Observation of Positive Effects of Freestanding Scattering Film in Dye-Sensitized Solar Cells

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ABSTRACT Dye-sensitized solar cells (DSSCs) with a nanocrystalline TiO_2 as a anode incorporating a free-standing and flexible light-scattering film composed of sub-micrometer-sized Al_2O_3 particles with a small amount of ion-transportable polymeric binder were prepared and compared to DSSCs composed of a nanocrystalline TiO_2/sub-micrometer-sized TiO_2 bilayer as an anode. The cell efficiency of the former was higher than that of the latter. This implies that the enhancement of the light absorption as that obtained with a general DSSC with light-scattering layer (sub-micrometer-sized TiO_2) is possible by combining a high-surface-area layer of nanocrystalline TiO_2 and free-standing light scattering film. The novel DSSCs with the free-standing light scattering film showed an additional resistance, which was characterized by the electrochemical impedance analysis. However, the cell performance was not seriously influenced by the additional resistance. When the free-standing scattering film was assembled with flexible type DSSCs, not only a greatly enhanced power conversion efficiency but also better long-term stability than the DSSC without the light scattering film were observed.

KEYWORDS: dye-sensitized solar cells • light-scattering film • free-standing • flexible • high efficiency • light-scattering effect

INTRODUCTION

Dye-sensitized solar cells (DSSCs) with a mesoporous network of interconnected TiO_2 nanocrystals are currently attracting widespread scientific and technological interest as a high-efficiency and low-cost alternative to conventional inorganic photovoltaic devices (1). With power conversion efficiencies above 10 %, DSSCs have been shown to exhibit potentially useful operating characteristics (2). To obtain highly efficient DSSCs, attempts have been made to fabricate devices with a relatively thick layer of nanocrystalline TiO_2 (1). However, the main issue inhibiting the development of DSSC technology is the scaling up of the devices to large modules (3). The essential requirement for the production of DSSC modules is to produce thin nanocrystalline TiO_2 films with a higher surface area, together with a higher light scattering layer (400−500 nm sized TiO_2), so that the production cost can be reduced by lowering the dye usage without sacrificing the cell performance (3). Although the small size of the TiO_2 nanoparticles (~20 nm) employed to ensure a high surface area makes conventional nanocrystalline TiO_2 films poor light scatterers, mixing the nanoparticles with larger particles or applying a scattering layer to the nanocrystalline film has been shown in simula-

tions and some experimental studies to increase the light harvesting by enhancing the scattering of light (4−6). For example, Wang et al. reported a TiO_2 photoelectrode with a multilayer structure, where each layer consisted of TiO_2 nanoparticles of different radii (7). Other promising concepts encompass the inclusion of large particles of TiO_2 or spherical voids in the nanocrystalline TiO_2 layer for the purpose of light scattering (8, 9).

Recently, lightweight plastic-type DSSCs have attracted much attention due to the drastic reduction in cost that they afford and their more extensive applications, such as mobile power for wearable electronic devices (10). Nanocrystalline TiO_2/scattering TiO_2 bilayer films for DSSCs have usually been prepared by the sequential casting of TiO_2 pastes with an organic binder on glass substrates, followed by burning at temperatures above 450 °C. In the case of a plastic substrate-based DSSC, however, this conventional preparation method using high-temperature annealing is not acceptable. Hence, the preparation of well-connected nanocrystalline TiO_2/scattering TiO_2 bilayer in a plastic substrate based DSSC is a very challenging issue. In addition, when plastic-based DSSCs are bent, there is some possibility of the dye-coated TiO_2 electrode and Pt electrode coming into contact with each other, resulting in an internal short.

In the present paper, we demonstrate some of the possibilities for making free-standing and flexible scattering films for DSSCs using submicrometer sized inorganic particles with a small amount of ion-transportable polymeric binder (Figure 1a). The organic/inorganic hybrid films can act not only as a scattering layer for the purpose of enhancing the light harvesting, but also as ion-transportable gel-like
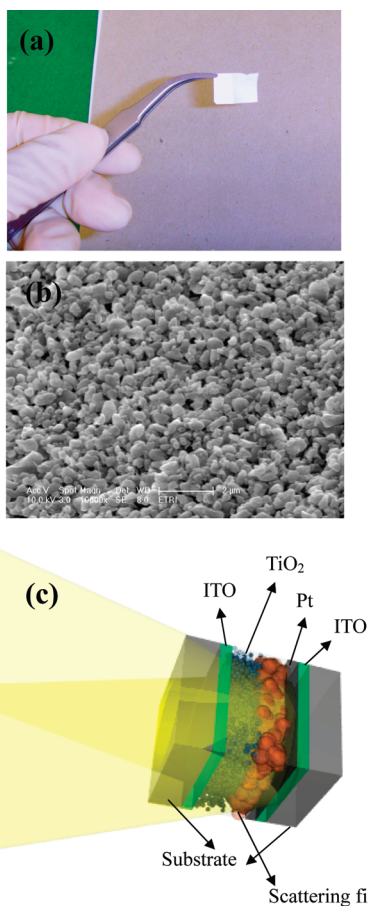
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FIGURE 1. (a) Photograph and **(b)** SEM image of the free-standing scattering film. **(c)** Cell structure of the DSSC with the freestanding scattering film.

FIGURE 2. Photocurrent density−voltage (J−V) curves for the DSSCs with and without the scattering film (30 μm thick).

membranes. The conventional DSSC with a scattering TiO_2 layer was compared to DSSCs with a free-standing scattering film. The free-standing scattering film was also assembled with flexible-type DSSCs and its positive effects were investigated.

EXPERIMENTAL SECTION

Anatase TiO_2 colloids were made via a sol−gel hydrolysis and autoclaving of titanium isopropoxide at 230 °C for 12 h in an acetic acid aqueous solution, as described elsewhere (11). TiO_2 nanoparticles were dispersed in α-terpinol with ethyl cellulose as a binder. Single-layer TiO_2 mesoporous films were used as photoanodes. A 10 μm thick, transparent, high-surface-area layer of 20 nm-sized TiO_2 particles was first printed on the fluorine-doped SnO_2 conducting glass (FTO) substrate. After heat treatment at 550 °C for 30 min, the nanocrystalline TiO_2 electrodes were immersed in 50 mM N719 solution. Counter electrodes were prepared by coating an FTO glass with a drop of H_2PtCl_6 and heating it at 400 °C for 15 min. For preparing flexible type DSSC, chemical sintering method at low temperature was used for flexible TiO_2 electrode following the procedure as described in the literature (12). As a low-temperature method for counter electrode, 40 mM hydrogen hexachloroplatinate (IV) hydrate in 2-propanol was spread evenly on a ITO-PEN substrate, and the surface was dried for 2 h at 120 °C. A 60 mM reducing agent was prepared by dissolving $NaBH_4$ in an H_2O and ethanol mixture (8:2 vol. ratio). Pt(IV)-coated plastics were immersed in the reducing agent solution until the surface became dark. The treated samples were washed by ethanol and water sequentially, and were dried for 2 h at 130 °C.

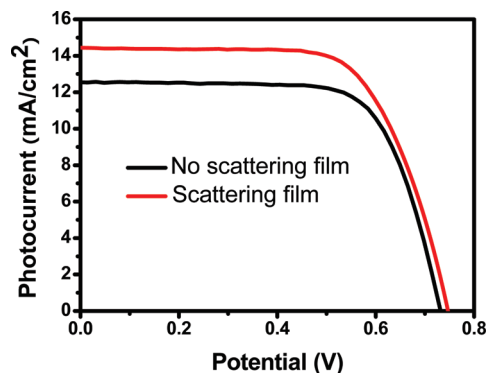To prepare the free-standing light scattering film, a mixture of 400 nm sized Al_2O_3 (Sumitomo, Japan) and PVdF-HFP (Kynar Powerflex) at a ratio of 95:5 was dissolved in acetone, followed by sonication for several hours. The well-dispersed inorganic/organic solution was cast on a glass substrate by screen printing with a doctor blade. After being immersed in water, a freestanding Al_2O_3 film was obtained. The Al_2O_3 film was inserted between the dye-adsorbed nanocrystalline TiO_2 electrode and Pt counter electrode. The dye-adsorbed nanocrystalline TiO_2 electrode, Al_2O_3 film, and Pt counter electrode were assembled into a sealed sandwich-type cell by heating with a hot melt of polymer film (Surlyn, Dupont 1702). A drop of the electrolyte solution was introduced into a hole drilled in the counter electrode of the assembled cell, followed by sealing the holes using microcover glass and Surlyn. The electrolyte was composed of 0.6 M butylmethylimidazolium iodide, 0.03 M I_2, 0.1 M guanidinium thiocyanate, and 0.5 M 4-tert-butylpyridine in a mixture of acetonitrile and valeronitrile (v/v, 85:15). For all experiments the cells were covered with a mask (area: 0.2 cm^2) that was slightly bigger than the dye-adsorbed nanocrystalline TiO_2 electrode. For each cell with different scattering film, 10 identical DSSCs were assembled and characterized. The J−V curves were measured at AM 1.5 illumination using a Keithley 2400 source measure unit. A 1000 W xenon lamp (Oriel, 91193) served as the light source and its intensity was calibrated using a Si reference cell (Fraunhofer ISE, certificate no. C-ISE269). IPCE was measured at the low chopping speed of 5 Hz using a system by PV Measurement, Inc., equipped with a halogen source and a broadband bias light for approximating one sun intensity. The IPCE system was calibrated using a silicon reference photodiode (G587, PV Measurement, Inc.).

RESULTS AND DISCUSSION

The scanning electron microscopy image of the freestanding scattering film with the Al_2O_3 submicroparticles shows that the particles are well distributed and completely packed (Figure 1b). Furthermore, the mircopores are believed to be occupied by the ion conducting polymer electrolyte (PVdF-HFP), which facilitate its diffusion. The wetted inorganic scattering film with the electrolyte showed good dimensional stability, because PVdF-HFP is not soluble in the organic solvents that were used. Figure 1c shows a schematic diagram of the DSSC with the scattering film.

The scattering film made by screen printing was typically about 15 μm ∼30 μm thick after the evaporation of the solvent. Figure 2 shows the typical current−voltage (J−V) characteristics of the sealed DSSCs with and without the freestanding scattering film under the illumination of simulated
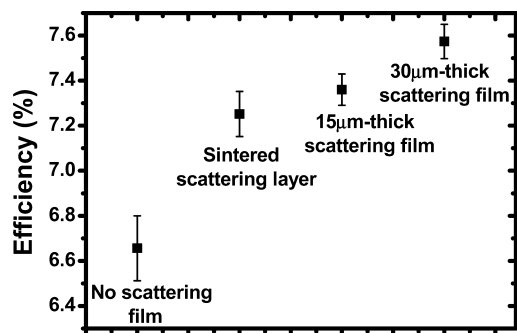
FIGURE 3. Summarized performances for the DSSCs.

FIGURE 4. IPCE of DSSCs with (dot line) and without (solid line) the 30 μm thick freestanding scattering film.

FIGURE 5. Electrochemical impedance spectra of DSSCs with and without the scattering film.

AM1.5 solar light (100mW/cm^2). In the case of the DSSC without the scattering film, the J_{sc}, V_{oc}, and FF values are 12.54 mA/cm^2, 730 mV, and 0.711, respectively, corresponding to an overall energy conversion efficiency of 6.5. Figure 2 also shows the typical $J-V$ curves of the DSSC with the free-standing scattering film. The J_{sc}, V_{oc}, and FF values of this device are 14.44 mA/cm^2, 745 mV, and 0.677, respectively, corresponding to an overall energy conversion efficiency of 7.3. As a result of the increase in the J_{sc} value, the conversion efficiency increased from 6.5 % for the DSSC without the scattering film to 7.3 %, for that with the scattering film. This result indicates that the free-standing, scattering film composed of Al$_2$O$_3$ and PVdF-HFP can induce the light scattering of incident solar light, which increases the light absorption efficiency.

The $J-V$ characteristics for the two sets of devices were studied to compare the light scattering effects of the free-standing, light-scattering film and general light-scattering layer with a 400 nm sized sintered TiO$_2$ layer. A 10 μm thick, transparent, high-surface-area layer of 20 nm sized TiO$_2$ particles was first printed on an FTO electrode, and this layer was subsequently coated with a 5 μm thick second layer of 400 nm light-scattering particles. The film was annealed at 550 °C for 30 min in air. Figure 3 shows that the light scattering due to the scattering layer enhanced the photocurrent density in the devices with the 5 μm thick TiO$_2$ scattering layer. When the 10 μm thick, transparent, high-surface-area layer of 20 nm sized TiO$_2$ was coupled with the 15 μm thick free-standing light-scattering film as a scattering layer, the cell efficiency was slightly higher than that of the DSSCs with the 400 nm sized sintered scattering layer. This implies that the same enhancement of the light absorption as that obtained with the general DSSC with light -scattering layer can be achieved by combining a high-surface-area layer of 20 nm sized TiO$_2$ and novel freestanding light-scattering film. When the 20 μm thick film was used, more enhanced light-scattering effect was observed.

Figure 4 supports enhancement of J_{sc} when light scattering film has been added. The maximum value of IPCE for DSSC occurs at around 540 nm, which is corresponding to the absorption peak for N719. Before the maximum value, no noticeable difference has been observed for samples whether they have scattering film or not. However, higher IPCE values have been recorded for samples with scattering
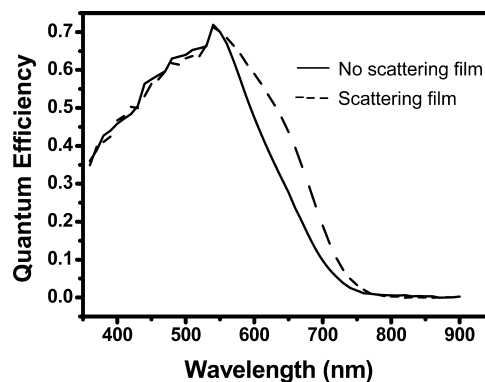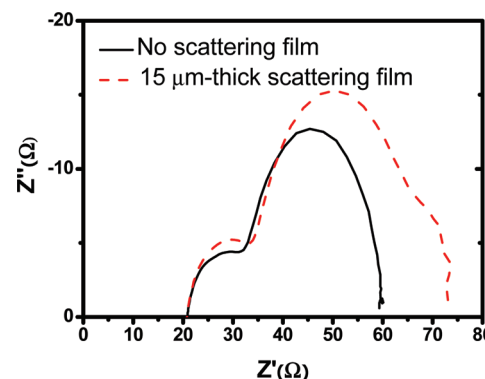
film. When the values are integrated from 540 to 800 nm, the samples with scattering film show 25−30 % more absorption.

Figure 5 shows the electrochemical impedance spectra for the DSSCs without a scattering layer and with a free-standing light scattering film. R_o in Figure 5 is the ohmic resistance of the dye-sensitized solar cells, representing the electron transport processes with a very short time constant. The first semicircle is the resistances at the TiO$_2$/FTO interface, between the TiO$_2$ particles, and at the interface of the Pt/electrolyte solution (13, 14). In the impedance spectra for the both DSSCs, R_o and the first semicircle were almost the same. The second semicircle represents the resistance component at the TiO$_2$/electrolyte solution and TiO$_2$/dye interfaces (14). In our experiments, the resistance in the DSSC with the scattering film was larger than that of the liquid electrolyte based cell, indicating that the former has additional resistance at the TiO$_2$/electrolyte interface or Pt/electrolyte interface because of the additional porous scattering layer. In addition, the response at low frequency is related to the diffusion process of the I$^-$/I$_3^-$ redox electrolytes. In the case of the liquid electrolyte-based cell, this component was not observed. However, the DSSC with the scattering film also shows an additional semicircle, which represents Nernstian diffusion, arising because of the reduced ion mobility.

Flexible DSSCs based on a transparent conductive substrate have attracted a lot of interest because of their lightweight, flexibility, and low cost in recent years. Because
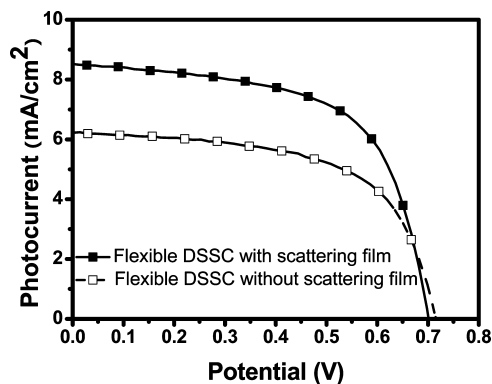
FIGURE 6. Photocurrent density−voltage ($J-V$) curves for the flexible DSSCs with and without the 30 μm thick freestanding scattering film.
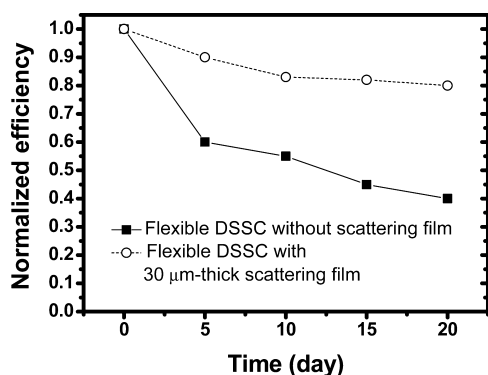

FIGURE 7. Long-term stability of DSSCs with liquid electrolyte and with the 30 μm thick freestanding scattering film.

the heat treatment temperature for the polymer substrates are generally limited to a temperature lower than 150 °C, the preparation of thick TiO_2 films with good connections between TiO_2 nanoparticles becomes a key issue. Good connections such as necking and chemical bonds between TiO_2 nanoparticles are usually obtained by sintering the TiO_2 film at a temperature of 500 °C. We believe that the freestanding light-scattering film is more suitable for flexible DSSCs because of the difficulty for preparation of thick TiO_2 film composed of 20 nm sized particle/400 nm sized particle bilayers. Figure 6 shows the $J-V$ characteristics of a flexible DSSC with and without the free-standing light scattering film. Under standard testing conditions, the cell based on the ITO/PEN substrate without the free-standing light scattering film gave a photocurrent of 6.22 mA/cm^2, an open circuit voltage of 715 mV, and a fill factor of 0.601, yielding a 2.67 % conversion efficiency. Meanwhile the cell with the free-standing light scattering film gave a photocurrent of 8.50 mA/cm^2, an open circuit voltage of 700 mV, and a fill factor of 0.611, yielding a 3.64 % conversion efficiency. The efficiency of the former is 36.3 % higher than that of the latter.

To investigate the long-term stability of DSSCs with scattering inorganic membrane, we carried out the aging test on the sealed DSSC. The cells were stored in air at room temperature and their efficiencies were measured once per 5 days. Figure 7 shows the long-term stabilities of the reference device and the device with the scattering inorganic membrane in air at room temperature. The cell efficiencies of the devices with and without the scattering membrane decrease to approximately 0.8 and 0.4 after 20 days, respectively. This provides good evidence for the positive effect of the scattering membrane on the long-term stability. This might be due to the fact that the liquid electrolytes easily volatilize and leak during long-term operation, resulting in a decrease of the energy conversion efficiency of the DSSC (15). These results prove that the present membrane can suppress leaking or evaporation of the liquid electrolyte, and therefore results in more improved device durability.

CONCLUSIONS

A new type of scattering layer for enhancing the light harvesting in DSSCs was introduced. In the case of flexible DSSCs, preparing double-layered TiO_2 anodes with a 20 nm sized TiO_2 layer and 400 nm sized scattering layer without thermal sintering is very difficult. The proposed flexible DSSC with freestanding scattering membrane shows not only a greatly enhanced power conversion efficiency, but also better long-term stability than the DSSC without the scattering membrane. The present results indicate that the method used herein has the potential to solve one of the major problem involved in preparing flexible DSSCs with a scattering layer.

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