

## Photovoltaic Performance of a Novel TiO<sub>2</sub> Electrode Consisting of a Mesoporous TiO<sub>2</sub> Layer and a Compact TiO<sub>2</sub> Blocking Layer for Dye-Sensitized Solar Cells

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**Abstract**—A double-layered TiO<sub>2</sub> photoelectrode consisting of a compact TiO<sub>2</sub> film as an electrolyte-blocking layer and a mesoporous TiO<sub>2</sub> as a dye-adsorbed layer was prepared using the sputtering and a doctor-blade methods. The compact TiO<sub>2</sub> blocking layer was deposited onto a transparent conducting oxide (TCO) substrate by reactive sputtering. Then, anatase mesoporous TiO<sub>2</sub> was synthesized by means of a surfactant-assisted sol-gel process. Comparison of the photovoltaic performances of the obtained solar cells (DSSCs) disclosed that the cells with a sputtering layer had higher conversion efficiencies than those without such a layer. Solar cells containing double-layered TiO<sub>2</sub> electrodes exhibited a higher efficiency (3.15%) relative to conventional cells composed of TiO<sub>2</sub> nanoparticles (1.75%). This behavior may result from the fact that mesoporous TiO<sub>2</sub>-based double layer has a higher surface area (304 m<sup>2</sup>g<sup>-1</sup>), thus leading to an increase in the amount of dye adsorbed, which in turn enhances the photocurrent. In addition, it is expected that the compact structure of the blocking layer manufactured using the sputtering process will prevent electron recombination at the TCO.

**Keywords**—Dye-sensitized solar cells; Double-layered structure; Electrolyte blocking layer; mesoporous TiO<sub>2</sub>

### I. INTRODUCTION

Since the first report on a low-cost dye-sensitized solar cell (DSSC) in 1991 by Grätzel and O'Regan [1], this type of device has been regarded as a promising candidate for next-generation solar cells. Research on the preparation of TiO<sub>2</sub> electrodes has been widely carried out. For DSSCs, such electrodes must have an extremely high surface area so that the dye molecule can be sufficiently adsorbed, thereby resulting in the generation of a high photocurrent. However, conventional TiO<sub>2</sub> particle layers provide an insufficient physical surface area per unit area (< 100 m<sup>2</sup>g<sup>-1</sup>), rendering low light harvesting by the monolayer of adsorbed dye on the TiO<sub>2</sub> surface. Recently, great attention has been dedicated to the study of mesoporous TiO<sub>2</sub> to address this problem. The application of such electrodes to solar cells has been found to be effective, and, it is known that a mesoporous TiO<sub>2</sub> layer displays a high specific surface area of over 400 m<sup>2</sup>g<sup>-1</sup> before calcination. However, the surface area can be reduced to about 173 m<sup>2</sup>g<sup>-1</sup> after calcination [2]. In the case of DSSCs, high-temperature sintering is necessary to remove organic binders and promote TiO<sub>2</sub> crystal growth. Therefore,

studies to maintain the high specific area of mesoporous TiO<sub>2</sub> after sintering are required to maximize the effect of the mesoporous structure.

In addition to the surface-area problem of conventional mesoporous TiO<sub>2</sub> electrodes, charge-recombination processes at the interface between the TCO and the TiO<sub>2</sub> layers have limited the enhancement of the photon-to-electron conversion efficiency [3, 4]. Much effort has been devoted to fabricating a compact TiO<sub>2</sub> film that can be used as a blocking layer to impede electrolyte invasion. Ito et al. reported the preparation of a compact TiO<sub>2</sub> blocking layer by the spray pyrolysis. However, this layer was unable to completely stop the electrolyte invasion because the film was not dense enough [5]. In another study, Yanagida et al. reported the preparation of a compact TiO<sub>2</sub> blocking layer obtained by depositing metallic Ti through the sputtering method and then oxidizing it by annealing on the surface [6]. However, this layer also failed to achieve a high performance due to a delicate crystal phase and a defective oxide film.

Recently, several reports on double-layered TiO<sub>2</sub> electrodes have been published. Some of these studies describe the preparation of high-performance double-layered TiO<sub>2</sub> DSSC electrodes [7, 8]. It has been reported that DSSCs consisting of various layers with different particle sizes exhibit a high efficiency.

To the best of our knowledge, no reports exist so far on the preparation of a double-layered TiO<sub>2</sub> electrode composed of a compact electrolyte blocking layer (prepared by using reactive sputtering) and a mesoporous TiO<sub>2</sub> electrode with high specific area after sintering.

In this present study, we prepared a double-layered TiO<sub>2</sub> electrode for DSSCs, which is composed of a mesoporous TiO<sub>2</sub> film with an extremely high specific surface area after calcination (used as a dye adsorbed layer), and a sputtered TiO<sub>2</sub> film (used as electrolyte-blocking layer). To investigate the effect of the double-layered electrode on the performance of the solar cells, we compared the solar conversion efficiency of DSSCs composed of single- and double-layered electrodes. We also investigated the conversion efficiency of the cells using conventional P25 electrodes as a standard.

### II. EXPERIMENTAL

#### A. Preparation of the TiO<sub>2</sub> Blocking Layer

A schematic diagram of the experimental apparatus has been published previously [9]. The TiO<sub>2</sub> blocking layer was

deposited onto a fluorine-doped tin oxide (FTO) glass by reactive inductively coupled plasma (ICP) assisted DC magnetron sputtering of the Ti target. Details of the sputtering parameters are described elsewhere [10]. The deposition time was 30 min with a rate of about 30 nm/min.

### B. Maintaining the Integrity of the Specifications

Titanium isopropoxide [ $\text{Ti}(\text{O}^i\text{Pr})_4$ , 97%, Aldrich], the triblock copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ,  $M = 5800$ , Aldrich) and 2,4-pentandione ( $\geq 99\%$ , Aldrich) were used without purification. After dissolving the triblock copolymer (used as a surfactant) in deionized water at 40 °C, sulfuric acid was added to the mixture. Then, titanium isopropoxide, chelated with 2,4-pentandione, was slowly added (dropwise) to the surfactant solution using a magnetic stirrer. This solution was first kept at 50 °C, and then the hydrothermally treated at 90 °C for 12 h.

A coating paste was prepared by mixing mesoporous  $\text{TiO}_2$  colloid, polyethylene glycol (PEG, Aldrich) and polyethylene oxide (PEO, Aldrich), whereby PEG and PEO were used as thickeners. The mesoporous  $\text{TiO}_2$  layer was deposited by using the doctor-blade technique on an FTO glass. For comparison, a traditional P25 film was also prepared by using the one-shot doctor-blade technique.

### C. Solar-Cell Fabrication

Prior to the adsorption of the dye, the  $\text{TiO}_2$  films were heated at 450 °C for 20 min and then immersed overnight at 80 °C in an ethanolic solution containing the ruthenium sensitizer dye  $\text{RuL}_2(\text{NCS})_2$  ( $L = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid,  $3 \times 10^{-4}$  M). The counter electrode was prepared by coating an FTO glass with a thin layer of 5 mM solution of  $\text{H}_2\text{PtCl}_6$  in isopropanol. The electrolyte (1-hexyl-2,3-dimethyl-imidazolium ( $\text{C}_6\text{DMI}$ ), 0.6 M), iodine ( $\text{I}_2$ , 0.05 M), lithium iodide ( $\text{LiI}$ , 0.1 M), and 4-tert-butylpyridine (0.5 M) in 3-methoxyacetonitrile were injected through a hole into the counter electrode.

### D. Electrodes and Photovoltaic Characterization

The primary particle size of the mesoporous  $\text{TiO}_2$  colloids was investigated by means of field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6330F) and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2000 FX II).

The electrode microstructures were studied using FE-SEM, and the crystal structures of the mesoporous and blocking layers were determined by wide-angle X-ray diffraction (XRD, MAC/Sci. MXP 18XHF-22SRA with  $\text{CuK}\alpha$  radiation) at room temperature. An accelerating voltage of 50 kV and an emission current of 100 mA were used. The surface area of the mesoporous  $\text{TiO}_2$  layer was determined via nitrogen adsorption and desorption isotherms were obtained at 77 K using Micrometrics ASAP 2000 equipment. All the materials were degassed at 200 °C and  $10^{-6}$  Torr for 6 h. The optical transmittance of the  $\text{TiO}_2$  blocking layer deposited with ICP was determined by using an ultraviolet-visible (UV/Vis) spectroscopy.

To measure the amount of dye adsorbed on the photo-electrodes, molecules of the dye were desorbed from the surface using a 0.1 M NaOH solution in water and ethanol (50:50, v/v). The absorption spectra of the solution were detected using a UV/Vis spectrometer [30].

The photovoltaic properties of the solar cells were determined using a Keithley 2400 source measuring unit. An Xe lamp (Oriel, 300 W) served as the light source and its light intensity was adjusted with an Si reference solar equipped with a KG-5 filter (Fraunhofer Institute, Germany) for an approximately AM-1.5 radiation, which corresponds to a solar elevation of 42° to the horizon. All samples were measured under global AM-1.5, 100  $\text{mW}/\text{cm}^2$  irradiation.

## III. RESULTS AND DISCUSSION

### A. Characterization of the Blocking Layer

Fig 1 shows the XRD pattern of a  $\text{TiO}_2$  blocking layer prepared by an ICP assisted DC magnetron sputtering. It can be seen that a crystalline anatase phase was obtained, even on the non-heated substrate. The high-density plasma contributed to the crystal formation without the need for substrate heating [10]. The preparation of an anatase mono crystalline phase without further heating is expected to minimize the adhesion problem when coating a working electrode of anatase phase on the blocking layer. The thickness of the film was 1  $\mu\text{m}$ , as measured using an  $\alpha$ -step profiler.

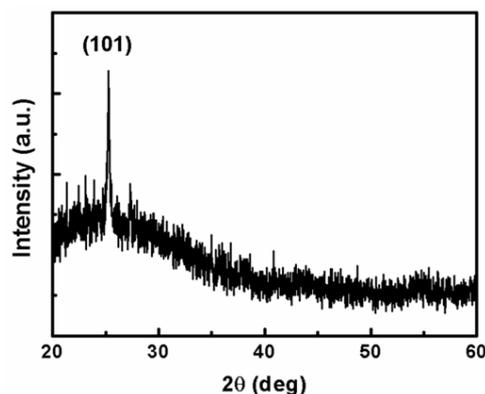


Figure 1. XRD patterns of the  $\text{TiO}_2$  blocking layer

In addition, the sputtered  $\text{TiO}_2$  blocking layer showed a high visible-light transmittance (ca. 80%), as shown in Fig. 2. The optical transmittance response was much greater than that obtained with a P25 film of the same thickness which had a visible light transmittance of 20%. Thus, we expect that sputtered  $\text{TiO}_2$  film can be used as a high-performance blocking layer, because the light is able to reach the dye adsorbed on the working electrode without any loss. As far as DSSC fabrication is concerned, ICP assisted DC magnetron sputtering it is very important for deposit formation.

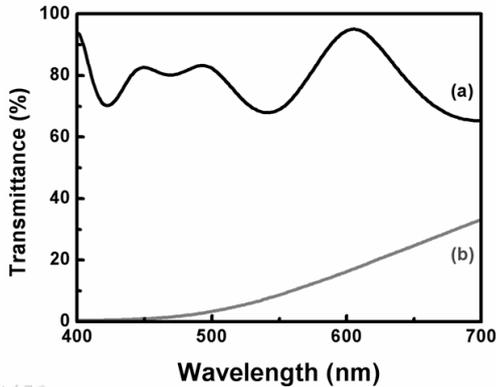


Figure 2. Visible light transmittance of (a) the TiO<sub>2</sub> blocking layer prepared by sputtering and (b) traditional P25 film

### B. Characterization of the Mesoporous TiO<sub>2</sub> Layer

Fig. 3 illustrates the FE-SEM image of a mesoporous TiO<sub>2</sub> film. It can be seen that this film exhibits a uniform and crack-free surface morphology, and from the  $\alpha$ -step measurements, it was confirmed that the thickness of the sample was about 4  $\mu\text{m}$ .

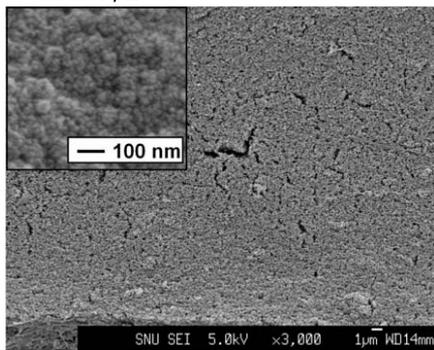


Figure 3. FE-SEM image of the mesoporous TiO<sub>2</sub> film

Fig. 4 shows XRD patterns of mesoporous TiO<sub>2</sub> before and after calcination. Although no calcination process was applied to the mesoporous materials, relatively broad diffraction peaks of the anatase structures appeared in the mesoporous TiO<sub>2</sub> [identified by the (101) peak at  $2\theta = 25.2^\circ$ ]. This result implies that the amorphous phase of mesoporous TiO<sub>2</sub> was converted into an anatase phase through the hydrothermal treatment. Previous work in our laboratory has demonstrated that the hydrothermal treatment is a critical factor in the formation of the anatase structure in the absence of calcination [11]. As shown in Fig. 4, no phase transformations occurred in the mesoporous TiO<sub>2</sub> during sintering at 500  $^\circ\text{C}$ .

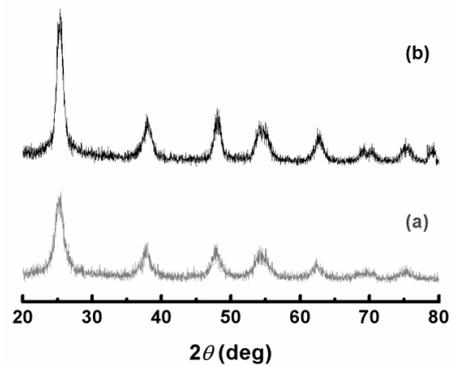


Figure 4. XRD patterns of the mesoporous TiO<sub>2</sub> (a) before and (b) after calcination

The specific area was analyzed before and after sintering, by means of N<sub>2</sub> adsorption-desorption analysis, to confirm the formation of the mesoporous TiO<sub>2</sub> film. As shown in Fig. 5 (a), the mesoporous TiO<sub>2</sub> sample exhibited the classical type-IV behavior with H<sub>2</sub> hysteresis between the adsorption-desorption curves. This is the characteristic behavior of a mesoporous material according to the IUPAC classification. A type H<sub>2</sub> hysteresis loop is commonly associated with a wormhole-like framework mesostructure or ink-bottle pores between close-packed spherical particles [12]. We expected that each wormhole-like pore of the mesoporous TiO<sub>2</sub> film will not be blocked up but linked to another one, so that dye molecules are readily adsorbed between the pores and the electrolyte can easily permeate into those pores.

As shown in Table 1, the mesoporous TiO<sub>2</sub> layer maintains the pores and its specific area (304 m<sup>2</sup>g<sup>-1</sup>) even after sintering. A much higher value of the specific area was obtained in this case relative to a P25 film with 80 m<sup>2</sup>g<sup>-1</sup> [Fig. 5 (b), Table 1]. This result indicates that the mesoporous TiO<sub>2</sub> photoelectrode should provide a larger sensitizer surface coverage compared to traditional TiO<sub>2</sub> nanoparticle electrodes.

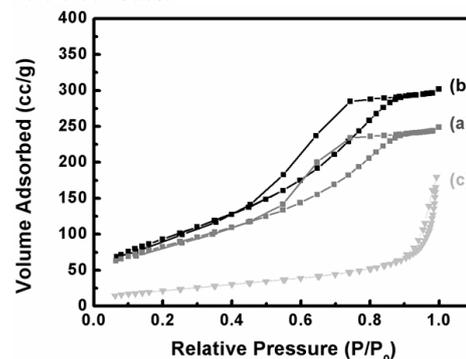


Figure 5. N<sub>2</sub> adsorption-desorption isotherms of the mesoporous TiO<sub>2</sub> (a) before and (b) after calcination, and (c) P25

TABLE I. SURFACE AREA AND PORE SIZE OF MESOPOROUS TiO<sub>2</sub> BEFORE AND AFTER CALCINATION, AND P25

		Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore size (nm)
Mesoporous TiO <sub>2</sub>	Before calcination	347	3.9
	After calcination	304	11.5
P25		80	10.6

### C. Photovoltaic Performance of Double-Layered TiO<sub>2</sub>

The photocurrent density-potential curves ( $J$ - $V$ ) obtained under AM 1.5 light intensities for the DSSCs assembled with the mesoporous TiO<sub>2</sub> electrode are presented in Fig. 6. The electrical parameters are summarized in Table II. For comparison, a DSSC composed of standard titania nanoparticles (Degussa P25) was also assembled. We found that the DSSC containing the mesoporous TiO<sub>2</sub> electrode had a significantly higher short-circuit photocurrent ( $J_{sc}$ ) as compared to a cell containing a P25 electrode of the same thickness. The photocurrent that is generated by a DSSC is directly related to the number of dye molecules that are absorbed on the TiO<sub>2</sub> electrode. Therefore, the greater the surface area, the larger the amount of photocurrent produced by the mesoporous-TiO<sub>2</sub> based DSSC. In addition, the porous structure of mesoporous TiO<sub>2</sub> allows the efficient penetration of the electrolyte. As a result, the solar-energy conversion efficiency of mesoporous TiO<sub>2</sub>-based DSSCs is higher than that of P25-based DSSCs for a comparable film thickness.

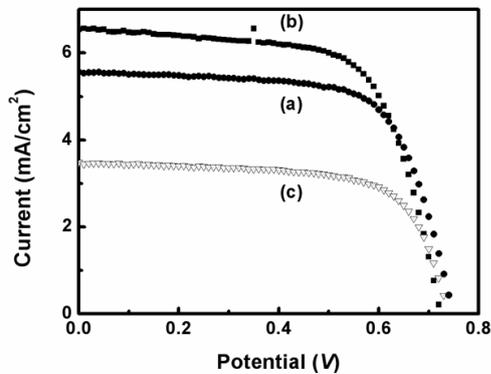


Figure 6. Photocurrent density-voltage ( $J$ - $V$ ) curves of DSSC with (a) single-layered mesoporous TiO<sub>2</sub> electrode, (b) double-layered TiO<sub>2</sub> electrode, and (c) single-layered traditional P25 electrode

In the case of double-layered TiO<sub>2</sub> prepared by coating a mesoporous TiO<sub>2</sub> layer onto a sputtered TiO<sub>2</sub> blocking layer, a solar conversion efficiency of 3.15% is finally obtained, as shown in Fig. 6. The short-circuit photocurrent ( $J_{sc}$ ) and open-circuit voltage ( $V_{oc}$ ) were 6.54 mA/cm<sup>2</sup> and 0.723 V, respectively. Such an electrode can improve the  $J_{sc}$  without lowering the  $V_{oc}$  in DSSCs with an 80% improvement of the conversion efficiency compared to P25-electrode-based cells. The sputtered TiO<sub>2</sub> layer has a denser structure compared to a nanoparticle layer of the same thickness. Hence, we believe that the sputtered TiO<sub>2</sub> layer is able to efficiently hinder the

electrolyte invasion. In addition, the sputtered layer can be used as a blocking layer without loss of light-harvesting efficiency because it has a high visible transmittance. Next, the mesoporous TiO<sub>2</sub> layer is able to adsorb more dye molecules than the conventional TiO<sub>2</sub> layer, which leads to a higher short-circuit current. Accordingly, the double-layered TiO<sub>2</sub> electrode causes an increase of the photocurrent without loss of photovoltage due to a high adsorption capacity of dye molecules and electrolyte blocking.

TABLE II.  $J$ - $V$  CHARACTERISTICS OF DSSC WITH A SINGLE-LAYERED MESOPOROUS TiO<sub>2</sub> ELECTRODE, A DOUBLE-LAYERED TiO<sub>2</sub> ELECTRODE, AND A SINGLE-LAYERED P25 ELECTRODE

	Sample		
	Single-layered mesoporous TiO <sub>2</sub>	Double-layered mesoporous TiO <sub>2</sub>	Single-layered P25
$V_{oc}$ (V)	0.75	0.72	0.74
$J_{sc}$ (mA cm <sup>-2</sup> )	5.57	6.54	3.49
FF	0.68	0.67	0.68
EFF (%)	2.83	3.15	1.75

## IV. CONCLUSION

In summary, we have successfully prepared a double-layered TiO<sub>2</sub> electrode composed of a compact TiO<sub>2</sub> blocking layer and a mesoporous TiO<sub>2</sub> layer. The sputtered TiO<sub>2</sub> layer exhibited a denser structure and higher visible-light transmittance when compared to a nanoparticle layer of the same thickness. Also, the mesoporous TiO<sub>2</sub> layer was able to adsorb more dye molecules than the conventional TiO<sub>2</sub> layer, which led to high energy-conversion efficiency. The double-layered TiO<sub>2</sub> electrode caused an increase in photocurrent without photovoltage drop due to the high adsorption capacity of sensitizers and electrolyte blocking. We found that the double-layered TiO<sub>2</sub> electrode gave rise to an 80% improvement in the energy-conversion efficiency as compared to a single-layered conventional TiO<sub>2</sub> electrode. Therefore, we believe that this method for preparing double-layered TiO<sub>2</sub> electrodes may play an important role in improving the performance of DSSCs.

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