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Preparations and Characterizations of TiO_2 Pastes for Flexible Dye-Sensitized Solar Cells

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New TiO_2 pastes for the fabrication of TiO_2 electrodes at low temperature were prepared from a TiO_2 nanoparticle colloidal solution including Ti-alkoxide precursors. In addition, TiO_2 pastes comprising 123 nm and 200 nm TiO_2 particles used as scattering particles were prepared. Single and double layered TiO_2 electrodes were deposited onto an ITO-PEN film by the doctor-blade method and subsequently sintered at 140° C and used to fabricate flexible Dye-sensitized Solar Cells (DSSCs). Due to the light scattering effect in the double layered TiO_2 electrode, the J_{sc} and efficiency of the flexible DSSCs were greatly enhanced.

Keywords Flexible dye-sensitized solar cells; light scattering effect; low-temperature TiO_2 electrode fabrication

1. Introduction

Dye-sensitized solar cells (DSSCs) have been widely investigated during the past decade [1,2]. Their major advantages are a lower production cost compared to traditional crystalline silicon solar cells and potentially higher conversion efficiency. Moreover, the lightness and flexibility of solar cells are important advantages, since they facilitate the transportation and photovoltaic power-supply system equipment and make possible. Replacing the traditional rigid substrate by flexible plastic electrodes allows for their low-cost fabrication by roll-to-roll mass production. Therefore, flexible photovoltaic cells have the potential to be used in a wide rage of applications, including plastic electronics. The low-temperature processing of porous

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thin films of oxide semiconductors such as TiO_2, ZnO and SnO_2 to conductive plastic film substrates plays an important role in the development of flexible DSSCs and remains an ongoing challenge [3–6]. The major drawback involved in the development of "plastic" DSSCs concerns the deposition of a TiO_2 film with an indium-tin oxide-coated polyethylene naphthalate (ITO–PEN) film, for which the thermal treatment temperature is limited to 150°C, because otherwise the polymer will undergo thermal degradation and the TiO_2 electrode will lose its transparency and become completely distorted. However, the deposition of a TiO_2 film deposition on an ITO–PEN film at 150°C results in the reduced electrical contact between the TiO_2 particles and low dye absorption. Due to the thermal instability of the plastic substrates, flexible DSSCs using them have a lower efficiency than those using glass substrates sintered at high-temperature (450–500°C). Therefore, many companies and academic institutions have been engaged in research and development to find a solution to this problem. Various attempts have been made to develop methods compatible with plastic substrates such as chemical deposition [7], the sintering of colloids at low temperature [8,9], the mechanical compression of crystalline particles [10,11], electrophoretical deposition [12,13], the lift-off technique [14], and hydrothermal crystallization [15]. Moreover, 28 GHz microwave irradiation has also been used for the rapid synthesis of a TiO_2 electrode without heating the plastic substrate over 150°C [16]. Although the overall conversion efficiency is low, in comparison to that of DSSCs using glass electrodes, the recent advances made in this area can be considered to be very promising.

Recently, many researchers have developed flexible metal substrates for counter electrodes and demonstrated highly efficient photovoltaic cells with various metal substrates [17,18]. The counter electrode requires a cathode catalyst for the reduction of tri-iodide (I_3^-) to iodide (I^-). Zn, Stainless steel, W, and Ti have been widely used for this purpose on flexible plastic substrates. On the other hand, semitransparent mesoporous counter electrodes have been fabricated using carbon materials and conductive polymer materials, including derivatives of poly (3,4-ethylenedioxythiophene) (PEDOT) and poly (3,4-ethylenedioxythiophene) – poly (styrenesulfonate) (PEDOT-PSS).

In the present research, we fabricated nanoporous mono- and double-layered TiO_2 films consisting of different TiO_2 pastes, which were composed of TiO_2 particles with average diameters of 20 nm, 123 nm, and 200 nm. TiO_2 films were deposited on transparent conductive polymers by the doctor-blade method, followed by heat treatment at 140°C. And the introduction of the scattering layers with the larger TiO_2 particles clearly improves the cell performances, especially the J_{sc} value for light collection in the device. The effects of the content of the Ti-alkoxide precursor solution and the scattering particles were analyzed by BET measurements, UV-Vis spectroscopy and simulation.

2. Experimental

2.1. *Materials*

TiO_2 powders (P-25, a mixture of Ca. 30% rutile state and 70% anatase state, BET surface area $50 \pm 10\,m^2/g$, mean particle size 20 nm) were purchased from Degussa AG, Germany. Titanium iso-propoxide (TIP), acetic acid, acetylacetone, poly (ethylene glycol) ethyl ether methacrylate (PEG-EEM), deionized water, iodine (I_2),

propylene carbonate (PC), ethylene carbonate (EC), acetonitrile (AN), and tetrabutylammonium iodide (TBAI) were purchased from Aldrich Co. and used without further purification. cis-Bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) dye (N3 dye) and 1-propyl-3-methylimidazolium iodide (PMII) as an ionic liquid were purchased from Solaronix SA.

ITO-PEN (thickness 200 μm, sheet resistance 13 Ω/□, transmittance 80%) as a transparent conductive plastic electrode and platinum-coated PEN (thickness 188 μm, sheet resistance 5 Ω/□) as a counter electrode were obtained from Peccell SA.

2.2. *Preparations of TiO_2 Pastes*

The TiO_2 pastes used for the low-temperature fabrication of TiO_2 films were prepared from a nanoparticle TiO_2 colloidal solution dispersed in ethanol including Ti-alkoxide precursor solution to facilitate the connection between the TiO_2 particles and the formation of thick TiO_2 films on plastic substrates. A TiO_2 colloidal solution consisting of commercially-available TiO_2 powder (P-25)/ethanol/acetylacetone at a molar ratio of 1:4:0.024 was prepared and then dispersed by magnetic stirring. A TIP precursor solution consisting of TIP/ethanol/water/acetylacetone at a molar ratio of 1:10:1:0.8 was prepared. To find the optimum amount of the Ti-alkoxide precursor solution, about 2.7 ml of the TiO_2 colloidal solution was mixed with various amounts (0.7 ml, 1.0 ml, and 2.0 ml) of the TIP precursor solution. Three types of pastes were prepared by stirring these solutions for 48 hours and named Paste A-1, Paste A-2, and Paste A-3, respectively. Pastes B and C were prepared by changing the P-25 to 123 nm and 200 nm sized TiO_2 particles, respectively.

2.3. *Fabrication of Single- and Double-Layered TiO_2 Electrodes*

The three different kinds of TiO_2 pastes (Paste A-2, Paste B, and Paste C) were used as the electrodes of the flexible DSSCs. The 123 nm and 200 nm sized TiO_2 particles used as scattering particles were prepared by the sol-gel method according to the procedures mentioned in the literature [17]. Pastes B and Paste C containing the 123 nm and 200 nm TiO_2 particles, respectively, were used as the scattering layers. Figure 1 shows the three types of TiO_2 electrodes deposited onto ITO-PEN film substrates by the doctor-blade method and subsequently sintered at 140°C. The structure of Type A consisted of a single-layered electrode, whereas Type B and C were double-layered electrodes.

2.4. *Fabrication of Flexible DSSC Devices*

We prepared flexible DSSC devices using N3 dye as a photosensitizer, sandwiched between the TiO_2 electrode and the Pt-coated PEN film as the counter electrode.

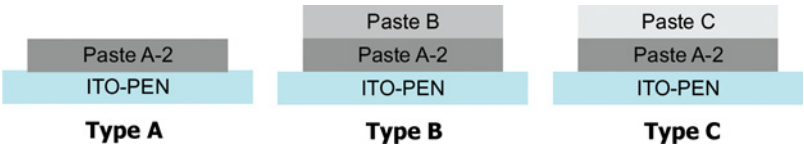

Figure 1. Three types of TiO_2 electrodes onto ITO-PEN film prepared for flexible DSSCs.

The TiO_2 electrodes were fabricated with three different structures, namely Type A, Type B, and Type C, to evaluate the light scattering effect of the double-layered TiO_2 films. Before assembling the two electrodes, the polymer electrolyte was cast onto the TiO_2 electrode impregnated with N3 dye and dried at 50°C for about 1 hour in an oven to evaporate the solvent. The polymer electrolyte contains I_2, TBAI, PMII, EC/PC (EC: PC = 4:1 v/v), and PEG-EEM as a polymer matrix in acetonitrile.

2.5. *Measurements*

The size distribution of the nanoparticles was measured by particle size analysis (PSA, BECKMAN COULTER LS 1332, USA) after being dispersed in ethanol. The crystal structures of the mono- and double-layered TiO_2 electrodes were analyzed by X-ray diffraction (XRD) with Cu Kα radiation (X'Pert PRO). The Brunauer-Emmett-Teller (BET) surface area & pore volume and mean pore size of the mono- and double-layered TiO_2 electrodes were determined by a Surface Area & Pore Size Analyzer (NOVA 4000e). The mono- and double-layered TiO_2 electrodes were characterized by means of Scanning Electron Microscopy (SEM) to investigate their surface and thickness. The transmittance and absorbance of the TiO_2 electrodes were measured using a UV-Vis-NIR spectrophotometer (Varian, Cary 5000). The photovoltaic characteristics of the DSSC devices were measured using a Solar Simulator (150 W simulator, PEC-L11/PECCELL) under simulated solar light with an ARC Lamp power supply (AM 1.5, 100 mW/cm^2). The solar simulator was calibrated to a verified Si reference cell. The active area of the DSSCs measured using a black mask was 0.25 cm^2.

3. Results and Discussion

3.1. *Characterizations of TiO_2 Pastes for Flexible DSSCs*

To optimize the amount of Ti-alkoxide precursor solution with respect to the TiO_2 colloidal solution, the films prepared using the various Ti-alkoxide precursor solutions were investigated. The properties of the TiO_2 films with the various Ti-alkoxide precursor concentrations calcined at 140°C were measured and their surface parameters and XRD patterns are given in Table 1 and Figure 2, respectively.

From the BET data, it can be seen that as the amount of Ti-alkocide precursor solution in Pastes A-1, A-2, and A-3 was increased from 0.7 ml to 2.0 ml, the surface area remained at around 55~59 m^2/g, and the pore volume slightly decreased from 0.49 to 0.15 cm^3/g. Figure 2 shows the X-ray diffraction-patterns of the TiO_2 films after calcination at 140°C. As shown in the figure, both anatase (101) and rutile (110) phases were observed. These results indicate that the TiO_2 colloidal solutions with Ti-alkoxide precursor solution lead to the formation of crystalline.

3.2. *Photovoltaic Properties of Flexible DSSC Devices using Various TiO_2 Pastes*

The photovoltaic performances of the flexible DSSCs using Pastes A-1, A-2, and A-3 are summarized in Table 2. As the amount of the Ti-alkoxide precursor solution increased, the open-circuit voltage (V_{oc}) decreased. Despite the decrease of V_{oc}, the best energy conversion efficiency of 2.74% was obtained for Paste A-2, as judged

Table 1. The BET data of TiO_2 films calcined at 140°C based on different Ti-alkoxide precursor solution amounts

	BET[1] surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
Paste A-1[2]	56.40	0.49	15.80
Paste A-2[3]	59.10	0.38	15.70
Paste A-3[4]	54.80	0.15	32.40

[1]Brunauer-Emmett-Teller.
[2]About 2.7 ml of TiO_2 colloidal solution mixed with 0.7 ml of Ti-alkoxide precursor solution.
[3]About 2.7 ml of TiO_2 colloidal solution mixed with 1.0 ml of Ti-alkoxide precursor solution.
[4]About 2.7 ml of TiO_2 colloidal solution mixed with 2.0 ml of Ti-alkoxide precursor solution.

by the cell efficiency, with a high short-circuit current (J_{sc}) value of 6.54 mA/cm^2 being obtained. Under these conditions, the surface area and pore diameter were measured to be 59.10 m^2/g and 15.70 nm, respectively.

3.3. *Characterization of Single- and Double-Layered TiO_2 Electrodes*

As previously tested, we fabricated single- and double-layered TiO2 electrodes using Paste A-2, Paste B, and Paste C and characterized them.

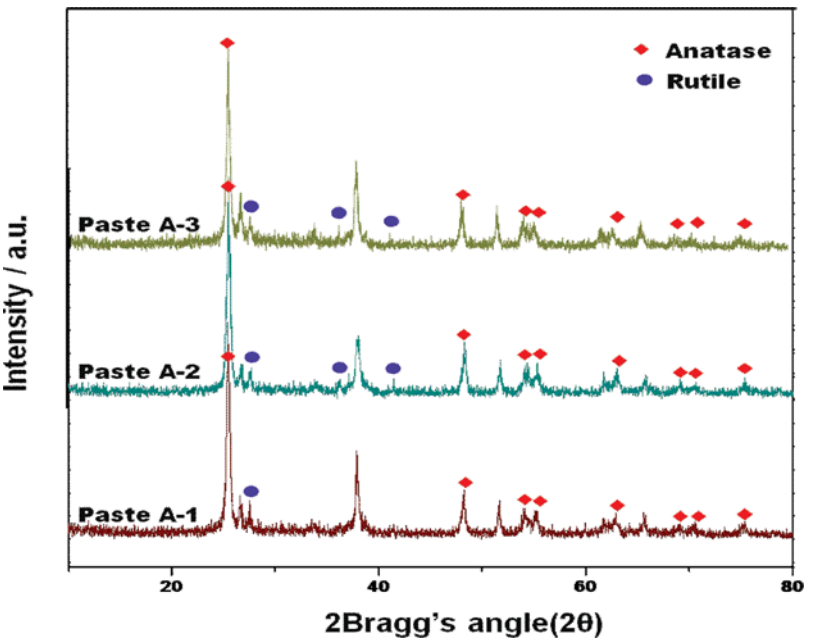

Figure 2. The X-ray diffraction-patterns of the TiO_2 films calcined at 140°C based on different Ti-alkoxide precursor solution amounts.

Table 2. Photovoltaic performances of flexible DSSCs using TiO_2 films based on various Ti-alkoxide precursor solution amounts using PEG polymer electrolyte under light density: 100 mW/cm^2; AM 1.5, active area: 0.25 cm^2

	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor	Efficiency (%)
Paste A-1[1]	0.68	4.84	0.62	2.06
Paste A-2[2]	0.66	6.54	0.63	2.74
Paste A-3[3]	0.64	6.07	0.64	2.51

[1]About 2.7 ml of TiO_2 colloidal solution mixed with 0.7 ml of Ti-alkoxide precursor solution.
[2]About 2.7 ml of TiO_2 colloidal solution mixed with 1.0 ml of Ti-alkoxide precursor solution.
[3]About 2.7 ml of TiO_2 colloidal solution mixed with 2.0 ml of Ti-alkoxide precursor solution.

Figure 3 shows the SEM images of the single- and double-layered TiO_2 electrodes with the scattering layers after sintering at 140°C. Small grains are observed within the highly porous 20 nm TiO_2 layer structure prepared using commercially available Degussa P25 TiO_2. In fact, this morphology is very similar to that of the porous nanocrystalline TiO_2 film prepared by the standard high temperature method at temperatures over 500°C, in which relatively large grains are clumped together within the 123 nm and 200 nm TiO_2 layer structures. The thicknesses of the single- and double-layered TiO_2 electrodes measured by SEM were about 8∼15 μm. For the Type B and C double-layered TiO_2 electrodes, the light scattering layers formed by Pastes B and C were observed to have a thickness of about 5∼7 μm, which is sufficient for the light scattering effect.

The UV-Vis absorbance and transmittance spectra of the single- and double-layered TiO_2 electrodes after sintering at 140°C are shown in Figure 4. Figure 4 (a) shows the absorbance spectra of the three types of TiO_2 electrodes on the

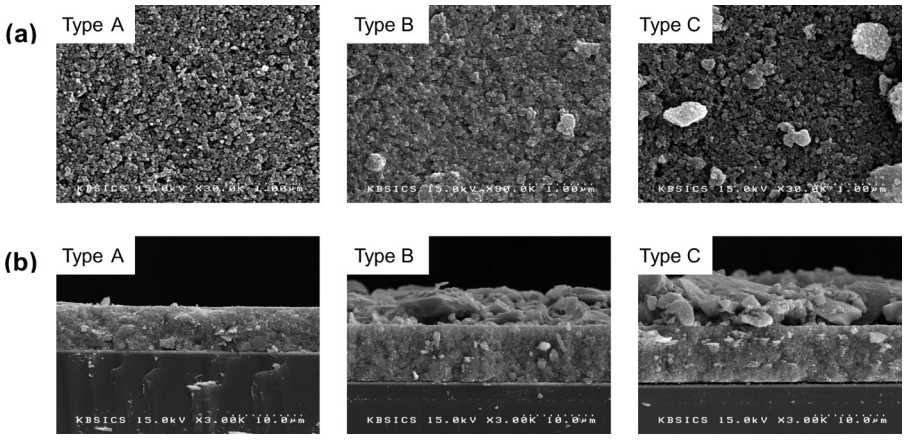

Figure 3. SEM images of the single- and double-layered TiO_2 electrodes of Type A, B, and C for the low temperature fabrication after sintering at 140°C.

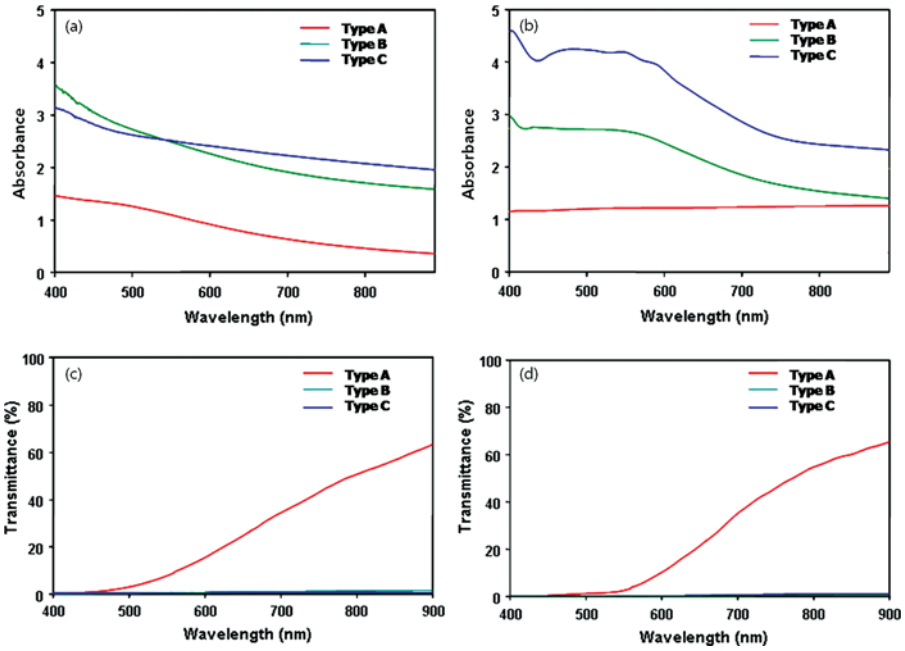

Figure 4. Absorbance and transmittance spectra of the single- and double-layered TiO_2 electrodes of Type A, B, and C after sintering. (a) absorbance spectra of the TiO_2 electrodes, (b) absorbance spectra of the N3 dye adsorbed the TiO_2 electrodes on the ITO-PEN film, and (c) transmittance spectra of the TiO_2 electrodes, (d) transmittance spectra of the N3 dye adsorbed the TiO_2 electrodes on the ITO-PEN film.

ITO-PEN film, and Figure 4 (b) shows that of the TiO_2 electrodes in which the N3 dye is adsorbed on the ITO-PEN film. The absorbance of the TiO_2 electrodes is remarkably increased by the introduction of the light scattering layers. The high absorbance of the double-layered TiO_2 electrodes in the region of 650–750 nm, because of the light scattering by Pastes B and C, is apparent in their absorbance spectra.

Figure 4 (c) and 4 (d) show the transmittances of the single- and double-layered TiO_2 electrodes after sintering at 140°C. The transmittances of the electrodes were decreased by the use of large TiO_2 particles or by the addition of the light scattering layers. Particularly, the type B and C electrodes based on Pastes B and C, respectively, showed a transmittance of nearly 0% in the visible and near-IR region. The introduction of the scattering layers with the larger TiO_2 particles, viz. the 123 nm- and 200 nm-TiO_2 layers, clearly improves the cell performances, especially the J_{sc} value for light collection in the device.

3.4. *Photovoltaic Properties of Flexible DSSC Devices using Single- and Double-Layered TiO_2 Electrodes*

The as-prepared TiO_2 films on the ITO-PEN film substrate were examined as working electrodes in flexible DSSCs. The I-V curves of the flexible DSSC devices constructed with the various TiO_2 electrodes and PEG-EEM electrolytes under AM 1.5 illumination are shown in Figure 5 and their photovoltaic characteristics

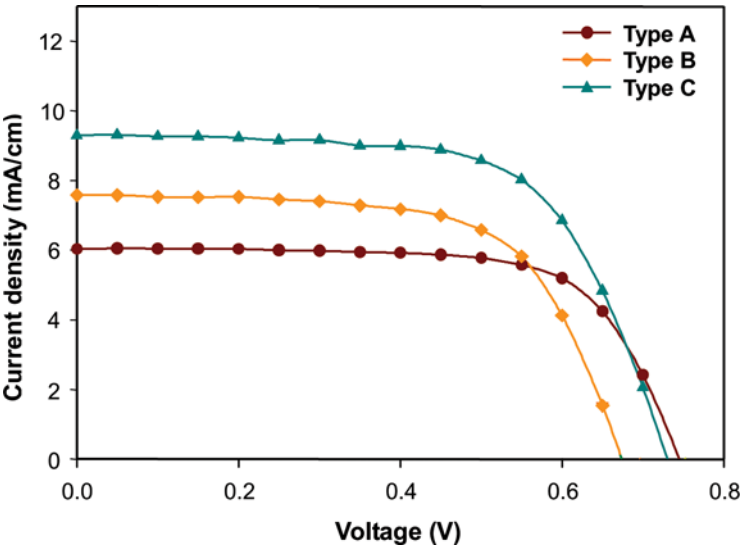

Figure 5. I-V characteristics of flexible DSSCs using the single- and double-layered TiO_2 electrodes of Type A, B, and C using PEG-EEM polymer electrolyte under light density: 100 mW/cm^2; AM 1.5, active area: 0.25 cm^2.

are summarized in Table 3. The highest conversion efficiency of 4.41% was achieved for the cells employing the films prepared with Pastes A-2 and Paste C for the scattering layer, in spite of the ITO-PEN film substrate. With the addition of the scattering layers, the J_{sc} value of the flexible DSSCs was greatly enhanced. The photocurrent of the Type C device was increased by up to 54%, from 6.03 to 9.29 mA/cm^2, compared to that of the Type A device without the scattering layers.

The use of film substrates requires nanoporous TiO_2 films to be used as the working electrode to improve the efficiency of energy conversion and the introduction of the nanoporous scattering layer is a particularly effective method of accomplishing this. The TiO_2 electrodes using Pastes D and E as the light scattering layers enhanced the photocurrent density and cell conversion efficiency of the flexible DSSCs using polymer electrolytes.

Table 3. Photovoltaic performances of flexible DSSCs using the single- and double-layered TiO_2 electrodes of Type A, B, and C using PEG-EEM polymer electrolyte under light density: 100 mW/cm^2; AM 1.5, active area: 0.25 cm^2

Type of structure	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor	Efficiency (%)
Type A[1]	0.75	6.03	0.69	3.12
Type B[2]	0.67	7.58	0.65	3.29
Type C[3]	0.73	9.29	0.65	4.41

[1]Single-layered TiO_2 film consisting of Paste A-2 with average diameters of 20 nm.
[2]Double-layered TiO_2 films consisting of different pastes (Paste A-2 and Paste B), which were composed of TiO_2 particles with average diameters of 20 nm and 123 nm, respectively.
[3]Double-layered TiO_2 films consisting of different pastes (Paste A-2 and Paste C), which were composed of TiO_2 particles with average diameters of 20 nm and 200 nm, respectively.

4. Conclusion

In this study, we examined the low-temperature fabrication of TiO_2 electrodes for use in flexible DSSCs using a Ti-alkoxide precursor solution prepared by the sol-gel method. Flexible DSSCs using PEG-EEM electrolyte with single- and double-layered TiO_2 electrodes were fabricated on an ITO-PEN film substrate and their performances were investigated.

By introducing the light scattering layer, the J_{sc} as well as the fill factor in the DSSCs were improved. Moreover, the overall power conversion efficiency of the DSSCs based on the ITO-PEN film substrate was increased to 4.41%. Especially, the flexible DSSCs using the low temperature calcination method achieved higher values of the open-circuit voltage, short-circuit current and cell conversion efficiency than those of the flexible DSSCs using commercial TiO_2 pastes.

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