Dye-sensitized solar cells (DSCs) capable of converting light to electricity are attracting widespread interest over the past decade due to their high efficiency, simplicity, and low fabrication cost. In DSCs, the photoanode comprises a dye-sensitized TiO₂ thick film coated on the fluorine-doped tin oxide (FTO) glass. The nanocrystalline TiO₂ film with interconnected mesoporous structure is required to increase the adsorption amount of molecular dye and facilitate the transport of electrons and electrolyte. A counter electrode with platinum layer serves as the cathode. The electrolyte is an iodide/triodide (I⁻/I³⁻) redox couple in an organic solvent or ionic liquid.

There are several ways to enhance the photovoltaic properties of DSCs. A known method is to reduce the charge recombination reaction. The charge recombination is an important loss (back-reaction) in DSCs resulting from the transfer of electrons from the FTO substrate to I₃⁻ ions in electrolyte. The charge recombination can be significantly suppressed by introducing a thin blocking layer, also called a compact layer. Metal oxide layers such as TiO₂, Nb-doped TiO₂, Nb₂O₅, and Al₂O₃ were reported to have a positive effect on the mitigation of the charge recombination. Among them, the compact TiO₂ layer is the most suitable candidate as the effective blocking layer. The TiO₂ blocking layers can be prepared by spray pyrolysis, hydrolysis of TiCl₄ aqueous solution, sputtering, dip-coating, spin-coating, doctor-blade coating, electrochemical deposition, and atomic layer deposition. Several other approaches have also been proposed to decrease the dark current and the recombination phenomena in DSCs such as the use of a UV post-treatment, a fine tuning of the electrolyte composition, and the use of a core-shell structure.

Generally, the photovoltaic properties of the DSCs with blocking layers are strongly influenced by the preparation approaches. The electrochemical deposition technique has some advantages over the others: structure and thickness of the film can be easily varied by controlling the depositing parameters like voltage, current, temperature, and bath composition.

The electrical contact between the thick TiO₂ layer and FTO substrate also plays an important role in enhancing the photovoltaic properties of the DSCs. A thin oxide layer coated on the FTO substrate was found to reduce the contact resistance due to the enhanced adhesion of main thick TiO₂ layer to FTO substrate. Therefore, we expect that a thin TiO₂ film consisting of a blocking layer (compact layer) and an anchoring layer (loose layer) may help to increase the photovoltaic properties of the DSC as revealed in Figure 1. In a previous communication, we verified that a thin bifunctional TiO₂ film having inner compact layer and outer anchoring layer coated on FTO glass could reduce the charge recombination and interfacial contact resistance between FTO and main TiO₂ layer. The photoelectron conversion efficiency (η) of dye-sensitized solar cell (DSC) using TiO₂-coated FTO deposited at 10 μA cm⁻² was 6.9%, which is higher than that of DSC using bare FTO (6.5%). The outer anchoring layer composed of nanorods deposited at 5 μA cm⁻² could significantly reduce the interfacial contact resistance between FTO and main TiO₂ layer. Therefore, η of DSC was further increased to 7.1% after applying the TiO₂-coated FTO deposited at 5 μA cm⁻².
substances. The TiO$_2$ paste used for photoanodes was in-house made by Tripod Technology. The prepared TiO$_2$ photoanodes were annealed at 450°C for 1 h in air. The thickness of resultant TiO$_2$ films was approximately 15 μm measured by the profiler. The adsorption of dye on the TiO$_2$ surface was carried out by soaking the TiO$_2$ electrodes in a dry ethanol solution of N719 dye (3 x 10$^{-4}$ mol L$^{-1}$, C$_6$H$_4$(N$_2$O)$_2$N$_2$S$_2$(Ru) at room temperature for 12 h. To obtain information on dye loading, dye desorption experiments were carried out by immersing dye-sensitized TiO$_2$ photoanodes in 10 ml of 0.1 M NaOH for 1 h followed by UV-visible absorbance measurements. The amount of dye after sensitization was measured to be approximately 8.5 μg L$^{-1}$. In this work, we used a two-step dip coating process to prepare a nanocluster Pt counter-electrode and the detailed procedure was described in a previous publication.

A dye-coated photoanode was assembled with a counter-electrode by using a sealing plastic (25 μm, SX-1170-25, Soralonix) to form a sandwich-type DSC. An electrolyte containing 0.6 mol L$^{-1}$ DMPH (1-propyl-2,3-dimethylimidazolium iodide), 0.1 mol L$^{-1}$ LiI (lithium iodide), 0.05 mol L$^{-1}$ iodine, and 0.5 mol L$^{-1}$ TBP (4-tert-butylpyridine) in MPN (3-methoxypropionitrile) solvent was then infiltrated into voids between the two electrodes of the cell. The active area of DSCs was 0.283 cm$^2$. The photovoltaic properties of the DSCs were carried out by scanning DSCs from the open-circuit voltage ($V_{oc}$) of the cell to the short-circuit condition ($V_{sc}$) at a scan rate of 5 mV s$^{-1}$ with a source meter (Keithley 2400) under one-sun illumination (AM1.5, 100 mW cm$^{-2}$) by an Xe solar simulator (Yamashita Denso, YSS-E40). Electrochemical impedance measurement was carried out at open-circuit voltage under one-sun illumination using a potentiostat/galvanostat (Eco Chemie, Autolab PGSTAT 10) with ac amplitude of 5 mV at a frequency range of 0.1–5 x 10$^4$ Hz.

Results and Discussion

The surface morphology of the electrodeposited TiO$_2$ film, which can be varied by tuning the current density during deposition, may affect the photovoltaic properties of the DSCS. Figure 2 shows the SEM images of the TiO$_2$ coated FTO substrates deposited at various current densities. The charge passed for both films deposited at 5 μA cm$^{-2}$ and 10 μA cm$^{-2}$ was set at 0.52 C cm$^{-2}$. Both films were annealed at 450°C for 1 h prior to the SEM observations. The bare FTO surface, which is not shown here, is composed of tin oxide crystals whose particles are around 150-300 nm in size. As can be seen from Figure 2, thin TiO$_2$ film can be homogeneously coated on the tin oxide crystals by means of the anodic electrodeposition technique. A thin TiO$_2$ film deposited at 10 μA cm$^{-2}$ shows a compact film morphology composed of granular nanoparticles, while that deposited at 5 μA cm$^{-2}$ shows a less compact film composed of short nanorods having diameter less than 15 nm. Interestingly, the cross-sectional SEM images of films reveal that both electrodeposited TiO$_2$ films are structurally more compact near the FTO surface, and become less compact further away from the surface. The film thickness for both deposited thin TiO$_2$ films was estimated to be approximately 30-50 nm from the cross-sectional SEM image (the inset of Figure 2). In general, the film thickness can be readily increased by increasing the charge passed. However, a thick compact film (underlayer) coated on the FTO substrate may decrease the optical transmittance and sheet conductivity of the FTO substrate.

A progressive change in film structure might result from the variation in voltage during galvanostatic deposition. Figure 3 shows the variation in voltage associated with time in the first 300 s during galvanostatic deposition of TiO$_2$ films at 5 and 10 μA cm$^{-2}$. Both films have a similar trend of variation in voltage during deposition. At the beginning of galvanostatic deposition, the voltage decreases and then stabilizes in the succeeding deposition. It is generally believed that the nucleation extremely depends on the overvoltage during electrochemical deposition. An increase in the overvoltage leads to an...
serve as an anchoring layer to improve the electrical contact between FTO and the main TiO₂ layer. Therefore, the DSC with TiO₂-coated FTO substrates showed better photovoltaic properties than the DSC with bare FTO substrate. On the other hand, a loose outer layer composed of nanorods could provide a superior semitransparency and a better electrical contact between FTO and main TiO₂ layer. The photovoltaic properties of a cell with thin TiO₂ film deposited at a lower current density of 5 μA cm⁻² was, therefore, superior to those of cell with thin TiO₂ film deposited at a higher current density of 10 μA cm⁻².

Acknowledgment

The authors gratefully acknowledge the financial support from the National Science Council, Taiwan, Republic of China (Project No: NSC 100-2221-E-151-059).

References