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# Supercritical fluid processing of mesoporous crystalline TiO$_2$ thin films for highly efficient dye-sensitized solar cells†

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In this study, a high light-to-electricity conversion efficiency of 5.14% was achieved by applying a TiO$_2$ thin film with a thickness of 1.87 μm as an electrode material under an AM 1.5 solar light (100 mW cm$^{-2}$). This high efficiency can be attributed to post-treatment by the supercritical fluid process and the addition of nanoparticles to the thin film. Supercritical fluid treatment is shown to significantly enhance the thermal stability of these thin films. Thus, the high porosity of the treated films was maintained even upon calcination at a high temperature. Additionally, the addition of crystalline light scattering nanoparticles in the thin film not only increases the crystallinity of the thin films but also ensures capture of the incident light and increases the efficiency of light harvesting. The thin film with well-preserved mesopores among the nanoparticles can capture the incident light efficiently and further increase efficiency of light harvesting, which leads to the remarkably high light-to-electricity conversion efficiency.

## Introduction

Dye-sensitized solar cells (DSSCs) are expected to be a regenerative low-cost alternative to conventional solid-state p–n junction solar cells.[1] Currently, this kind of solar cell reaches an efficiency exceeding 11% using nanocrystalline TiO$_2$ as the electrode material.[2] However, such high efficiencies are not easy to achieve, and are still far from the theoretical efficiency of 33%.[3] Recent research has been directed towards improving the efficiency by developing new sensitizers, new electrolytes and new electrode materials. A variety of semiconductor oxides such as ZnO,[4] SnO$_2$,[5] Nb$_2$O$_5$,[6] and TiO$_2$[7,8] have been tried as electrode films in DSSCs, but only TiO$_2$, especially in its anatase phase, has shown high light-to-electricity efficiency.[8] In order to further improve their photovoltaic properties, the electrode TiO$_2$ films have been modified by using surface coatings or light scattering particles/layers.[9,10] However, the utilization of a supercritical fluid process in the preparation of the electrode TiO$_2$ films for DSSCs has not been reported to date. In this study, a series of TiO$_2$ thin films composed of mesopores and nanoparticles were prepared by a spin-coating process and then treated by a supercritical fluid process with a small volume of titanium tetraisoproxide [Ti(OPr$^i$)$_4$]. These treated TiO$_2$ thin films were

introduced into a DSSC and obtained a remarkably high efficiency of 5.14% (film thickness = 1.87 μm) under illumination of simulated AM 1.5 solar light (100 mW cm$^{-2}$). The effects of adding particles to the electrode thin film and the post-treatment by the supercritical fluid process on the photovoltaic performances are discussed.

## Experimental

### Preparation of TiO$_2$ films

A sol with a molar composition of 1.0 : 0.02 : 2.4 : 35 Ti(OPr$^i$)$_4$ : P123 : HCl : EtOH was prepared according to the procedure reported previously.[11,12] 0.5 g of P25 (Degussa, Germany, 30% rutile and 70% anatase, particle size 25 nm) was added to 5 mL of the above sol and dispersed using an ultrasonic horn for one hour. Titania films were coated on fluorine doped SnO$_2$-coated conductive glass (Nippon sheet glass, 8–10 Ω sq$^{-1}$) at room temperature by a spin-coating method. The resulting films was subsequently aged at room temperature and then at 60 °C for 24 h to facilitate the evaporation-induced self-assembly process before being annealed at 150 °C for 24 h.

### Supercritical fluid treatment

The post-treatment of the films by the supercritical CO$_2$ (sc-CO$_2$) was carried out following the procedure reported previously.[12] In a N$_2$ glovebox, the films were placed into a 20 mL high-pressure cell with a small volume of Ti(OPr$^i$)$_4$ (<0.02 mL). The cell was then attached to a stainless steel reservoir (60 mL) via a three-way valve. A high-pressure pump (ISCO Instruments, PA) was used to pump CO$_2$ (99.99%) through the reservoir into the reaction cell. The cell was pressurized to between 34.5 and 58.6 MPa with CO$_2$ and placed in a furnace at temperatures ranging from 60 to 100 °C. The reaction was allowed to proceed under these conditions

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† Electronic supplementary information (ESI) available: SEM image of mesoporous titania film with a thickness of about 2.6 μm showing the cracked surface. See DOI: 10.1039/b706569h

for approximately 30 min. The films were calcined at a temperature of 400 °C for about 3 h before the characterization and solar cell fabrication.

**Warning**: High-pressure equipment such as that required for the experiments described in this paper should be equipped with a relief valve and/or a rupture disk to minimize risk or personal injury.

### Characterization of the TiO₂ films

X-Ray diffraction (XRD) patterns were recorded $\theta$–$2\theta$ mode on a Philips X'pert PW3710 diffractometer. The microstructure of the samples was characterized by transmission electron microscopy (TEM) (JEOL 2000EX TEM at 200 kV). Samples scratched from the substrate were suspended in ethanol by sonication. Carbon-coated copper grids were used as the sample holders. To evaluate the morphology of the film surface, scanning electron microscopy (SEM) was performed on a JEOL JSM-5510 scanning microscope operating at 10 kV.

### Preparation of a dye-sensitized thin film of mesoporous TiO₂

The TiO₂ thin films were calcined at 400 °C and used as the electrode materials in DSSCs. A 50 mM aqueous solution of TiCl₄ (Wako Chemical) was dropped onto the TiO₂ thin film and kept at 70 °C for more than 30 min. After TiCl₄ treatment, the film was calcined at 400 °C for 30 min in air. The thickness of the TiO₂ films was determined by using an Alpha-Step 300 profiler (Tencor Instruments). The apparent surface area of the TiO₂ film electrode was measured with a microscope (Nikon, model C-PS) was 0.24–0.27 cm² (*ca*. 0.5 cm × 0.5 cm).

Dye N719 [*cis*-di(thiocyanato)-*N*,*N*′-bis(2,2-bipyridyl-4-carboxylate-4′-tetrabutyl ammonium carboxylate) ruthenium (II), Solaronix] (0.3 mM) was dissolved in ethanol (Kanto Chemical Co.). The TiO₂ thin films were immersed into the dye solution and then kept at 25 °C for 3–5 d so that the dye could be adsorbed onto the surface of the TiO₂ electrodes. After dye adsorption, the color of TiO₂ thin films changed to a deep red.

### Solar cell assembly

The dye-sensitized TiO₂ electrode was incorporated into a thin layer, sandwiched solar cell. The area of the TiO₂ electrodes was 0.5 × 0.5 cm. The counterelectrode was Pt sputtered on a transparent conducting glass using an ion coater (Eiko engineering, IB-5). A polyethylene spacer (30 and 60 μm thickness) was used to prevent the cell from short-circuiting when the counter and working electrodes were clamped together. The electrolyte consisted of 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI), 0.1 M LiI, and 0.05 M I₂ in acetonitrile (AN) with 0.5 M 4-*tert*-butylpyridine (TBP). Reagent-grade LiI (Wako) and I₂ (Wako) were used for the electrolyte. TBP (Aldrich) and AN (Aldrich and Tokyo Kasei) were distilled before use. DMPImI was synthesized from 1,2-dimethylimidazolium (Tokyo Kasei) and *n*-propyl iodide (Tokyo Kasei).

### Photovoltaic characterizations

The photovoltaic measurements were conducted by using a Xe lamp light source simulating the AM 1.5 spectrum (Wacom,

WXS-80C-3, 100 mW cm⁻²). The incident light intensity was calibrated with a standard solar cell for amorphous silicon solar cells produced by the Japan Quality Assurance Organization. Action spectra of the incident monochromatic photon-to-current conversion efficiency (IPCE) was measured by using a CEP-99W system (Bunkon-keiki Co., Ltd.).

## Results and discussions

The function of the solar cell is characterized by several parameters, such as the short-circuit photocurrent ($J_{sc}$), the open-circuit photovoltage ($V_{oc}$), the fill factor (FF), and the light-to-electricity conversion efficiency ($\eta$). Fig. 1 shows typical photocurrent–voltage characteristics and the photocurrent action spectrum of a sealed cell composed of mesoporous TiO₂ and P25 nanoparticles which were treated by the supercritical fluid process. A light-to-electricity conversion efficiency of 5.14% was reached for a sealed cell with a thickness of 1.87 μm (1 Sun, AM 1.5, 100 mW cm⁻², without a mask and anti-reflection film on the surface of the cells). The $J_{sc}$, $V_{oc}$, and FF are 9.97 mA cm⁻², 0.748 V and 0.689, respectively. In order to avoid the irradiation of light from the
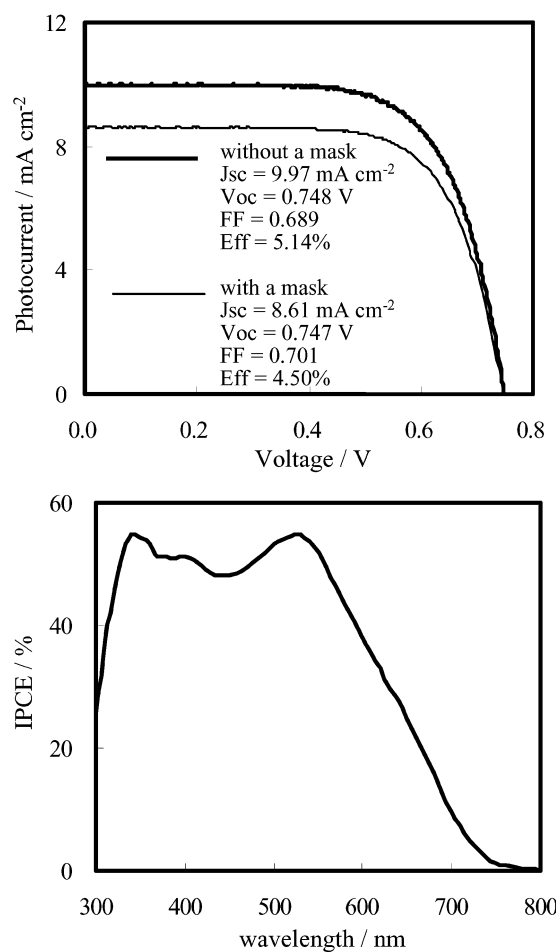


**Fig. 1** Illustration of the *I*–*V* characteristics of a sealed cell composed of mesoporous TiO₂ and P25 nanoparticles treated by the supercritical fluid process. The film thickness and size of a sealed cell are 1.87 μm and 0.5 cm × 0.5 cm, respectively. The sealed cell was measured under AM 1.5 solar light (100 mW cm⁻²).

glass substrates, a black photomask was used to put on the cell surface. The $J_{sc}$ decreased from 9.97 to 8.61 mA cm$^{-2}$, while the $V_{oc}$ remained almost unchanged. A monochromatic incident photon-to-current conversion efficiency (IPCE) of 54.5% was reached at 520 nm, confirming a high $\eta$ for the cell with a thin thickness.

Several research groups have reported highly efficient dye-sensitized solar cells composed of mesoporous TiO$_2$ thin films. Using the dip coating process, Grätzel's group prepared mesoporous TiO$_2$ films with a thin thickness of 1 μm and used it as the electrode material for DSSCs.[13] An efficiency of 4.04% was obtained with a black photomask under AM 1.5 solar light. An efficiency of 5.05% was reached by using mesoporous TiO$_2$ as the electrode film by Kartini et al.,[14] but the film thickness was not reported. Hou et al.[15] also reported a highly efficient DSSC made of mesoporous TiO$_2$ with a thickness of 2.5 μm and an efficiency of 5.31% was achieved under non-standard conditions (500 W Xe lamp). More recently, we also reported an efficiency of 10% based on mesoporous TiO$_2$ with a thickness of ca. 27 μm.[16] Even though mesoporous TiO$_2$ has successfully been used as the electrode material in DSSCs, the highly efficient dye-sensitized solar cells made of thin thickness films are still full of challenges because of the potential due to applications in cellular phones, ID cards and watches, in which the glass substrate is replaced by plastic materials and lightweight, thin, and low-cost DSSCs. Here, an efficiency of 5.14% was achieved by using a thin thickness TiO$_2$ film as the electrode material. This high efficiency is attributed to the modification of TiO$_2$ electrodes by adding nanoparticles into the film and post-treatment with a super-critical fluid process.

Fig. 2 depicts the results of characterization of the electrode TiO$_2$ films prepared by the spin-coating process. The films were scratched off a glass substrate and observed by TEM. Fig. 2(a) shows a TEM image of sc-CO$_2$ treated TiO$_2$ thin films without the addition of P25 nanoparticles. When calcined at a high temperature, the ordered mesoporous frameworks of metal oxide thin films are prone to collapse because of the crystallization of the metal oxides in the mesoporous walls. The well-preserved hexagonal-packed mesopores after calcina-tion at a temperature of about 400 °C indicates the high thermal stability of the treated films, which is consistent with our previous observations.[11,12] As shown in Fig. 2(b) and 2(c), it can be clearly seen that nanocrystalline particles with an average size of approximately 25 nm, which is consistent with the size of P25 particles, were well dispersed within the films. The nanoparticles were well connected by mesoporous titania formed during the evaporation-induced self-assembly process from the starting sol. The precursor gel was believed to occupy the interparticle voids and the limited space would give some influence on the alignment of the micelles formed and resulted in the irregular mesoporous structure of these titania films. After calcination at a temperature above 400 °C, the meso-pores in the films without the sc-CO$_2$ treatment were seen to partially collapse due to the crystallization of the inorganic framework, and the decomposition and release of the surfactant in the mesopores. In agreement with our previous observations,[11,12] the sc-CO$_2$ treatment could significantly enhance the thermal stability of mesoporous titania films. The
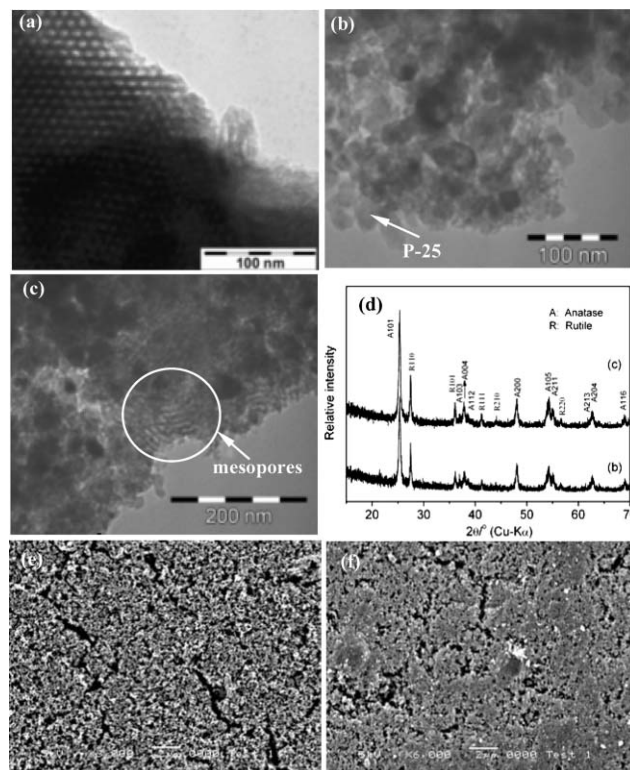


**Fig. 2** TEM images of electrode films (a) mesoporous TiO$_2$ treated by the sc-CO$_2$, and films composed of mesoporous and nanoparticles (b) without the sc-CO$_2$ treatment and (c) with the sc-CO$_2$ treatment. (d) XRD patterns of TiO$_2$ electrode films of (b) and (c). (e) and (f) SEM images corresponding to TiO$_2$ films of (b) and (c), respectively. All of the films were calcined at 400 °C for 3 h before characterization.

well-preserved mesopores among the P25 nanoparticles when subjected to high temperature calcination increased the specific surface area of these films. Fig. 2(d) shows the diffraction patterns of titania films with and without the sc-CO$_2$ treatment. The resulting crystal phases of these titania films were mainly anatase, with the presence of a small amount of rutile introduced by the P25 nanoparticles. Compared to that of the sample without the sc-CO$_2$ treatment, the $d_{101}$ diffraction of anatase in the sample treated by the sc-CO$_2$ method is much stronger. The increase in intensity of the $d_{101}$ diffraction peak indicates the higher crystallinity of anatase after the treatment. SEM images of the titania films show rough surfaces which resulted from the interparticle pores making it easy for the dye molecules to penetrate into the films [Fig. 2(e) and 2(f)]. While compared to the films without sc-CO$_2$ treatment, a thin layer of scattered TiO$_2$ particles can be clearly observed on the surface of the TiO$_2$ film treated by the sc-CO$_2$ with a small volume of Ti(OPr$^i$)$_4$.

To compare the effect of adding nanoparticles to the thin films and post-treatment by the supercritical fluid process on the photovoltaic performance, three cells with a similar thickness were fabricated and measured under the same conditions. As depicted in Fig. 3A curve a, the electrode film of a cell composed of mesoporous TiO$_2$ is transparent, and the $J_{sc}$, $V_{oc}$ and $\eta$ are 2.85 mA cm$^{-2}$, 0.675 V and 1.26%, respectively. After the TiO$_2$ nanoparticles (P25) were added to
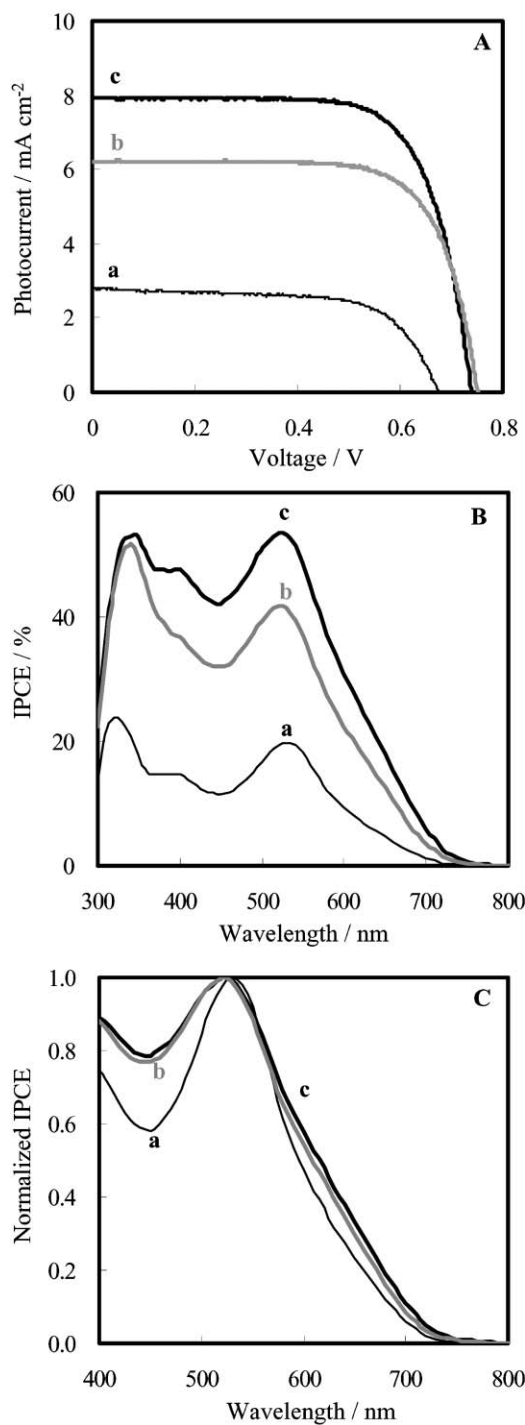
**Fig. 3** (A) Illustration of the I–V characteristics, (B) IPCE and (C) normalized IPCE of three sealed cells composed of TiO$_2$ films. (a) Mesoporous TiO$_2$ film with 1.44 μm thickness treated by sc-CO$_2$; (b) the film composed of mesoporous TiO$_2$ and P25 nanoparticles with a thickness of 1.36 μm without sc-CO$_2$ treatment and (c) the film composed of mesoporous TiO$_2$ and P25 nanoparticles with a thickness of 1.42 μm treated by sc-CO$_2$. All results were obtained without a black photomask and anti-reflection film on the surface of cell under 1.5 AM solar light (100 mW cm$^{-2}$).

the sol and coated on the conducting glass, the opaque film was composed of mesoporus TiO$_2$ and P25 nanoparticles. It can be seen from curve b of Fig. 3A that the photovoltaic

properties of the cell composed of the opaque film were improved significantly. The $J_{sc}$, $V_{oc}$ and $\eta$ increase to 6.21 mA cm$^{-2}$, 0.72 V and 3.36%, respectively. This can be attributed to the high crystallinity of the thin films derived from the crystallized nanoparticles and the efficient light harvest in the cell resuling from the light scattering by the nanoparticles in the TiO$_2$ electrode films.[9] Curve c of Fig. 3A shows the I–V curve of a cell composed of mesoporous TiO$_2$ and P25 nanoparticles which was treated by the supercritical fluid process. It clearly shows that the $J_{sc}$ and $\eta$ increase to 7.92 mA cm$^{-2}$ and 4.18%, indicating that the photovoltaic properties of the cell can be improved obviously by the post-treatment. As mentioned above, the mesopores TiO$_2$ in the film without the sc-CO$_2$ treatment collapsed after calcination at temperatures above 400 °C, while the thermal stability of the mesoporous TiO$_2$ films treated by the sc-CO$_2$ could be enhanced significantly and the porosity of the treated films was still well-preserved. The well-preserved mesopores among the P25 nanoparticles increase the specific surface area of these films and tend to adsorb more dye molecules, resulting in increased photocurrent density. Fig. 3B shows the dependence of the absolute and normalized values of the IPCE on wavelength for the three cells mentioned above. Compared to the cell made of transparent TiO$_2$ film, the IPCE of the cell composed of mesoporous TiO$_2$ and P25 nanoparticles (opaque film) increased significantly from 19.8% to 41.7%. After the film was treated by the sc-CO$_2$, the IPCE further increased to 53%. This result indicates that the addition of nanoparticles to the films followed by the sc-CO$_2$ is contributing to the increase in the efficiency of light harvest. Fig. 3C exhibits plots of the IPCE data normalized with respect to the intensity of the peak at 520 nm. Clearly, the cell composed of mesoporous TiO$_2$ and P25 nanoparticles exhibits a higher IPCE in both the short (400–520 nm) and long (550–800 nm) spectral ranges. This indicates that the light absorption by the iodide species (I$_3^-$) in the electrolyte is accentuated in the short-wavelength range and thus, red light is more effectively utilized in the films containing mesoporous and particles.[17,18]

The photovoltaic performances of DSSCs largely depend on the film thickness. As depicted in Fig. 4, the efficiency of the
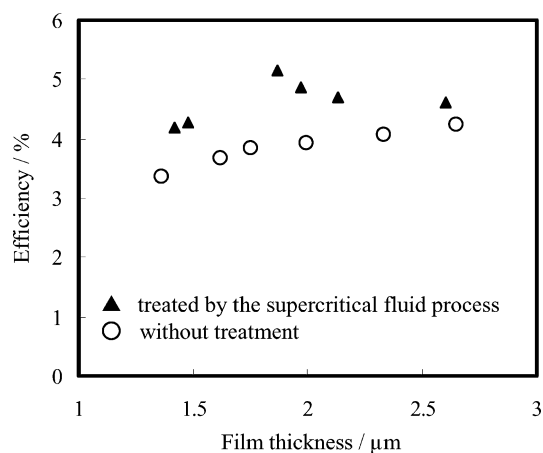


**Fig. 4** The dependence of efficiency on film thickness with and without treatment by the supercritical fluid process.

cells exhibits an obviously linear increase with an increase in film thickness, in which the cells were composed of mesoporous $TiO_2$ and P25 nanoparticles without the sc-$CO_2$ treatment. On the contrary, for a film thickness of less than 1.9 μm the efficiency shows a significant linear increase with an increase in the thickness of films treated with sc-$CO_2$. However, above 1.9 μm the efficiency decreases when the thickness of films further increases. This might be related to the sc-$CO_2$ treatment. For the films with thicknesses of less than 1.9 μm, Ti species generated from $Ti(OPr^i)_4$ molecules could easily penetrate into these films under sc-$CO_2$ conditions, which would efficiently enhance the porosity and crystallinity of these films. Thus, more dye molecules would be absorbed into the well-preserved mesopores and the electrolyte solution could also easily access these mesopores, which would significantly enhance the light-to-electricity conversion efficiency. While for the films thicker than 1.9 μm, the supercritical $CO_2$ could treat only the outer layers of the films due to its limited penetration ability. However, as suggested by Grätzel and coworkers,[19] the outer layers do not contribute significantly to the photogeneration of conduction-band electrons, due to the filtering of light by the dyed particles located close to the FTO glasses. Thus, there is only a slight increase in the energy conversion efficiency for the thicker $TiO_2$ electrode films. Moreover, with increasing film thickness, some cracks on the surface of the film were observed (see ESI†). This might be another reason why the efficiency tends to slightly increase for films with a thickness of above 1.9 μm.

The effect of scattering particles in the thin film and post-treatment by a supercritical fluid process on light capture is illustrated in Scheme 1. The electrode made of mesoporous $TiO_2$ is a transparent film, thus, the majority of incident light cannot be captured in the films. This is a reason why the IPCE value is less than 20% and $J_{sc}$ is only 2.65 mA cm$^{-2}$ for a cell composed of transparent film. After adding nanoparticles into the film, a opaque film was obtained. As shown in Scheme 1(b), the majority of incident light can be captured in the presence of scattering particles in the film, resulting in an increase in the efficiency of light harvesting. This is also evidenced by the result of IPCE measurements. The IPCE value increased from 19.8% to 41.7% when the opaque $TiO_2$ film composed of mesoporous $TiO_2$ and P25 nanoparticles was used as the electrode material. According to report by Tachibana et al.,[20] large size particles can be used as light scatterers to increase efficiency of light harvesting. However, in this study, the efficiency of light harvesting was also increased by addition of
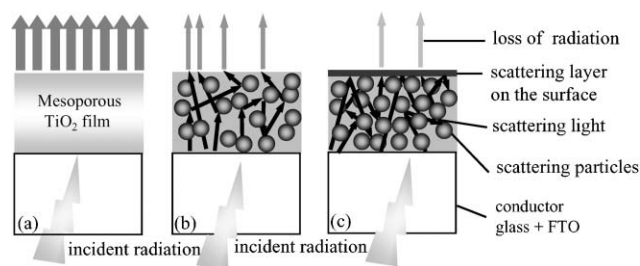
P25 nanoparticles. This might be attributed to aggregation of partial P25 particles and formed big size "particles" in the electrode preparation process. As mentioned above, the mesopores in the film without the sc-$CO_2$ treatment were collapsed after they were calcined at temperatures above 400 °C, resulting in the formation of intervals in the film and a decrease of the light harvesting efficiency. On the contrary, the sc-$CO_2$ treatment could significantly enhance the thermal stability. Thus, the porosity of the treated films was still well-preserved after they were calcined at a high temperature. The film with well-preserved mesopores among the nanoparticles can capture the incident light efficiently and increase the efficiency of light harvest. On the other hand, a scattering layer on the surface of the thin films was formed after the thin film was treated by the supercritical fluid process, as observed in SEM image [Fig. 2(f)]. As a result, the loss of incident radiation decreased and the efficiency of light harvesting further increased.

## Conclusions

In this study, a high light-to-electricity conversion efficiency of 5.14% was achieved by applying a $TiO_2$ thin film with a thickness of 1.87 μm as an electrode material, in which the film is composed of mesoporous $TiO_2$ and P25 nanoparticles and then treated by a supercritical fluid process. This high efficiency can be attributed to both the post-treatment by the supercritical fluid process and the addition of nanoparticles in the thin film. The films treated by the supercritical fluid process could significantly enhance their thermal stability. Thus, the porosity of the treated films was still well-preserved upon calcination at a high temperature. On the other hand, the addition of light scattering particles in the thin films ensures capture of the incident light and increases the efficiency of light harvest. The films with well-preserved mesopores among the nanoparticles can capture the incident light efficiently and further increase the efficiency of light harvest. Moreover, a scattering layer on the surface of the thin films was formed after the thin film was treated by the supercritical fluid process, and resulted in decreased loss of incident radiation and increased further the efficiency of light harvesting. The photovoltaic properties of the DSSCs, composed of $TiO_2$ thin films with a treatment by the supercritical fluid process, are expected to be further improved through the use of a new electrolyte and a new dye. Therefore, $TiO_2$ thin film treated by the supercritical fluid process can be used as an electrode material in DSSCs which may provide a means of obtaining higher efficiency of plastic substrate-based DSSCs.

**Scheme 1** Light capture in the electrode films. (a) Mesoporous $TiO_2$ film treated by the sc-$CO_2$, and the film composed of mesoporous and particles without sc-$CO_2$ treatment (b) and with sc-$CO_2$ treatment (c).

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