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Shape- and Morphology-controlled Metal Organic Framework Template for High-Efficiency Solid-state Dye-Sensitized Solar Cells

Won Seok Chi‡, Dong Kyu Roh‡, Chang Soo Lee, Jong Hak Kim*

This report provides a facile process to produce shape- and morphology-controlled MIL-125(Ti), a subclass of metal organic frameworks (MOFs) using poly(ethylene glycol) diglycidyl ether (PEGDGE) as a structure directing agent. Upon deliberate calcination, MIL-125(Ti) is converted to mesoporous hierarchical TiO2 (hier-TiO2) with anatase phase, a large surface area and a variety of nanostructures. The morphology changes from 200-nm circular plates to 1-µm bipyramid with increasing PEGDGE amount, indicating the pivotal role of PEGDGE as a shape controller. When the hier-TiO2 is deposited onto a nanocrystalline TiO2 (nc-TiO2) layer as the scattering layer, the dye-sensitized solar cell (DSSC) with a quasi-solid-state polymer electrolyte records a high conversion efficiency (7.1% at 100 mW/cm2), which is much higher than that of DSSCs with nc-TiO2 layer only (4.6%) or with a commercial scattering TiO2 (cs-TiO2) on a nc-TiO2 layer (5.0%). A solid-state DSSC using a single component solid polymer, i.e., poly((1-(4-ethenylphenyl)methyl)-3-butyl-imidazolium iodide (PEBII), also exhibits excellent efficiency of up to 8.0%. The improved efficiency results from the pivotal role of the hier-TiO2 in improving the surface area and light harvesting properties, as demonstrated by N2 adsorption/desorption isotherm, reflectance spectroscopy, incident photon-to-current efficiency (IPCE), and electrochemical impedance spectroscopy (EIS) analyses.

Introduction

There has been a large focus on dye-sensitized solar cells (DSSCs) as a promising alternative to conventional silicone solar cells because of their high efficiency, low cost, and easy fabrication. Most of the current research has focused on enhancement of device performance, which can be achieved through the development of novel sensitizers, metal oxide photoanodes, catalytic counter electrodes, or electrolytes. Among these, the photoanode is an especially important component as it directly affects dye absorption, light trapping ability, charge recombination, and interfacial contact between electrode and electrolyte. Typically, mesoporous TiO2 is employed as a photoanode material because of its suitable energy level, superior dye absorption ability, and ease of structure control.

As a main element of photoanodes, a nanocrystalline TiO2 layer is generally deposited on a transparent conducting oxide substrate for dye adsorption. However, this approach has some disadvantages such as low surface area, poor interconnectivity, and smaller light scattering ability because of the poorly organized morphology resulting from small and regular particle size without effective pores. To address these issues, light scattering particles with a large size were deposited onto a nanocrystalline TiO2 layer to harvest reflecting light. This method increased the light scattering ability as well as the dye loading amount of the photoanode, resulting in enhanced solar energy conversion efficiency in DSSCs.

Despite the high-energy conversion efficiency of DSSCs based on a conventional liquid electrolyte, solid-state or quasi-solid-state DSSCs have recently received great attention because of the need for long-term stability, flexible design, and lightweight cells. In particular, DSSCs with enhanced energy conversion efficiency and long-term stability need to be developed for future applications such as building integrated photovoltaics. Not only for DSSC, but also for energy storage devices such as rechargeable batteries, the design of solid-state electrolyte is of pivotal importance to obtain durable performance as well as high efficiency. One important consideration for such DSSCs is to obtain deep penetration of solid electrolytes with large molecular volume into the TiO2 mesopores, which is largely affected by the pore size, porosity, and pore interconnectivity. Despite much progress in incorporating solid-state or quasi-solid electrolytes, there have not been extensive efforts to enhance the device performance by modification of photoanode structures.

Metal organic frameworks (MOFs) have been widely investigated for their attractive unique properties, which can be tuneable by the design of the coordination between metal ions.
and organic linkers. MOFs can possess infinite features such as frameworks geometries, pore sizes, and functionalities by tailoring both organic ligand and metal selection. Their highly flexible potential make them candidates for wide applications in the field of gas adsorption separation, catalysts, sensors, and batteries, which are in demand for sustainable and renewable energy devices.\textsuperscript{32-34}

Recently, MOFs have been researched as promising photovoltaic materials in DSSCs. Cu-based MOFs were substituted as a new sensitizer instead of N719 dye using a layer-by-layer technique.\textsuperscript{35} Mg-MOF was introduced into a polymer composite electrolyte by UV radiation, which increased the photoenergy conversion efficiency through interactions between carboxyl groups in Mg-MOF and hydroxyl groups in the TiO\textsubscript{2} surface layer.\textsuperscript{36} Furthermore, a metal-organic gel electrolyte composed by coordination of Al\textsuperscript{3+} and 1,3,5-benzenetricarboxylate provided good accommodation ability.\textsuperscript{37} For electrode application, MOFs worked as both template and precursor to provide functional materials with a high surface area retaining particle morphology. Cobalt sulfide nanoparticles derived from surfactant assisted the preparation of zeolite imidazole framework-67 (ZIF-67) with high surface area and good catalytic properties. As a result, CoS-derived counter electrode-based DSSCs showed a higher solar power conversion efficiency than Pt-based counter electrodes.\textsuperscript{38} Leaf-like ZIF film was also converted to a porous ZnO nanosheet photoanode, which enabled high dye loading, efficient electrolyte diffusion, rapid dye adsorption by nanoparticles, and good light harvesting ability.\textsuperscript{39} Also, hierarchical ZnO parallelepipeds were prepared from MOF-5, a subclass of MOF series, and used as a scattering layer in the DSSCs.\textsuperscript{40} However, most previous studies are based on a ZnO photoanode with which it is difficult to achieve a high efficiency because of the low surface area and dye loading.

In this study, we report a facile way of preparing multifunctional, hierarchical, anatase TiO\textsubscript{2} with large surface area and various morphologies directly derived from MIL-125(Ti), a subclass of MOF series. In particular, poly(ethylene glycol) diglycidyl ether (PEGDGE) was employed as a structure-directing agent to form various MIL-125(Ti) structures. Upon deliberate calcination, MIL-125(Ti) was converted to hierarchical TiO\textsubscript{2} (hier-TiO\textsubscript{2}) with a large surface area and a variety of nanostructures. The hier-TiO\textsubscript{2} synthesized was used to form top scattering layers on a nanocrystalline TiO\textsubscript{2} (nc-TiO\textsubscript{2}) layer for use in DSSC applications, and these hier-TiO\textsubscript{2} layers were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), N\textsubscript{2} adsorption–desorption isotherm analysis, UV-visible light absorption, and reflectance spectroscopy. The performance of DSSCs was investigated by measuring current density–voltage (J-V) curves, incident photon-to-current efficiency (IPCE), and electrochemical impedance spectroscopy (EIS).

### Experimental section

#### Materials

Titanium (IV) butoxide (TBT), terephthalic acid (4-benzeneedicarboxylate, BDC), poly(ethylene glycol) diglycidyl ether (PEGDGE), poly(ethylene glycol) (PEG10k, 10,000 g/mol), lithium iodide (LiI), 1-methyl-3-propylimidazolium iodide (MPII), iodine (I\textsubscript{2}), dimethylformamide (DMF), methanol, ethanol, and acetonitrile were purchased from Aldrich and used without further purification. Ruthenium dye (533-bisTBA, N719) was purchased from Solaronix, and commercially available TiO\textsubscript{2} paste (Dyesol paste, 18NR-T) was purchased from Dyesol. FTO conductive glass was purchased from Pilkington, France.

#### Preparation of MIL-125(Ti)

First, 3.5 g of terephthalic acid was completely dissolved in DMF solvent. Different amounts (0, 0.06, 0.6, and 1.2 ml) of PEGDGE, 1.82 ml of titanium butoxide, and 7 ml of methanol were sequentially added to this solution, followed by stirring for 20-30 min to produce homogeneous mixtures. The resultant solutions were hydrothermally reacted in an autoclave at 150°C for 24 h. The synthesized MIL-125(Ti) was centrifuged at 10,000 rpm for 30 min and washed with fresh methanol several times. The final products were dried in a vacuum oven overnight at 50°C to completely evaporate the DMF. MIL-125(Ti) synthesized using 0, 0.06, 0.6, and 1.2 ml of PEGDGE was named MIL-125(Ti)\textsubscript{1}, MIL-125(Ti)\textsubscript{2}, MIL-125(Ti)\textsubscript{3}, and MIL-125(Ti)\textsubscript{4}, respectively.

#### Conversion of MIL-125(Ti) to hierarchical TiO\textsubscript{2} (hier-TiO\textsubscript{2})

The synthesized MIL-125(Ti) was calcined at 380°C for a long time (i.e., 5 h) with a slow increase in temperature (i.e., 10°C/min) to produce a mesoporous anatase structure while controlling the release of gas from the MIL framework.\textsuperscript{41} Setting temperature moderate was the most important to generate a highly mesoporous structure, while maintaining the basic framework of MIL-125(Ti) without pore blocking and formation of big pores by the connection of small pores.

#### Preparation of photoanodes

As-prepared hier-TiO\textsubscript{2} particles (0.1 g) were dispersed in 1 ml absolute ethanol solvent by sonication and stirring for 5 h. After distribution of particles in solution, 0.4 ml of α-terpinol and 0.05 g of ethyl cellulose were added to the suspension solutions to increase the viscosity. The resultant solutions were sonicated for 30 min and stirred overnight for perfect dissolution of organic materials in the TiO\textsubscript{2} suspension. Ethanol solvents were evaporated during stirring while maintaining a homogeneous state, resulting in the formation of highly viscous TiO\textsubscript{2} paste. As-prepared TiO\textsubscript{2} pastes were doctor-bladed onto the nc-TiO\textsubscript{2} layer and heated in a drying oven at 50°C for 1 h and 80°C for 1 h. This process was performed to prevent crack formation after calcination. Finally, the TiO\textsubscript{2} photoanodes were calcinated at 500°C for 30 min. TiCl\textsubscript{4} post-treatment was not necessary because of the good physical and adhesion properties.
Fabrication of DSSCs

DSSCs with active area of 0.16 cm$^2$ were fabricated according to our previous studies. First, the FTO (Pilkington Co. Ltd., 8 Ω) glass pieces were cut (1.5 cm × 2 cm) and cleaned with acetone and ethanol under sonication. For the blocking layer, Ti(IV) bis(ethyl acetatoaceto) disopropoxide solution in 1-butanol was spin-coated onto FTO glass and then the glass was heated stepwise to 450°C and maintained at this temperature for 30 min. A 6- to 7-μm thick TiO$_2$ layer was prepared on the blocking layer on FTO substrate using commercial TiO$_2$ paste (Dyesol paste, 18NR-T) by the doctor-blade method and then calcinated at 450°C for 30 min, resulting in the formation of a transparent TiO$_2$ photoanode. The TiO$_2$ photoanodes were immersed in dye solution containing 13 mg N719 in 50 ml absolute ethanol solution and incubated in an oven at 50°C for 3 h. The resulting photoanodes were washed with pure ethanol several times and dried by air gun. The Pt counter electrode was prepared by spin-coating solution containing 7 mM H$_2$PtCl$_6$·H$_2$O in 2-propanol onto the FTO glass, followed by heat treatment at 450°C for 30 min. The quasi-solid-state electrolyte was prepared using PEG10k (M$_w$ = 10,000 g/mol), MPIL, LiI and I$_2$ in acetonitrile solvent. Poly[(1-(4-ethenylphenyl)methyl)-3-butyl-imidazolium iodide] (PEBII) without any additives was used as the single component solid electrolyte. The prepared electrolytes were directly cast onto the photoanode. Both electrodes were superimposed and pressed between two glass plates to slowly evaporate the solvent and produce a thin electrolyte layer. The cells were placed in a vacuum oven for 1 day to allow complete evaporation of the solvent and then sealed with an epoxy resin.

The photovoltaic properties of DSSCs were characterized using a Keithley Model 2400 and a 1000 W xenon lamp (Oriel, 91193). The light intensity was homogeneous over a 20 × 20 cm$^2$ area. The mismatch between the simulated light and natural sunlight was calibrated by adjusting the photocurrent density of a Si solar cell (Fraunhofer Institute for Solar Energy System, Mono-Si + KG Filter, Certificate No. C-ISE269) for a sunlight intensity of unity (100 mW/cm$^2$). More than three identical DSSCs were fabricated and tested to increase the reliability of the characterizations, and all of the DSSCs were characterized at room temperature using a thermoelectric cooler to maintain the temperature. EIS data were measured using an electrochemical work station (Keithley Model 2400) with a frequency range from 0.01 Hz to 0.1 MHz and AC amplitude of 0.2 V.

Measurement of dye loading

N719 dye–sensitized TiO$_2$ photoanodes with an active area of 1.0 cm$^2$ were immersed in 10.0 ml of 0.1 M NaOH in a 1:1 (by volume) mixed solvent of ethanol and deionized water. The resulting solutions were stirred until the N719 dye molecules detached fully from the surface of the TiO$_2$ photoanodes. Finally, the original N719 dye loading on the photoanodes was calculated based on UV-visible spectroscopy analysis of the solutions using the absorbance peak value at 515 nm according to the Beer–Lambert law (A = εlc), where A is the absorbance at 515 nm, ε = 14,100 M$^{-1}$ cm$^{-1}$ is the molar extinction coefficient of the N719 dye at 515 nm, l is the length of the analytical light path, and c is the concentration of the N719 dye.

Characterization

Materials synthesis was characterized by Excalibur Series FT-IR (DIGLAB Co.) instrument over a frequency range of 4,000–400 cm$^{-1}$. Each element was investigated by XPS equipped with a K-alpha (Thermo, UK) with a monochromated Al Kα X-ray source. UV-vis spectroscopy was performed with a spectrophotometer (Shimadzu) in the range of 300–800 nm. The thermal stability of materials was determined by TGA (Mettler Toledo TGA/SDTA 851e, Columbus, OH) under air atmosphere from 50°C to 700°C at a rate of 20°C/min. The morphology of materials was characterized by energy-filtering transmission electron microscopy (EF-TEM, Carl Zeiss, LIBRA 120, Germany).

Results and Discussion

Hydrothermal reaction of the solution containing TBT, BDC, and PEGDGE was conducted at 150°C for 24 h to synthesize MIL-125(Ti) with various structures and sizes. To confirm successful preparation of MIL-125(Ti), the FT-IR spectra were measured as shown in Figure 1a. The strong absorption band at 1381 cm$^{-1}$ and weak absorption band at 1437 cm$^{-1}$ corresponded to a symmetric stretching vibration bands from 400–800 cm$^{-1}$ indicate the –O–Ti–O vibrations. The intensity of the carboxylic acid functional group of MIL-125(Ti) in the range of 1300–700 cm$^{-1}$ gradually increased with increasing amount of PEGDGE in the reaction solution, indicating surface modification of MIL-125(Ti) by PEGDGE.

TGA is a useful tool that can be used to confirm the transition process from MIL-125(Ti) to TiO$_2$. As shown in Figure 1b, the first weight loss was observed under the calcination process up to 100°C, and is due to residual solvents that were primarily water adsorbed onto MIL-125(Ti). In the rage of 100–300°C, the second slow weight loss was caused by removal of DMF molecules and unreacted organic chemicals captured within MIL-125(Ti) pores. Above 300°C the stable MIL-125(Ti) started to undergo phase transition and structural reorganization to TiO$_2$ without external configuration of particles, probably due to the loss of hydroxo groups. It was confirmed that MIL-125(Ti) instantaneously decomposed to TiO$_2$ at 450°C and maintained the resultant TiO$_2$ structure under further heat treatment.
XRD patterns of MIL-125(Ti) series produced by different amounts of PEGDGE were measured to identify the crystal phase of materials, as shown in Figure 1c. The crystal structure was composed of μ-OH corner-sharing TiO$_6$ octahedra chains through Ti$^{4+}$ ions, which were interconnected by BDC molecules to develop three-dimensional architecture pores. The crystal structure and phases of MIL-125(Ti) series were consistent with previously reported values. However, the relative peak intensity was primarily affected by the amount of PEGDGE used for hydrothermal process. With increasing amount of PEGDGE, the peaks at diffraction angles (2θ) of 9.7°, 15.3°, 19.5°, and 25.0° increased whereas the peaks at 6.7°, 11.6°, 15.0°, 16.5°, and 17.9° decreased. This indicates that the growth of MIL-125(Ti) crystalline structure was affected by PEGDGE and thus the crystal was reconstructed, leading to a change in particle morphology and surface area. After calcination, the pure anatase TiO$_2$ phase structure was observed for all MIL-125(Ti)-based hierarchical TiO$_2$ (denoted as hier-TiO$_2$) regardless of the PEGDGE content, as shown in Figure 1d. The peaks at 25.3°, 37.9°, 47.8°, and 54.7° corresponded to reflections from the (101), (004), (200), and (105) crystal planes of anatase TiO$_2$, respectively.

The MIL-125(Ti) series, controlled by the amount of PEGDGE in the synthesis procedure, presented various particle sizes (200 nm–1 µm) and shapes (circular plate to truncated bipyramids), as seen in Figure 2a-d. Hydrothermal reaction of a homogenous solution composed of TBP and BDC in DMF/methanol mixture without PEGDGE produced a small particle size (200 nm) and circular plate morphology. Use of the modulator PEGDGE resulted in more phase separation between solvent and precursor, leading to an aggregated structure and larger particle size up to 1 µm. Furthermore, the direction perpendicular to the circular plate generated new growth and facet formation that was exposed on the crystal structure, triggering formation of truncated bipyramids.
Figure 2e-h shows the SEM images of mesoporous anatase \( \text{TiO}_2 \) particles derived from MIL-125(Ti) via dispersion in ethanol solution and casting onto glass substrate. Distributed hier-
\( \text{TiO}_2 \) particles were densely packed and maintained their morphology, even after calcination with crystal structure alternation. Only \( \text{TiO}_2 \) particle sizes were reduced by shrinkage of MIL-125(Ti), in which the pores were formed from frameworks of intertwined Ti metal and organic linker after calcination. These submicro and microsized hier-
\( \text{TiO}_2 \) particles are expected to efficiently enhance the light scattering ability.

To more clearly identify the morphology and size of MIL-125(Ti) and hier-
\( \text{TiO}_2 \) particles, TEM observations were conducted as shown in Figure 3. MIL-125(Ti) exhibited a large size of greater than 500 nm without evident pore structure due to the very small pore size of less than 2 nm. The framework structure gradually changed from circular plates to truncated bipyramids, consistent with the above SEM observations. Upon calcination, well-defined \( \text{TiO}_2 \) particles were generated with organized mesopores and large surface area, which would be effective for enhancing dye loading and pore filling of the polymer electrolyte. All hier-
\( \text{TiO}_2 \) particles retained highly interconnected pores with shrunken particle sizes. These special characteristics of mesoporous anatase \( \text{TiO}_2 \) would act to boost solar energy performance, which needs a large surface area and excellent light scattering properties.

Under the mild calcination conditions, MIL-125(Ti) series were completely converted to anatase mesoporous hier-
\( \text{TiO}_2 \) particles. The specific surface area of MIL-125(Ti) and hier-
\( \text{TiO}_2 \) particles is summarized in Table S1, as determined by N\(_2\) adsorption-desorption measurements using the BET method. Because of the small-scale frameworks coordinating the organic linker and metal ions, the MIL-
125(Ti) series exhibited a high surface area of over 1300 m\(^2\)/g, which is comparable to recently reported values.\(^{48-50}\) After calcination, the pores of MIL-125(Ti) were shrunken, such that anatase \( \text{TiO}_2 \) particles had an area of over 100 m\(^2\)/g, but retained the particle frameworks. As shown in Figure 4a, Type-IV isotherms with H1-type hysteresis loops at \( P/P_0 = 0.5-0.8 \) were observed for all hier-
\( \text{TiO}_2 \) particles, indicating the presence of large mesopores. The average pore diameters of hier-
\( \text{TiO}_2 \) particles were quite similar at approximately 6–10 nm, as estimated using the BJH method (Figure 4b).
UV-visible absorption spectra were measured to investigate changes in dye loading of bilayer photoanodes of hier-TiO$_2$ on nc-TiO$_2$. The results are summarized in Table 1. The hier-TiO$_2$ layered photoanodes exhibited greater dye loading than neat nc-TiO$_2$ monolayered photoanode due to the increased film thickness and increased surface area. In particular, the deposition of hier-TiO$_2$ layer on nc-TiO$_2$ photoanodes resulted in a nearly two-fold increase in dye loading (from 77 to 139 nmol/cm$^2$), which would help to significantly improve the efficiency of the DSSCs.

Figure 4c shows photographs of different hier-TiO$_2$/nc-TiO$_2$ bilayer photoanodes and neat nc-TiO$_2$ monolayer photoanode. By the naked eye it was obvious that the photoanodes became opaque after the deposition of hier-TiO$_2$ on transparent nc-TiO$_2$, demonstrating efficient light reflectance and scattering. The reflective abilities of hier-TiO$_2$/nc-TiO$_2$ bilayers and neat transparent nc-TiO$_2$ monolayer were measured by UV-vis reflectance spectroscopy in the visible range from 300−800 nm as shown in Figure 5a. The photoanode with a transparent nc-TiO$_2$ monolayer presented low reflective ability with retaining values between 10% and 20% and maximum reflectance at 390 nm. On the other hand, higher reflective properties were observed for the bilayer photoanodes composed of scattering hier-TiO$_2$ on nc-TiO$_2$ layer over the entire range, recording over 50% reflectance. All of the photoanodes with a scattering layer exhibited similar reflectance ability without large differences. This reflectance ability could strongly affect the performance of the DSSCs, which might be dependent on light trapping ability of the photoanode for recycling light.

Surface and cross-sectional SEM images of the photoanodes layered by the doctor blading technique are shown in Figure S1 and S2. The surface SEM images of hier-TiO$_2$ on nc-TiO$_2$ photoanodes were not significantly different from those of neat hier-TiO$_2$ particles (Figure 2e,h), indicating that the original morphology and particle size were not perturbed by the organic binder (i.e., ethyl cellulose and α-terpinol) and the doctor blading technique. However, the interconnectivity between the TiO$_2$ particles could be enhanced to provide increased electron transportation. The dual porous structure of the hier-TiO$_2$ layer formed by small inner pores in the particles as well as large pores between the particles would be effective in improving energy conversion efficiency based on a multifunctional effect. In general, commercial scattering layers are deposited with less than 4 µm thickness because of their own resistance and lower
effectiveness of pore filling. However, we were able to increase the thickness of the hier-TiO$_2$ layer up to approximately 6 µm by controlling the viscosity of the paste and using the doctor blading technique, resulting in improved DSSC efficiency. This is because the hier-TiO$_2$ scattering layer has a greater ability to improve dye adsorption and light utilization, without having any negative effect on the pore filling of polymer electrolyte even at higher film thickness.

The solid-state or quasi-solid-state DSSCs are more advantageous than the liquid electrolyte-based counterpart because of the need for long-term stability, a flexible design, and light-weight cells. DSSCs based on a hier-TiO$_2$ layer were fabricated using a quasi-solid-state polymer electrolyte consisting of PEG10K, MPII, Lil, and I$_2$. This quasi-solid-state polymer electrolyte is based on the ethylene oxide group and a high molecular weight (10,000 g/mol) enough to produce better mechanical stability and faster ion transportation via the Grotthus hopping compared to the ones reported by other groups. The J-V curves of the DSSCs with different photoanode structures were measured at 100 mW/cm$^2$ as shown in Figure 5b and their photovoltaic parameters, including short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF), and overall energy conversion efficiency ($\eta$), are summarized in Table 1. The hier-TiO$_2$ bilayer photoanodes enhanced the solar energy conversion efficiency to as high as 7.1%, which is much higher than that of the nc-TiO$_2$ monolayer photoanode (4.6%). The obtained cell efficiency was not significantly changed at room temperature up to several days. There were no significant differences in FF and $V_{oc}$ values among the DSSCs. Thus, the much higher efficiency of hier-TiO$_2$ based DSSCs is mostly attributed to an improvement in the $J_{sc}$ value, resulting from increased dye loading and light scattering effect. Although there was a slight difference among the hier-TiO$_2$ based DSSCs, hier4-TiO$_2$ showed the highest efficiency, which will be characterized in next section using EIS and IPCE measurements.

The electrochemical analysis provides important information on the internal and interfacial resistances in equivalent circuits. The EIS spectra of DSSCs fabricated with hier-TiO$_2$ based photoanodes are shown in Figure 5c and summarized in Table 1. The resistance parameters consisted of Ohmic series resistance of conducting glass substrate ($R_s$), interfacial charge transfer resistance between counter electrode and electrolyte ($R_{ct}$), interfacial charge transfer resistance between the photoanode and electrolyte ($R_2$), and mass transport.
plotted by dividing entire IPCE values by the highest IPCE value to but is related to light scattering efficiency at wavelengths above 525 photoanode at both low (< 525 nm) and high (> 525 nm) wavelengths, which is indicative of enhancement of both dye loading and light scattering properties. The light scattering effect increased with an increase in TiO₂ particle size, consistent with the reflectance results in the wavelength range between 600 and 700 nm. Despite lower dye loading, the hier4-TiO₂ based DSSC showed the highest efficiency as a result of better light scattering properties at higher wavelength regions, indicating that light scattering is more important than dye loading for the scattering layer.

IPCE is defined as the ratio of the number of electrons in the external circuit produced by incident photons to the number of generated charge carriers at a given wavelength. Hence, the light scattering effect can be evaluated by measuring the IPCE spectra of DSSCs. The IPCE spectrum is directly related to the Jₚ value measured in J-V curves, which is largely determined by dye loading, electron transport, and light harvesting. The IPCE spectra of DSSCs with a quasi-solid-state polymer electrolyte and various photoanodes were measured at 100 mW/cm² as a function of the illumination wavelength, as shown in Figure 5d. To ensure size dependency as well as dye loading ability, the normalized IPCE curves were also plotted by dividing entire IPCE values by the highest IPCE value to give a maximum IPCE value of 1 (Figure S3). The IPCE values of the DSSCs fabricated with hier-TiO₂/nc-TiO₂ bilayer photoanodes were always much higher than those of nc-TiO₂ monolayer or the cs-TiO₂/nc-TiO₂ double layer photoanode. This indicates that DSSCs based on hier-TiO₂ photoanodes exhibited enhanced light utilization ability through light scattering layer deposition. The maximum IPCE value was observed at 525 nm, corresponding to the absorption peak of N719 dye, due to visible π* to π metal to ligand charge transfer. The IPCE value is a result of the amount of dye absorption at lower wavelengths below 525 nm, but is related to light scattering efficiency at wavelengths above 525 nm. The DSSCs with bilayer photoanodes exhibited higher IPCE values compared to those with a neat nc-TiO₂ layer-based photoanode at both low (< 525 nm) and high (> 525 nm) wavelengths, which is indicative of enhancement of both dye loading and light scattering properties. The light scattering effect increased with an increase in TiO₂ particle size, consistent with the reflectance results in the wavelength range between 600 and 700 nm. Despite lower dye loading, the hier4-TiO₂ based DSSC showed the highest efficiency as a result of better light scattering properties at higher wavelength regions, indicating that light scattering is more important than dye loading for the scattering layer.

We also tested the effectiveness of hier-TiO₂ as a light scattering layer by fabricating solid-state DSSCs employing a single component solid PEBII electrolyte, as shown in Figure 6. PEBII solidifies as a result of free radical polymerization of an ionic liquid, and the ionic conductivity reached 2.0 × 10⁻⁴ S cm⁻¹ at room temperature due to the well-organized structure coupled with the π–π stacking interactions. Thus, PEBII functioned well as the solid electrolyte even without any additives such as iodide salt or iodine (I₂). The efficiency of solid-state DSSCs based on a hier-TiO₂/nc-TiO₂ double layer reached 8.0%, which is among the highest values reported for N719-based solid-state DSSCs. This again demonstrated that the hier-TiO₂ layer is highly efficient because of its multifunctionality; namely, (1) a large surface area that allows high levels of dye loading and thereby enhances the light harvesting efficiency, (2) a morphology that reflects the light back
into the nc-TiO$_2$ layer, and (3) higher porosity that allows deep penetration of large molecular volume polymer electrolyte.

**Conclusion**

We have reported a synthesis of anatase hier-TiO$_2$ nanostructures derived from shape- and morphology-controlled MIL-125(Ti) via direct conversion by a calcination process. MIL-125(Ti) functioned as both template and precursor with control of structure and particle size though the use of PEGDGE as the structure-directing agent in the hydrothermal reaction. Use of large amounts of PEGDGE produced a larger particle size and changed the morphology from a circular plate to bipyramid. The hier-TiO$_2$ possessed high porosity as well as good interconnectivity, making it effective as the scattering layer in a bilayer photoanode for DSSC. The DSSC fabricated with hier-TiO$_2$/nc-TiO$_2$ bilayer photoanode and a quasi-solid-state polymer electrolyte exhibited greatly improved solar cell performance efficiency as high as 7.1%, compared to that of the nc-TiO$_2$ monolayer photoanode based DSSC (4.6%). The efficiency of solid-state DSSCs fabricated using a single component PEBII solid polymer also reached a high value of 8.0% (4.6%). The efficiency of solid-state DSSCs fabricated using a single component PEBII solid polymer also reached a high value of 8.0% (4.6%).

This strategy is very versatile and can be applied to other types of including structure controllable MOF materials. Furthermore, this contribution to the development of high-performance DSSCs, including hier-TiO$_2$/nc-TiO$_2$ bilayer photoanode effective as the scattering layer in a bilayer photovoltaic device application and provided a significant contribution to the development of high-performance DSSCs, including structure controllable MOF materials. Furthermore, this strategy is very versatile and can be applied to other types of photovoltaics such as perovskite solar cells to obtain better performance with scattering effect as well as high absorption ability.

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**Notes and references**

Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, South Korea. Fax: +82-2-312-6401; Tel: +82-2-2123-5757; E-mail: jonghak@yonsei.ac.kr

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‡ These authors contributed equally to this work.
51. Y. Wang, P. Sun, S. Cong, J. Zhao, G. Zou, Carbon, 2015, 92, 262-270.
A shape- and morphology-controlled MIL-125(Ti) was synthesized using poly(ethylene glycol) diglycidyl ether (PEGDGE) as a structure directing agent. Upon deliberate calcination, MIL-125(Ti) was converted to mesoporous hierarchical TiO$_2$ (hier-TiO$_2$) with anatase phase and a large surface area. Dye-sensitized solar cell (DSSC) fabricated with the hier-TiO$_2$ photoanode and a solid electrolyte exhibited a high efficiency of 8.0%.