 during the electrodeposition.

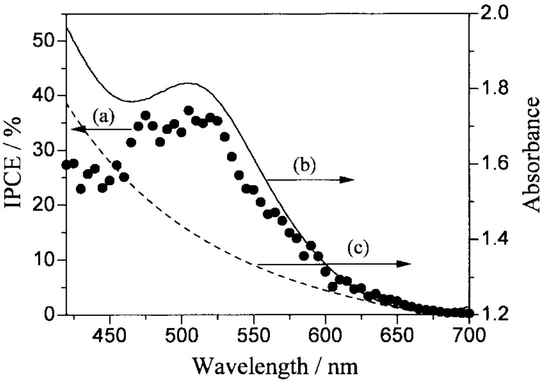

Figure 3. Photocurrent action spectrum (curve a) at the electrodeposited TiO_2 thin film electrode sensitized with N3 dye measured in an ethylene carbonate/acetonitrile (v/v = 4/1) containing 0.5 M KI and 0.03 M I_2 under monochromatic light illumination, in comparison with its absorption spectrum (curve b). The absorption spectrum of the bare TiO_2 film (curve c) is also shown for comparison.

The present work is partly defrayed by the Grant-in-Aid for Scientific Research on Priority-Area-Research “Electrochemistry of Ordered Interfaces” from the Ministry of Education, Science, Sports and Culture of Japan (09237105). S. K. wishes to thank the Ministry of Education, Science, Sports, and Culture for the award of a research scholarship. D. P. A. gratefully acknowledges the generous financial support extended by AIEJ for his stay at Gifu University. K. Y. is grateful to JSPS Research Fellowship for Young Scientists. We are deeply indebted to Dr. C. Natarajan (Osaka Gas Co., Ltd.) for many useful hints.

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