ORIGINAL ARTICLE

Multi-layering of a nanopatterned TiO₂ layer for highly efficient solid-state solar cells

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A facile process to prepare multi-layered nanopatterned photoanodes (MNPs) is presented with well-arrayed mesoporous inorganic oxide layers. The MNPs were prepared with multiple stacking of nanopatterned TiO₂ layers using a sacrificial polystyrene (PS)-thin film layer, which not only guided the stacking TiO₂ layer but also was removed completely by calcination without generating cracks. The prepared MNPs exhibited large enhancement of the light harvesting property by increasing the number of nanopatterned TiO₂ layers, through multiple reflection of the incident light from the periodic embedded channels formed between the nanopatterned layers. The photovoltaic efficiency was optimized with a 3-layered nanopatterned photoanode exhibiting a 73% J_{sc} and a 65% power conversion efficiency enhancement compared with a cell with a flat TiO₂ layer for I₂-free solid-state dye-sensitized solar cells.

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INTRODUCTION

Micro- and nano-patterned structures have demonstrated unprecedented light modulation effects; these structures have received considerable attention in metamaterial structures¹ and various light harvesting devices.^{2–10} In this context, patterned photoanodes in solar cells have been studied as a line structure,¹¹ a 3D micro-pyramid,¹² an embedded micro-line,¹³ and moth-eye structures¹⁴ in an effort to improve light harvesting efficiency in photovoltaic devices.^{2,3,15} In addition, the photonic crystal^{7,16,17} and plasmonic nanostructures^{18,19} have been explored intensively. Nonetheless, the absorption of incident light is still low, and a challenge remains to create light harvesting structures that provide high-light reflection and absorption over a broader range. Patterned structures exhibit enhanced surface area and are able to trap the incident light to enhance light harvesting;^{20,21} therefore, patterned structures are a key component in a solar cell. Among the various solar cells, iodine-free solid-state dye-sensitized solar cells (ssDSSCs) based on a conductive polymer as hole transporting materials have been attracting much interest recently owing to their low toxicity, light overall weight, long-term durability and processibility.^{11,22,23} However, the photoconversion efficiency of ssDSSCs is low due to the wasted light that is transmitted through the photoanode. In our previous work, we introduced a nanopatterned TiO₂ photoanode, showing 40% and 33% enhancements of the short-circuit current (J_{sc}) and power conversion efficiency (PCE), respectively, compared with a flat TiO₂ photoanode in ssDSSCs.¹¹ However, the light harvesting capabilities of ssDSSCs, which have only one nanopatterned layer, are limited because a significant amount of light could still be transmitted through the single nanopatterned layer.

Therefore, a challenge worth addressing is to build multi-layered nanopatterned photoanodes (MNPs) for higher light harvesting.

Herein, for the first time, we present a method of multi-stacking of nanopatterned mesoporous TiO₂ layers and the application of them in an I₂-free ssDSSC. The light harvesting was found to be significantly enhanced by multi-reflection of the incident light from the periodic embedded channels formed between the nanopatterned layers in the photoanode of an I₂-free ssDSSC. Furthermore, a complementary effect between light harvesting and electron transport in MNPs was analyzed to optimize the stacking of the nanopatterned TiO₂ layers.

EXPERIMENTAL PROCEDURE

Nanopatterning photoanode

Nanopatterning of TiO₂ films: The dense, compact TiO₂ blocking layer (Figure 1) with a 200-nm thickness was prepared by spin-coating a titanium diisopropoxide bis(acetylacetonate) solution (2 wt% in butanol) onto FTO (fluorine-doped tin oxide) glass (Pilkington, St Helens, UK, 8 Ω) at 2000 r.p.m. for 30 s, followed by calcination at 450 °C for 30 min. Commercially available paste (TiO₂ Paste 18NR-T, Dyesol, Queanbeyan, Australia) was cast onto the compact TiO₂ layer using a doctor-blade technique, and then, the polydimethylsiloxane (PDMS) stamp was manually placed onto a paste-coated photoanode with proper pressure. The thickness of the MNPs was controlled by diluting the original TiO₂ paste with organic solvent (terpineol), whereas the flat sample was fabricated by the TiO₂ paste without dilution. Thus, the weight percentage of TiO₂ pastes in terpineol were 100 wt% (1NP), 80 wt% (2NP), 65 wt% (3NP) and 50 wt% (4NP). The photoanode was maintained at 25 °C for 16 h or 70 °C for 3 h, and then, the stamp was peeled off. The nanopatterned photoanode was annealed at 60 °C for 1 h and then sintered at 500 °C for 30 min before cooling to 30 °C for 8 h. After successive sintering processes, the polymer-thin film was formed by spin-coating of 0.5 wt%

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Figure 1 The nanopatterning process for the multi-layered nanopatterned photoanode and the structure of high performance solid-state DSSCs. (a) The first-nanopatterned TiO₂ layer was prepared using TiO₂ paste and the PDMS nanostamp. (b) Calcination at 500 °C and spin-coating of the polystyrene polymer solution onto the prepared first-nanopatterned TiO₂ layer. (c) Coating of the TiO₂ paste and nanopatterning after rotating the substrate for the second-nanopatterned TiO₂ layer. (d) two-layered, (e) three-layered and (f) four-layered nanopatterned photoanodes after the calcination process at 500 °C. (g) The prepared solid-state DSSCs with nanopatterns and the conductive polymer.

polystyrene (PS, Sigma Aldrich, St Louis, MO, USA) solution in tetrahydrofuran (Aldrich Chemicals, 99.8%), ~50 μ l each cell at 2000 r.p.m. for 30 s. The MNPs were produced by repeating the nanopatterning process with rotation of the PDMS nanostamp (2NP: 90°, 3NP: 45° and 90°, 4NP: 45°, 90° and 135°). The used PDMS was washed with ethanol and could be reused.

Fabrication of ssDSSCs

The nanopatterned photoanode was immersed in the N719 dye (Solaronix SA, Aubonne, Switzerland) solution (0.5 mM in ethanol) for 24 h at room temperature, washed with ethanol and then dried. For the pore-filling of the HTM, the synthesized monomer (2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT)) was dissolved in anhydrous ethanol. One drop of dilute solution (1 wt%) was cast and dried under ambient conditions. One drop of a more concentrated solution (3 wt%) in ethanol was directly cast onto the photoanode and then dried under the same conditions. This process was also repeated three times. After complete drying of the solvent, the DBEDOT-incorporated photoanode was placed into a vial and capped, followed by being thermally polymerized at 55 °C for 24 h in an oven to produce a highly conductive polymer (poly(3,4-ethylenedioxythiophene) (PEDOT)). One drop of the ethanol solution, consisting of 1-methyl-3-propylimidazolium iodide (1.0 M, MPII, Aldrich Chemicals), 4-tert-butylpyridine (0.2 M, TBP, Aldrich Chemicals), and lithium bis(trifluoromethane)sulfonimide (0.2 M, LiTFSI, Aldrich Chemicals), was cast onto the dye-sensitized TiO₂ photoanode with conductive polymers. After complete evaporation of the solvent in a vacuum oven, sandwich-type ssDSSCs were fabricated through the attachment of the Pt-coated counter electrode and sealing.

Characterization

The morphology and energy-dispersive x-ray spectrometry mapping of MNPs were observed using a field-emission scanning electron microscope (model JSM-7001F, JEOL, Tokyo, Japan). The reflectance and transmittance were measured via an UV/Vis/NIR spectrophotometer equipped with a Spectralon coated integrating sphere (60-mm diameter) using BaSO₄ (PerkinElmer, Waltham, MA, USA, model: Lambda 750). The photoelectrochemical

performance characteristics were measured using an electrochemical workstation (Keithly Model 2400, Cleveland, OH, USA) and a solar simulator (1000 W xenon lamp, Oriel, 91193, Irvine, CA, USA). The light distribution was homogeneous over an 8 in $\times$ 8 in area, and the illumination intensity was calibrated using a Si solar cell (Fraunhofer Institute for solar Energy System, Mono-Si+KG filter, Certificate No. C-ISE269, Freiburg, Germany) to a sunlight intensity of 1 sun (100 mW cm⁻²). This calibration was re-verified using a NREL-calibrated Si solar cell (PV Measurements, Boulder, CO, USA). The incident photon-to-current efficiency (IPCE) measurement was performed using a 300-W Xe light source and a monochromator (Polaronix K3100 IPCE Measurement System, McScience, Suwon, Korea). The amount of adsorbed dye was determined via a dye desorption experiment after immersion of the TiO₂ film in a solution of NaOH (5 mM) in an ethanol/water (1:1 v/v) mixture. The concentration of desorbed dye in solution was analyzed using a UV/Vis/NIR spectrophotometer (Supplementary Figure S6 and Supplementary Table S3). Intensity-modulated photovoltage spectroscopy and intensity-modulated photocurrent spectroscopy measurements were performed on an electrochemical workstation equipped with a frequency response analyzer under a modulated green-light emitting diode (535 nm) driven by a source supply, which could provide both DC and AC illumination components (frequency range: from 10 000 to 0.01 Hz).

RESULTS AND DISCUSSION

Nanostructures and morphologies of MNPs

The MNPs were prepared via multiple stacking of nanopatterned TiO₂ layers using sacrificial PE-thin film layers, each of which was removed upon calcination after the stacking of the subsequent nanopatterned TiO₂ layer onto the bottom TiO₂ layer. Figure 1 shows a schematic illustration of the MNP fabrication process using a PDMS elastic nanostamp (3 cm $\times$ 4 cm) with a period of 600 nm. First, an electron-blocking layer was prepared on a FTO substrate, after which the substrate was coated with a commercially available TiO₂ paste (Dyesol 18NR-T) using a doctor-blade method. The PDMS

Figure 2 SEM images of the TiO₂ multi-layered nanopatterned photoanodes (MNPs). (a) The top surface of the nanopatterned TiO₂ layer after the first nanopatterning (scale bar, 1 μ m) and a photograph of the light diffraction of the nanopatterned photoanode (inset). (b) The two-layered nanopatterned photoanode (2NP; scale bar, 1 μ m), (c) 3NP (scale bar, 5 μ m) and (d) 4NP (scale bar, 7 μ m). Photographic images of light diffraction of the MNPs (inset, left top) and actual photoanodes at different directions (left bottom). Cross-sectional SEM image of (e) 4NP (scale bar, 5 μ m) and of (f) the interface of the MNPs (scale bar, 300 nm).

nanostamp was pressed firmly with pressure onto the TiO₂ paste-coated substrate. After drying at room temperature, the nanostamp was removed, and then, the patterned TiO₂ layer was annealed for 30 min at 80 °C to remove the remaining solvent. Next, the patterned TiO₂ photoanode was sintered at 500 °C for 30 min. Figure 2a shows the image of the one-layered nanopatterned photoanode (1NP), showing a clear periodic pattern over the entire large area (Supplementary Figure S1).

To stack an additional nanopatterned TiO₂ layer, a PS polymer solution (0.5 wt%) was spin-coated onto the 1NP to form nano-channels between the 1NP and the incoming nanopatterned TiO₂ layers. As the PS can be removed by sintering at 500 °C, it can preserve void channels for the efficient trapping of light in MNPs. After coating with PS, TiO₂ paste was coated onto the PS-coated 1NP, and the same patterning process used for the preparation of 1NP was performed with the same PDMS nanostamp. The PDMS pattern direction for the

second TiO₂ layer was rotated from the base layer (1NP) to increase the length of the light path. After peeling-off the PDMS nanostamp, the double-layered photoanode was sintered at 500 °C for 30 min, resulting in a two-layered nanopatterned photoanode (2NP). During the calcination step, the solvent and the PS were completely removed, as verified by Fourier-transform infrared spectroscopy: the vibrational peaks for the PS (1028, 1601, 2850 and 3027 cm⁻¹) disappeared after 30 min of calcination at 500 °C (Supplementary Figure S3). Furthermore, removal of PS from the MNPs upon calcination was directly observed energy-dispersive x-ray spectrometry mapping results (Supplementary Figure S4 and Supplementary Table S1). The carbon content was undetected from the composition of PS-coated MNPs after calcination, indicating that PS and any carbon residue from the decomposition of PS were removed completely by the calcination at 500 °C for 30 min.

The sacrificial PS layer was useful, as it was removed completely by calcination without generating cracks to produce the periodic void channels inside the 2NP, which are useful for the trapping of light. In contrast, the acrylate polymers, in this case poly(methyl methacrylate), generated cracks after calcination, possibly because the brittleness of poly(methyl methacrylate). Therefore, PS was used to form the MNPs (Supplementary Figure S2).

To prepare the MNPs, the processes described above were repeated. The pattern directions were rotated against the first-nanopatterned TiO₂ layer by rotating the direction of the PDMS nanostamp. Thus, the 3-layered nanopatterned photoanode (3NP) and 4-layered nanopatterned photoanode (4NP) have a rotated direction of the nanopatterns from the bottom first-nanopatterned TiO₂ layer to harvest more light from the light transmitted through the patterned layers.

The prepared MNPs showed a homogenous top surface without cracks (Figures 2 and 3a), despite the fact that it was subjected to multiple patterning-calcination cycles. Figures 2a–d show scanning electron microscopy images of the patterned TiO₂ photoanodes, with

periodic lines 300-nm wide on average and a height ranging from ca. 190 to ca. 50 nm. Note that the feature sizes are in good agreement with the wavelength of the visible light to ensure efficient trapping of sunlight. Furthermore, well-formed multi-stacked nanopatterns with a layer-by-layer structure with two to four layers in the nanopatterned photoanode were produced (Figures 2a–d). As the pattern directions of the nanopatterned TiO₂ layers were rotated with respect to each other, the MNPs should provide greater light harvesting by trapping the light inside of the nano-channels of the TiO₂ layer. As shown in the insets of Figures 2a–d, the diffracted light from the MNPs was rotated according to the number of patterned layers. Interestingly, both 3NP and 4NP showed clear pattern structures at the surface and cross-section of all layers (Figure 2). The cross-sectional scanning electron microscopy image of the 4NP structure showed that the multi-stacking process afforded well-adhered nanopatterned layers (Figures 2e and f).

The as-prepared MNPs were dipped into a solution of N719 dye in acetonitrile and *tert*-butanol to adsorb a sensitizer. Next, a solution containing 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) was

Figure 3 Optical analysis of multi-layered nanopatterned photoanodes (MNPs). (a) Photograph of a large-area four-layered nanopatterned photoanode (4NP) with light harvesting capabilities in all directions (scale bar, 1 cm). (b) Schematic illustration of light trapping with MNPs. (c) Light absorption spectra of dye-adsorbed MNPs. (d) Reflection spectra of the MNPs without dye-adsorption. Flat (black), 1NP (red), 2NP (blue), 3NP (magenta) and 4NP (green).

directly dropped onto the dye-adsorbed TiO₂ photoanode, followed by a solid-state polymerization^{11,22,23} at 60 °C to produce the conductive polymer, PEDOT as a HTM, to prepare an I₂-free ssDSSC.

Enhanced light harvesting properties of MNPs

As shown in Figure 2a, the 1NP sample showed light reflection only in one direction. However, the MNPs showed multi-direction reflections according to the number of pattern layers, as shown in Figures 2b–d. The 3NP and 4NP samples showed light reflection in three and four different directions with the rotation of the photoanodes. The incident light reaching the patterned layer can be diffracted at the first pattern layer from the top. The transmitted light from the first patterned layer is reflected back toward the first layer by the second patterned layer. The light harvesting mechanism with multi-reflection at the interface between the first and second, the second and third, and the third and fourth nanopatterned TiO₂ layers is illustrated in Figure 3b. Thus, the periodic MNPs can reflect the light back multiple times to the stacked patterned layers. For this reason, the optical path length and light absorption properties can be enhanced significantly by the MNPs, and thus, these MNPs can trap and harvest more light compared with the 1NP, although the thickness of these structures is the same: 12 μm. The optical properties of the MNPs prove that our approach for highly light-harvestable photoanodes of DSSCs is feasible. The incident light reaching the grating is diffracted in a backward direction from the periodic line-patterned photoanode. The angle of the diffracted light can be determined from the following equation (1),

$$m\lambda = n_{\text{active}}p(\sin\theta_i + \sin\theta_d) \quad (1)$$

where: m , λ , n_{active} , p , θ_i and θ_d are the diffraction order, wavelength of the incident light, refractive index of the TiO₂ layer, period of the pattern, incident angle, and diffraction angle, respectively. The value of n_{active} of the nanopatterned TiO₂ layer was determined to be 2.256,²⁴ and p is ~600 nm, as determined from the scanning electron microscopy image in Figure 2. The diffracted light can have m -values of 0, ± 1 and ± 2 and m -values of 0 and ± 1 when $250 \text{ nm} \leq \lambda \leq 600 \text{ nm}$ and $600 \text{ nm} \leq \lambda \leq 760 \text{ nm}$, respectively. At higher m -values, the θ_d of the diffracted light can be bent by 90°, leaving the light unable to be absorbed by the dye-adsorbed TiO₂ layer. The θ_d for the first-order reflection was 10.6° and 34.2° at the incident light of $\lambda = 250$ and 760 nm, respectively. The θ_d for the second-order reflection was 21.7° and 87.2° when $\lambda = 250$ and 676 nm, respectively. Therefore, the nanopatterned TiO₂ layer can reflect the light back to the photoanode and thus enhance the optical path length, improving light absorption.

The light reflection properties of the MNPs were characterized to evaluate the light harvesting properties, as shown in Figures 3c and d. The MNPs were prepared over a large area ($3 \times 4 \text{ cm}^2$) of FTO glass using PDMS nanostamps, indicating the enhancement of the light harvesting property by increasing the number of nanopatterned TiO₂ layers. As shown in Figure 3, the light was reflected significantly in the nanopatterned TiO₂ layer. Because the MNPs multiply reflect light and trap incoming light, they could enhance the optical path length for the broad wavelength range of the incident light.

The reflection was characterized using a UV/Vis/NIR spectrophotometer equipped with an integrating sphere, and the absorption was calculated by the measured transmission (T , Supplementary Figure S5) and reflection (R) ($A(\%) = 100 - T - R$).¹² The reflection spectra of each sample are shown over the spectral range of 350–700 nm in Figure 3d. The flat TiO₂ photoanode without a nanopattern exhibited a reflectance that was <20% in the visible range. However, the increases in light reflection of the MNPs were 29% (1NP), 37% (2NP), 43% (3NP) and 51% (4NP) compared with

Table 1 Performances and relative reflectance of iodine-free ssDSSCs fabricated with multi-layered nanopatterned photoanodes at 100 mW cm⁻²

Sample ^a	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)	Relative reflectance ^b	
					(400–700 nm)	
Flat	10.7	0.68	0.68	4.96	1	
1NP	14.6	0.67	0.66	6.46	1.29	
2NP	16.8	0.67	0.66	7.43	1.37	
3NP	18.5	0.66	0.67	8.17	1.43	
4NP	19.2	0.65	0.65	8.09	1.51	
Ref. 22	14.2	0.64	0.60	5.4	—	
Ref. 11	19.2	0.65	0.60	7.03	1.20	
Ref. 14	18.2	0.68	0.59	7.3	—	

Abbreviations: 1NP, one-layered nanopatterned photoanode; 2NP, two-layered nanopatterned photoanode; 3NP, three-layered nanopatterned photoanode; 4NP, four-layered nanopatterned photoanode; PCE, power conversion efficiency; ssDSSC, solid-state dye-sensitized solar cell. ^aAll the devices were fabricated by using a transparent TiO₂ layer without a scattering layer. The cells were investigated with an active area of 0.18 cm². ^bRelative optical data with reference to the reflectance of the flat photoanode, as characterized using a UV/Vis/NIR spectrophotometer.

the flat TiO₂ photoanode, as determined from the integration of the reflectance in the visible range (Table 1). This increased reflectance of the photoanode provides strong evidence on the light harvesting properties of the multi-stacked nanopattern with an increased number of layers. In addition, the absorption of dye-adsorbed photoanodes was increased according to the increase in the number of nanopatterned TiO₂ layers, as shown in Figure 3c. This result indicates that the MNPs provide the significant improvement in light absorption capabilities with enhanced light trapping ability owing to the multi-stacked nanopatterns. The MNPs exhibited a high-light absorption, increasing by 16% (1NP), 24% (2NP), 26% (3NP) and 27% (4NP) compared with a flat TiO₂ photoanode (Supplementary Table S2). As a result, the 4NP showed the highest light reflection and absorption among the MNPs.

MNPs in solar cells

The cell performance is characterized and the parameters of the cells are summarized in Figure 4 and Table 1, respectively. By increasing the number of nanopattern layers, the photocurrent (J_{sc}) also increased, possibly because of the enhanced amount of trapped light, as anticipated from the given absorption and reflection properties. The J_{sc} of MNP-ssDSSCs were 14.6 mA cm⁻² (1NP), 16.8 mA cm⁻² (2NP), 18.5 mA cm⁻² (3NP) and 19.2 mA cm⁻² (4NP), which are ~36% (1NP), 57% (2NP), 73% (3NP) and 79% (4NP) greater than that of the flat TiO₂ photoanode. The enhancement of J_{sc} provides strong evidence of the light harvesting properties in MNP-ssDSSCs because the thickness of the MNPs was controlled by the dilution TiO₂ paste. Furthermore, these tendencies are well matched with the IPCE curves of the DSSCs, which were measured at a chopper frequency of 5 Hz in alternating-current mode. (Figure 4b) The IPCE values of the DSSCs with MNPs were always greater than those of the DSSCs without nanopatterns in the wavelength region of 300 to 750 nm, which is the absorption range of the N719. The increase in the IPCE value over the whole visible range resulted in an increase in the J_{sc} of ssDSSCs with MNPs.

Increasing the number of nanopatterned TiO₂ layers has a significant influence on the photovoltaic performance (Figure 4c). The presence of a nanopatterned TiO₂ layer has an important role in the facilitation of the photocurrent. The J_{sc} was significantly improved from ca. 10.7 to 19.2 mA cm⁻² with the addition of nanopatterned

Figure 4 Photovoltaic characterization of an iodine-free ssDSSC with MNPs according to the number of nanopatterning layers of the photoanode. (a) Current–voltage (J – V) curves of DSSCs with MNPs at 100 mW cm^{-2} . (b) IPCE of each device. Flat (black), 1NP (red), 2NP (blue), 3NP (magenta) and 4NP (green). (c) Dependence characteristics of the J_{sc} , V_{oc} , FF and PCE of the devices with different numbers of nanopatterned layers of the photoanode.

TiO₂ layers. In contrast, the open circuit voltage (V_{oc}) decreased slightly from 0.68 to 0.65 with an increase in the number of nanopatterned TiO₂ layers. The slightly decreased V_{oc} is related to recombination owing to the voids of the interfaces between the nanopatterns.

As a result, the PCEs with the 3NP- and 4NP-ssDSSCs reached 8.17 and 8.09%, respectively, at 100 mW cm^{-2} , which were approximately 65 and 63% greater than that without nanopatterns, respectively. The 3NP-ssDSSCs showed the highest PCE of 8.17% at 100 mW cm^{-2} according to the V_{oc} (0.66), J_{sc} (18.5 mA cm^{-2}) and FF (0.67). These results represent improvements of 73 and 65% in J_{sc} and PCE, respectively, compared with the cells without nanopatterns. In contrast, the PCE of 4NP-ssDSSCs was lower than that of 3NP-

ssDSSCs, despite the fact that the J_{sc} of the cell with 4NP was higher than that of 3NP. The V_{oc} of the 4NP-ssDSSCs was lower than that of the 3NP-ssDSSCs, possibly because the electron recombination could be increased due to the nanopatterns. To understand the cause of increased recombination in MNPs, we determined the electron lifetimes, diffusion coefficients and diffusion length by means of intensity-modulated photovoltage spectroscopy and intensity-modulated photocurrent spectroscopy (Supplementary Figure S7). The electron lifetimes decreased with an increase in the number of nanopattern layers. This phenomenon could be attributed to the increased trapping sites and recombination centers originating from the periodic channels embedded inside of the nanopatterned layers of the MNPs. Such voids can disturb the electron transport and lead to recombination of charge carriers in the MNPs of ssDSSCs. The decrease in the electron lifetime was correlated with the decreased V_{oc} upon the increase in the number of nanopatterned layers. In addition, the diffusion coefficients of ssDSSCs with nanopatterns were lower than that of the flat TiO₂ photoanode cell. Given that the MNPs were composed of stacked nanopatterns with more embedded voids inside the nanopattern layers, more electrons could be trapped. Accordingly, the higher J_{sc} and PCE of 3NP can be mainly attributed to (i) the higher light absorption and reflection for high-light harvesting efficiency compared with the flat TiO₂ photoanode and (ii) the reduced electron recombination in the ssDSSC with 3NP compared with that of 4NP. These processes result in the optimization of the complementary effect between the light harvesting and the electron recombination process by the nanopatterned layers. The preparation and optimization for multi-stacking of nanopatterned layers could be extended to other applications, such as the photo-catalytic layer²⁵ and transparent conducting oxide substrates.^{26,27}

CONCLUSION

In conclusion, nanopatterned mesoporous TiO₂ layers were multi-stacked to produce periodic embedded channels between nanopatterned layers using PE-thin film. When the MNPs were applied, the light harvesting from an I₂-free ssDSSC was significantly enhanced by multi-reflection of incident light from the periodic embedded channels. Among the MNPs, the 3NP-ssDSSCs showed the highest PCE with high-light harvesting efficiency. The enhancements were 73% in J_{sc} and 65% in PCE for the 3NP-ssDSSCs, reaching a PCE of 8.17% at 100 mW cm^{-2} . This result represents one of the highest efficiencies observed for N719 dye based I₂-free ssDSSCs. The nano-architecturing approach for MNPs with mesoporous semiconductor nanoparticles represents a promising method that can both facilitate the manufacturing of photovoltaic devices with remarkable light harvesting properties and improvements in light modulation in many optoelectronic devices. Moreover, the results here provide insights into light trapping methods for multi-stacked nanopatterned layers, with a possible complementary effect of light harvesting and electron transport.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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