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Research Article

Improvement of Short-Circuit Current Density in Dye-Sensitized Solar Cells Using Sputtered Nanocolumnar TiO_2 Compact Layer

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The effect of a nanocolumnar TiO_2 compact layer in dye-sensitized solar cells (DSSCs) was examined. Such a compact layer was sputtered on a glass substrate with an indium tin oxide (ITO) film using TiO_2 powder as the raw material, with a thickness of ~100 nm. The compact layer improved the short-circuit current density and the efficiency of conversion of solar energy to electricity by the DSSC by 53.37% and 59.34%, yielding values of 27.33 mA/cm^2 and 9.21%, respectively. The performance was attributed to the effective electron pathways in the TiO_2 compact layer, which reduced the back reaction by preventing direct contact between the redox electrolyte and the conductive substrate.

1. Introduction

Dye-sensitized solar cells (DSSCs) are of particular interest in the field of solar energy, because of their low cost, simplicity of fabrication, and high solar energy conversion efficiency [1–5]. They have a basic structure that comprises two conductive substrates (another is coated catalyzer, for example, platinum), an absorbing layer of semiconductor materials, dye molecules, and a redox electrolyte. The principle of operation of DSSCs is that electrons are injected from the photoexcited dye into the conductive band of the semiconductor and forward flows to an external loop under illumination, while the electrolyte reduces the oxidized dye and transports the positive charges to the counter electrode. Extensive research has been performed to improve each component of DSSCs.

Gold nanoparticles (GNPs) have been used in solar cells because of their particular optical and electrical properties. They reportedly increase the generation of charge carriers, photocurrent, and efficiency of conversion of solar energy in DSSCs [6–8]. Several materials have been employed in the compact layer, or blocking layer; they include TiO_2 [9–11], Nb_2O_5 [12], ZnO [13], $CaCO_3$ [14], and $BaCO_3$ [15], which reduce the area of contact between the conductive substrate and the redox electrolyte. Among them, TiO_2 is commonly preferred because of its favorable antichemical and antiphoto corrosion abilities. The introduction of the compact layer between the conductive substrate and the porous films may improve the adherence between them and the transfer of electrons by increasing the number of electron pathways.

In this study, short-circuit current density is increased by introducing a compact layer to improve the performance of DSSCs. The photovoltaic characteristics of DSSC with and without a nanocolumnar TiO_2 compact layer were investigated by making spectral response and illuminated current density-voltage (J-V) measurements.

2. Experiment

Colloidal TiO_2 was prepared from 6 g nanocrystalline powder (Degussa, P25 titanium oxide, Japan), 0.1 mL of TritionX-100, 0.2 mL of acetylacetone, and 3 mL of aqueous GNPs in 7 mL deionized water, which were stirred together for 14 hrs. Subsequently, the mixture was spin-coated on indium tin oxide (ITO) glass substrate to a thickness of around 15 μm, and a 0.3 × 0.3 active area was defined. Thereafter, the photoelectrode was immersed in a 3×10^{-4} M solution of dye (cis-bis(isothiocyanato) bis (2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) (N_3) in ethanol

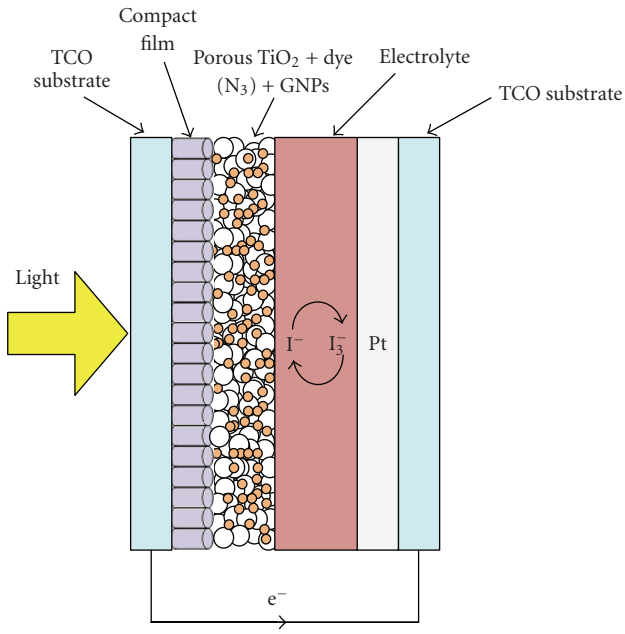


Figure 1: Schematic cross section of the DSSCs with nanocolumnar TiO_2 compact layer.

for 24 hrs, before being sintered at 450°C for 30 min, to increase its anatase content (anatase : rutile = 85 : 15) [16]. The compact layer was formed on an ITO glass substrate by sputtering the target using P25 TiO_2 powder as a raw material. The electrolyte was composed of 0.05 M iodide and 0.5 M lithium iodide with and without 0.5 M 4-tert-butylpyridine (TBP) in propylene carbonate. Then, a 100 nm thick layer of platinum was sputtered onto ITO substrate as a counter electrode. Cells were fabricated by placing sealing films (SX1170-60, SOLARONIX) between the two electrodes, and just leaving two via-holes for injection electrolyte. The sealing process was carried out on a hot plate at 100°C for 3 min. Then, the electrolyte was injected into the space between the two electrodes through the via-holes. Finally, the via-holes were sealed using the epoxy with low vapor transmission rate. Figure 1 schematically depicts the complete structure.

A field emission scanning electron microscope (FESEM) (LEO 1530) was adopted to examine the cross-section and surface morphology of the cells. The *J-V* characteristics were measured using a Keithley 2420 programmable source meter under irradiation by a 1000 W xenon lamp. The incident photon to electron conversion efficiency (IPCE) was measured using a spectrometer (DM-201, DONGWOO OPTRON) also under illumination by the 1000 W xenon lamp. Finally, the irradiation power density on the surface of the sample was calibrated as 100 mW/cm2.

3. Results and Discussion

Figures 2(a) and 2(b) present the cross-sectional and surface SEM images of the TiO_2 compact layer on ITO glass substrate. The mean size of the porous TiO_2 particles and the size of the nanocolumns of the 100 nm thick TiO_2 compact layer, were about 12 nm. The diameter of the sputtered TiO_2 compact layer had a diameter similar to that of the porous TiO_2 film that absorbed the dye molecules. Accordingly, the porous TiO_2 film formed a superior contact with the nanocolumnar TiO_2 compact layer and the electrolyte could not come into direct contact with the ITO substrate. The back transfer of electrons was thus reduced.

Figure 3 shows a typical XRD pattern of a TiO_2 compact layer that is deposited on ITO glass substrate by sputtering. Two dominant anatase diffraction peaks, (101) ($2\theta = 25.28°$) and (004) ($2\theta = 37.73°$), are observed. The results are consistent with the SEM image of nanoporous TiO_2 in Figure 2(a). Anatase-based TiO_2 has been regarded as the best semiconductor oxide for DSSCs, because an anatase film has a larger surface area per unit volume than a rutile film,and so is better able to absorb dye, has a longer electron diffusion coefficient, and has a shorter electron transit time [3, 17, 18].

Figure 4 plots the *J-V* characteristics of DSSCs with and without a TiO_2 compact layer that was injected with different electrolytes. Table 1 presents the characteristic parameters of these DSSCs. The cell has an active area of $0.3 \times 0.3\ cm^2$ and no antireflective coating. The short-circuit current density and the efficiency of conversion of solar energy to electricity of traditional DSSCs with a TiO_2 compact layer were improved by 53.37% and 59.34%, respectively. Therefore, the improvement in the overall performance of DSSCs was due to the introduction of a nanocolumnar TiO_2 compact layer.

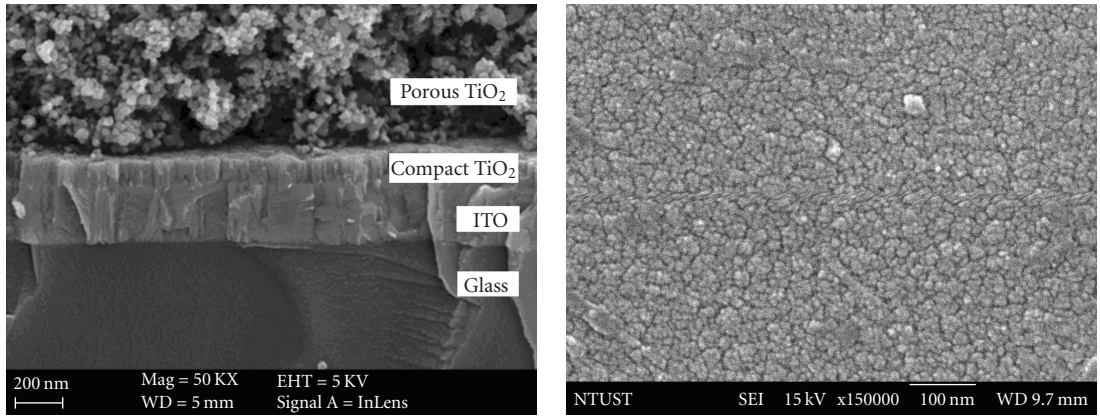
The increase in the short-circuit current density and the number of electrons that could reach the ITO substrate was attributed to the presence of effectively continuous electron pathways, which reduced the recombination of electrons, between the porous TiO_2 film and the ITO substrate. Furthermore, in this work, the GNPs were doped in porous TiO_2 films, raising the Fermi level [7, 8] as a Schottky barrier, and then the exiting electrons flowed spontaneously into the TiO_2 conductive band through the barrier, inhibiting the back-transfer of electrons [19]. Hence, the solar conversion efficiency of DSSCs with a compact layer was higher than that of traditional DSSCs.

Figure 5 plots the IPCE spectra obtained with and without a TiO_2 compact layer. It demonstrates that the energy conversion efficiency of DSSCs with a TiO_2 compact layer was overall higher than that of DSSCs without a TiO_2 compact layer. In particular, the difference between the efficiency with a compact layer and that without was approximately 20%. The IPCE also can be determined using the following equation [20, 21]:

$$\mathrm{IPCE}(\lambda) = \mathrm{LHE}(\lambda) \cdot \varphi_{\mathrm{inj}} \cdot \eta_{\mathrm{coll}}, \quad (1)$$

where LHE denotes the light harvesting efficiency of the dye molecule; φ_{inj} is the electron injection efficiency of the excited dye into the TiO_2, and η_{coll} is the collection efficiency of the system.

The procedures, equipment, and working environment of DSSCs were the same in all experiments: the parameters φ_{inj} and LHE were held almost constant, so the IPCE value

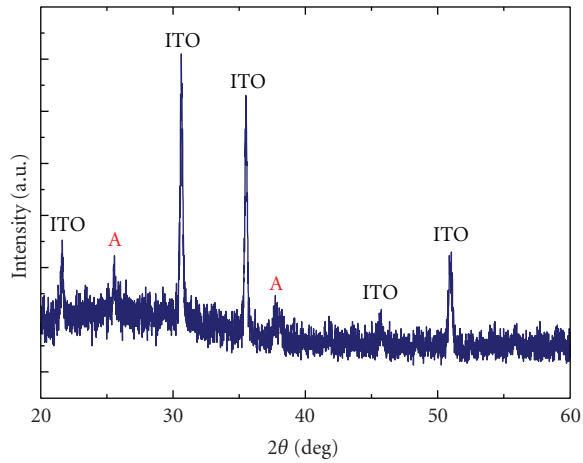


(a) (b)

Figure 2: (a) The SEM cross-section image of photoanode with compact layer. (b) The SEM morphological image of TiO_2 compact film.

Table 1: The parameters of DSSCs with and without TiO_2 compact layer (CPL) at different electrolytes.

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	F.F.	η (%)
CPL + LiI	0.563	27.33	0.599	9.21
LiI	0.526	17.82	0.617	5.78
CPL + LiI + TBP	0.681	11.82	0.609	4.90
LiI + TBP	0.692	5.31	0.561	2.06



A: anatase

Figure 3: XRD pattern of compact layer on ITO substrate.

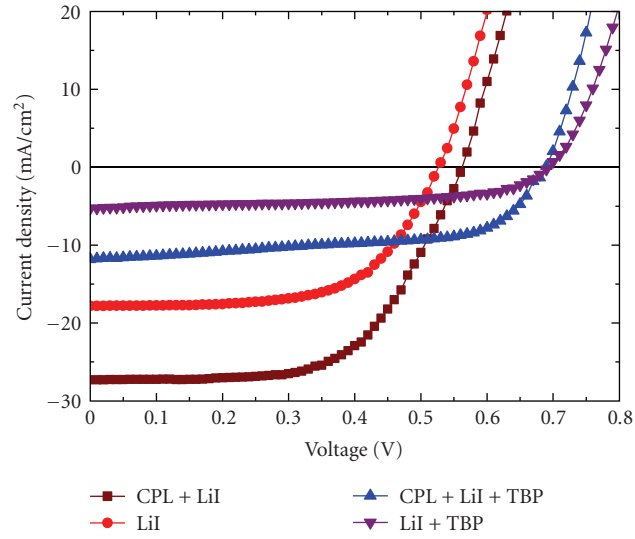


Figure 4: The J-V characteristics of DSSCs with and without compact layer at different electrolytes.

was thus determined by η_{coll} according to (1). Consequently, the parameter η_{coll} of DSSCs with a compact layer exceeded that of those without because the former contained more effective electron pathways.

4. Conclusions

This work discusses the improvement associated with the introduction of a nanocolumnar TiO_2 compact layer between the porous TiO_2 film and the conductive substrate in DSSCs. The short-circuit current density and the efficiency of conversion of solar energy to electricity were thus improved by 53.37% and 59.34%, respectively. The enhanced performance of DSSCs with a compact layer was attributed to the increase in contact area between porous TiO_2 and the ITO substrate and the presence of effectively continuous electrons pathways in the sputtered TiO_2 compact layer, which reduced back transfer by preventing direct contact between the redox electrolyte and the conductive substrate. Therefore, the short-circuit current density and efficiency

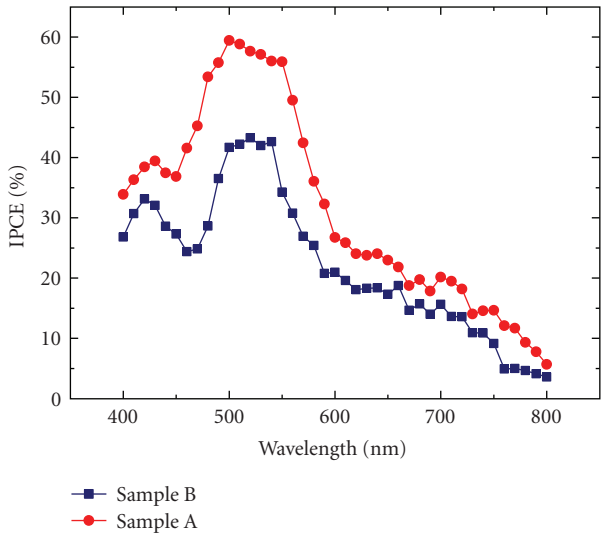


Figure 5: Photocurrent action spectra of DSSCs with and without compact layer.

of conversion of solar energy to electricity were increased to 27.33 mA/cm^2 and 9.21%, respectively, under illumination by a 1000 W Xe lamp.

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