Tailoring the Mesoscopic TiO$_2$ Layer: Concomitant Parameters for Enabling High-Performance Perovskite Solar Cells

Taehyun Hwang$^{1†}$, Sangheon Lee$^{1†}$, Jinhyun Kim$^1$, Jaewon Kim$^1$, Chunjoong Kim$^2$, Byungha Shin$^3$ and Byungwoo Park$^1*$

Abstract
Architectural control over the mesoporous TiO$_2$ film, a common electron-transport layer for organic-inorganic hybrid perovskite solar cells, is conducted by employing sub-micron sized polystyrene beads as sacrificial template. Such tailored TiO$_2$ layer is shown to induce asymmetric enhancement of light absorption notably in the long-wavelength region with red-shifted absorption onset of perovskite, leading to $\sim$20% increase of photocurrent and $\sim$10% increase of power conversion efficiency. This enhancement is likely to be originated from the enlarged CH$_3$NH$_3$PbI$_3$(Cl) grains residing in the sub-micron pores rather than from the effect of reduced perovskite-TiO$_2$ interfacial area, which is supported from optical bandgap change, haze transmission of incident light, and one-diode model parameters correlated with the internal surface area of microporous TiO$_2$ layers. With the templating strategy suggested, the necessity of proper hole-blocking method is discussed to prevent any direct contact of the large perovskite grains infiltrated into the intended pores of TiO$_2$ scaffold, further mitigating the interfacial recombination and leading to $\sim$20% improvement in power conversion efficiency compared with the control device using conventional solution-processed hole blocking TiO$_2$. Thereby, the imperatives that originate from the structural engineering of the electron-transport layer are discussed to understand the governing elements for the improved device performance.

Keywords: Perovskite solar cell, Nanostructural engineering, Light management, Modeling, Shunting path

Background
Organic-inorganic hybrid perovskites (CH$_3$NH$_3$PbI$_3$) have drawn enormous attentions due to their superior optoelectronic properties and versatilities in applications [1, 2]. For photovoltaic devices, many strategies have been attempted to improve the power-conversion efficiency. One among many deals with refining the perovskite film itself to reduce the trap states and unwanted electron-hole recombination. Generally, defects in grains or grain boundaries act as trap sites for the charge carriers and consequently decrease the charge collection efficiency [3–6]. Indeed, much effort aimed at the single-crystal perovskites caused successful results for the high photon-to-charge conversion efficiency [7–10]. Therefore, examining the strategies to control the crystallization for the defect reduction is necessary to achieve better-performing perovskite photovoltaics.

Defect-reduced perovskite films can be realized by directly modifying the perovskite synthesis conditions (e.g., reaction environment, precursor stoichiometry, crystallization atmosphere, etc.) [11–13] or by altering the mesoscopic structure of the underlying layers over which the perovskite film synthesis is conducted. The perovskite films are generally deposited upon mesoscopic scaffolds composed of oxide nanoparticles like TiO$_2$, into which the perovskite precursors infiltrate and form small crystallites whose dimensions are defined by the internal pore size of mother scaffold. Enlarging the pores in the scaffold, and hence, increasing the infiltrated perovskite grains is expected to reduce the defects

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by grain boundaries. At the same time, the internal electric field that is formed at the semiconductor junction may further assist the charge separation. Light trapping by the nanostructural engineering will also yield an additional merit for the performance enhancement [14].

To exploit the potential benefits of large-sized single crystalline perovskite, we herein controlled the nanostructures of mesoscopic TiO$_2$ layer to infiltrate the enlarged CH$_3$NH$_3$PbI$_3$(Cl) grains. Introduction of sacrificial templates during photoelectrode fabrication, one of the facile methods to obtain the controlled pore size and internal surface area [15–18], was applied to render submicron sized pores where the large perovskite grains can be accommodated. The concomitant effect of perovskite crystallinity, perovskite-TiO$_2$ interfacial area, and light trapping was investigated to understand the change of photovoltaic parameters resulted from the templating method. Furthermore, since the templated porous layer with hundred-nanometer large open pores inevitably raises the necessity for the complete compactness of hole-blocking layers against charge recombination at the FTO-perovskite direct contact, an alternative blocking layer was applied, providing additional power-conversion efficiency improvement. The essential issues in nanostructural engineering were discussed with the correlated solar-cell parameters.

**Methods**

**Preparation of Polystyrene (PS)-TiO$_2$ Mixture Solution**

The PS-TiO$_2$ mixture solution was prepared by mixing the ethanol-based PS solution (PS microsphere with 200 nm in diameter) and the TiO$_2$ paste (anatase-phase TiO$_2$ nanoparticles with ~20 nm in diameter) with various ratios (PS/TiO$_2$ = 1:10, 1:5, and 1:2 in wt. % ratio). The PS-TiO$_2$ solution was then diluted with identical solvent (PS-TiO$_2$/ethanol = 2:5 in wt. % ratio) for spin-coating. To prepare the bare TiO$_2$ solution without polystyrene for a reference, the TiO$_2$ paste was diluted with anhydrous ethanol to the corresponding wt. % ratio.

**CH$_3$NH$_3$PbI$_3$(Cl) Deposition**

The PbI$_3$ pre-coating was performed following our previous report [19]. The 3:1 molar ratio of MAI/PbCl$_2$ in DMF (perovskite precursor solution; 2.64 M of MAI and 0.88 M of PbCl$_2$) was then spin-coated at 2000 rpm for 60 s on the PbI$_2$ pre-coated layer or the TiO$_2$ compact layer and annealed at 100 °C for 50 min. To enhance the coverage and obtain the similar thicknesses of the perovskite capping layers in the PS-templated TiO$_2$ cases, spin-coating conditions were optimized. Spin-coating speed was reduced from 6500 to 1500 rpm for PbI$_2$ and from 2000 to 1500 rpm for the perovskite precursor solution. The precursor concentration was increased (from molar ratio of 2.64:0.88 to 4.08:1.36 between MAI and PbCl$_2$) with the increased annealing time (from 50 to 135 min), and the optimization was checked in the aspect of the perovskite crystallization from diffraction. As a control group, molar ratio of 2.64:0.88 between MAI and PbCl$_2$ was also used on the 1:10 PS-templated TiO$_2$, and we referred it as “1:10 (unoptimized)” since the perovskite did not fully cover the top of the 1:10 PS-templated TiO$_2$. Every perovskite deposition was processed in air.

**Solar Cell Fabrication**

A fluorine-doped tin oxide (FTO) substrate was cleaned, and the TiO$_2$ compact layer was deposited using the 150 and 300 mM solutions of titanium diisopropoxide bis(acetylacetonate) in 1-butanol through the spin-coating followed by the annealing at 500 °C [20]. Then, the substrate was immersed in a 40 mM TiCl$_4$ aqueous solution and treated in 70 °C oven for 30 min, followed by annealing at 500 °C. Bare TiO$_2$ or PS/TiO$_2$ solution was spin-coated at 2500 rpm for 30 s, and the substrate was annealed at 500 °C to remove the polystyrene templates. Then, TiCl$_4$ treatment was performed again, and MAPbI$_3$(Cl) layer was deposited as mentioned in the previous paragraph. Hole transport layer was coated using the spiro-OMeTAD solution (72.8 mg in 1 mL of chlorobenzene) with the addition of 17.5 μL of Li-TFSI stock solution (520 mg in 1 mL of acetonitrile) and 28.8 μL of tert-butylpyridine [20]. Finally, Au electrode was thermally evaporated.

The TiO$_2$ compact layer was separately prepared by rf-magnetron sputtering as an alternative blocking layer [21], instead of using conventional titanium diisopropoxide bis(acetylacetonate) solution. The deposition was performed using the TiO$_2$ target (anatase, 99.99%; 5-cm diameter) at temperature under an Ar atmosphere with the operating pressure of 13 mTorr and rf power of 120 W. Except for the blocking layer deposition, all the other procedures were exactly identical to the solar cell fabrication conditions described above.

**Characterization**

The crystal structure was examined by X-ray diffraction (XRD) (D8 Advance: Bruker). The images of secondary electrons and back scattered electrons were collected from field-emission scanning electron microscope (FESEM) (Merlin Compact: Zeiss), with the energy-dispersive X-ray spectroscopy (SEM-EDS). The absorbance and transmittance of the films were recorded through a UV-Vis spectrophotometer (Cary 5000: Agilent Technologies) with the integrating sphere, and the optical bandgap was evaluated from the $a^2$ vs. $hv$ (photon energy) analysis. Photocurrent density-voltage ($J$-$V$) curves...
were obtained by the solar cell measurement system (K3000: McScience) with a solar simulator (Xenon lamp, air mass (AM) 1.5 at 100 mW cm$^{-2}$). During the measurement, black mask of 0.09 cm$^2$ was applied, and the scan rate was fixed to 150 mV s$^{-1}$ (reverse direction).

**Results and Discussion**

For the achievement of high photon-to-charge conversion efficiency in solar cell operation, the high light absorption followed by the electron-hole generation and facile separation of carriers into each electrode should be guaranteed throughout the cell structure. Thus, the essential parameters that can affect these phenomena should be considered [22–25]. For high photoresponse, the composition and morphology of MAPbI$_3$ can be altered to broaden the absorption spectra [26–29]. For the electron-hole pair separation, internal electric field driven from the semiconductor junction can be utilized, and it is supported by the result that the MAPbI$_3$ phase forms the depletion region at the interface with TiO$_2$ in approximately hundreds of nanometers [30]. Having sufficiently large pores in the scaffold, the size of which is comparable to the depletion layer in the perovskite, therefore shall give a microstructural modification of infiltrated perovskite grains with the size desirable in terms of electron-hole separation. A comprehensive outline for the approach suggested above is given in Fig. 1, depicting the nanostructural engineering of TiO$_2$ accompanying the perovskite deposition for the intended large crystal infiltration.

To amend the pore size of TiO$_2$ layers and finally to adjust the grain size of infiltrated perovskite, a sacrificial template is facilely incorporated into the commercially available nanoparticle-based TiO$_2$ pastes by mixing with sub-micron sized polystyrene (PS) beads, varying the composition from PS/TiO$_2$ = 1:10 to 1:2 [15–18]. Rather thick TiO$_2$ porous film (∼800 nm) is used for solar cell in this case to investigate the effects of interface between perovskite and TiO$_2$ on the cell performance [2, 22]. Micropores left after the PS removal are successfully filled with PbI$_2$ by the pre-coating step, and the remaining PbI$_2$ crystals are stacked on TiO$_2$ (Fig. 2a–d and Additional file 1: Figure S1). These pre-coating method guarantees the enlarged grains and crystallinity of the converted perovskite since the original PbI$_6$ octahedron in the PbI$_2$ structure maintains its framework after the reaction with MA$^+$ and I$^-$ in the precursor [19]. As shown in Fig. 2e and Additional file 1: Figure S1, layered-PbI$_2$ crystals are converted into perovskite, filling the intended ∼200-nm micropores. Also, the conversion into MAPbI$_3$(Cl) is completed while maintaining the [110] orientation without remnant, as verified from the diffraction in Fig. 3a (magnification in Additional file 1: Figure S2(a)).
The back-scattered electron (BSE) imaging is a useful tool to identify the compositional contrast which originates from the atomic-number difference \[31\]. The BSE images in Additional file 1: Figure S3 confirm that regular ellipsoidal perovskites are clearly formed in the intended micropores. Furthermore, it is used to confirm the PbI\(_2\) pre-coating influence on the perovskite infiltration into the mesoporous TiO\(_2\) layer (mp-TiO\(_2\)) \[32\]. The PbI\(_2\) pre-coating indeed do not interfere with the perovskite infiltration into the mp-TiO\(_2\) (without PS) based on the BSE intensity comparison between Additional file 1: Figure S3(b) and (c). This is further examined by the elemental mapping (SEM-EDS): the distributions of Pb and I are the same whether the PbI\(_2\) pre-coating is performed or not (Additional file 1: Figure S4(a) and (b)) and whether the TiO\(_2\) layer is altered by the PS sacrificial template or not (Additional file 1: Figure S4(b) and (c)). The BSE intensity and the EDS mapping confirm that the interfacial area between the perovskite and TiO\(_2\) is decreased with the increased PS fraction, since the nanoparticulated-TiO\(_2\) film consisting of \(~20\) nm-sized-nanoparticle has a larger internal surface than the TiO\(_2\) film with the intended \(~200\)-nm micropores. The enlarged perovskite grain by PS incorporation is supported accordingly from the above results.

Haze transmission is the ratio of the diffused transmittance to the total transmittance, and discloses the degree of incident light scattering \[33\]. The PS-templated TiO\(_2\) looks opaque, and the haze increases as the PS ratio rises (Fig. 3b). Also, asymmetric elevation of absorbance is observed from MAPbI\(_3\)(Cl) with increasing PS ratio as shown in Fig. 3c. This is due to the increased light scattering from TiO\(_2\) and perovskite by the intended large crystals. In addition, the bandgap of mixed-halide perovskite is red-shifted by \(~10\) meV from the Tauc plot (Fig. 3d). This optical bandgap change is also observed when the identical mixed-halide precursor solution is used for the bare and 1:10 cases (“unoptimized” which is explained in the experimental section). This red-shift is not from the different quantity of Cl since the (110) peak of MAPbI\(_3\)(Cl) is identical between the bare and 1:10 case (Additional file 1: Figure S2(b)) \[34\].
When the concentration of mixed-halide solution is increased by ~50% while maintaining the MAI/PbCl\(_2\) ratio as 3:1 to improve the perovskite coverage for the PS-templated TiO\(_2\) cases, the (110) peak shifts to the high scattering angle (Additional file 1: Figure S2(a), identical to Fig. 3a with proper magnification). The lattice parameters \(a\) and \(c\) in tetragonal (space group I\(_{4}\)/m) are changed, respectively, from 0.892 to 0.886 nm and from 1.261 to 1.251 nm. The apparent optical bandgap can vary by the Cl concentration in MAPbI\(_3\)(Cl), Burstein-Moss effect (carrier concentration), quantum confinement effect, and/or grains and grain boundaries [9, 10, 26, 35–37].

The Burstein-Moss and quantum confinement effects are not pertinent to this system considering that the composition of perovskite was confirmed to be the same for all the cases, and the grain size was out of the regime where the quantum confinement effect works in [36, 37]. Therefore, the optical bandgap change is expected to be caused by the increased perovskite crystal sizes and Cl concentrations (based on the tetragonal unit-cell size). To verify the grain-size effect on the absorption shift, MAPbI\(_3\)(Cl) perovskite is deposited with the identical concentration of mixed-halide solution to the bare (without PS) on planar TiO\(_2\) layer (Additional file 1: Figure S5). From the diffraction and SEM images of MAPbI\(_3\)(Cl) film, MAPbI\(_3\)(Cl) grown on the TiO\(_2\) planar layer exhibits micrometer-sized lateral grains with the ~30-meV red-shift compared to the bare (without PS) in the absorption onset (inset in Fig. 3d), and this additionally supports the absorption-edge shift with respect to the perovskite grain size.

The MAPbI\(_3\)(Cl) solar cells are fabricated on each PS-templated TiO\(_2\) with varying PS ratios (Fig. 4 and Additional file 1: Figure S6) to understand the grain size and interfacial effects on the solar cell performance. The best and the average values of short-circuit current density \(J_{sc}\), open-circuit voltage \(V_{oc}\), fill factor (FF), and power-conversion efficiency (\(\eta\)) are summarized in Table 1. For PS/TiO\(_2\) = 1:10 case, the \(\eta\) is rather decreased in spite of ~13% improvement of \(J_{sc}\), which is due to the inferior \(V_{oc}\) and FF. Inferior \(V_{oc}\) in this case should be resolved to overcome...
the low efficiency, and we have considered several approaches, specifically focusing on the defect reduction that can cause recombination in the perovskite and at the interfaces [38–42]. However, as the PS ratio is increased, these parameters are recovered by ~20 mV and ~4% with the additional increase of $J_{sc}$ leading to approximately 10% increase of $\eta$ for the PS/TiO$_2$ = 1:2 case compared with the control devices without PS templating.

Analyses of $J$-$V$ curves based on the one-diode model provide useful parameters helpful to figure out the interfacial effects. The $J$-$V$ curves are fitted using the ideal one-diode model described in Additional file 1: Figure S7, and the resultant fit curves are shown with the dashed lines in Fig. 4 with the extracted solar-cell parameters in Table 2 [43, 44]. (Fitting results of $J$-$V$ under dark conditions are shown in Additional file 1: Figure S8.) The fit result shows that the dark-saturation

**Table 1** The effect of polystyrene (PS) ratio on the perovskite solar cell performance

| Substrate | $J_{sc}$ [mA cm$^{-2}$] | $V_{oc}$ [V] | FF [%] | $\eta$ [%] |
|-----------|-------------------------|-------------|--------|----------|
| w/o PS    | 17.9 (16.8)             | 0.719       | 53.4   | 6.87     |
| 1:10      | 20.5 (18.9)             | 0.633       | 52.7   | 6.84     |
| 1:5       | 20.6 (19.3)             | 0.635       | 54.5   | 7.13     |
| 1:2       | 20.5 (19.7)             | 0.667       | 56.6   | 7.74     |

Short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF), and power-conversion efficiency ($\eta$) of perovskite solar cells, without PS and with various ratios of PS-templated TiO$_2$. TiO$_2$ blocking layer is deposited by solution. (Data in the bracket are the averaged ones from more than four cells in each condition.)

**Table 2** Photovoltaic parameters extracted from the ideal one-diode model

| Substrate | $J_{sc}$ [mA cm$^{-2}$] | $J_{ph}$ [mA cm$^{-2}$] | $R_s$ [\(\Omega\) cm$^2$] | $R_{sh}$ [\(\Omega\) cm$^2$] | $R_{rec}$ [\(\Omega\) cm$^2$] | $\eta$ [%] |
|-----------|-------------------------|-------------------------|-----------------------------|----------------------------|-----------------------------|--------|
| w/o PS    | 9.39 x 10$^{-6}$        | 3.85 x 10$^{-6}$        | 5.90                        | 152.0                      | 1520.0                      | 1.94   |
| 1:10      | 1.92 x 10$^{-3}$        | 2.07 x 10$^{-3}$        | 6.95                        | 286.6                      | 287.2                       | 3.53   |
| 1:5       | 7.84 x 10$^{-4}$        | 7.07 x 10$^{-4}$        | 8.15                        | 305.6                      | 304.7                       | 3.13   |
| 1:2       | 2.77 x 10$^{-3}$        | 2.07 x 10$^{-3}$        | 9.65                        | 440.4                      | 441.8                       | 2.85   |

Dark-saturation current density ($J_s$), photogenerated current density ($J_{ph}$), series resistance ($R_s$), shunt resistance ($R_{sh}$), recombination shunt resistance ($R_{rec}$), and ideality factor ($n$), respectively, from the cell of the highest efficiency in each condition (AM 1.5 at 100 mW cm$^{-2}$). (Parameters are described in the following Additional file 1: Figure S7.)
current density ($J_0$) and the ideality factor ($n$) are worsened from $10^{-5}$ to $10^{-3}$ mA cm$^{-2}$ and 2 to 3, respectively, when PS is introduced. The back electron transfer from the FTO front electrode to the perovskite by the ~200-nm penetration may cause the recombination path, as seen in SEM image of Fig. 2e [45].

However, the series resistance ($R_s$) is improved from 5.9 to 2.0 Ω cm$^2$, and the recombination shunt resistance ($R_{sh,recom}$) (reflecting $R_{sh}$ at $J_{ph} = 0$) is increased from 152.0 to 441.8 Ω cm$^2$, which may have led to the enhanced FF. As the PS templating reduces the internal surface area by occupying the internal space for TiO$_2$ nanoparticle-based porous structure, improvement of $R_s$ and $R_{sh,recom}$ can reasonably be postulated to result from the decrease of interfacial trap sites, which shall be proportional to the internal surface area of TiO$_2$ scaffold unless the nature of trap sites at the TiO$_2$-perovskite interface are much affected by PS templating. To check whether such explanation works, the correlation of $R_s$ and $R_{sh,recom}$ with the internal surface area of TiO$_2$ layer is plotted in Fig. 5.

The internal surface area of PS-mediated TiO$_2$ layer for various PS fractions is calculated based on a simple Monte-Carlo method [46], and the possible overlap between beads is considered rather than assuming the beads as hard-sphere. The random distribution of 200-nm spheres in 10 × 10 × 1 μm$^3$ volume is simulated by assuming the probability profile of sphere-to-sphere overlap to show exponential decay, the exponent of which is assumed following the Hertzian model of elastic potential energy for contact of two identical elastic spheres at a given overlap displacement [47]. A previous report on the surface area change by polystyrene particle templating is also given as a more realistic guidance for comparison. In Fig. 5, the experimental PS/TiO$_2$ weight ratios are converted to volume ratios from the assumed densities of polystyrene (1.05 g cm$^{-3}$), TiO$_2$ (3.91 g cm$^{-3}$) and porosity of mesoscopic TiO$_2$ film (68.1%) [15, 48]. By introducing the PS microbeads, the internal surface area is

### Table 3
The effect of TiO$_2$ blocking layer by sputter deposition on the perovskite solar cell performance

| Substrate | $J_{sc}$ [mA cm$^{-2}$] | $V_{oc}$ [V] | FF [%] | $\eta$ [%] |
|-----------|-----------------|--------------|--------|---------|
| w/o PS    | 18.3            | 0.749        | 55.2   | 7.56    |
| 1:2       | 20.8            | 0.694        | 58.3   | 8.41    |

Short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF), and power-conversion efficiency ($\eta$) of perovskite solar cells from w/o PS and PS/TiO$_2$ = 1:2. The TiO$_2$ blocking layer is deposited by sputtering.

### Table 4
Photovoltaic parameters from the cells with the TiO$_2$ blocking layer by the sputter deposition

| Substrate | $J_0$ [mA cm$^{-2}$] | $J_{ph}$ [mA cm$^{-2}$] | $R_s$ [Ω cm$^2$] | $R_{sh}$ [Ω cm$^2$] | $R_{sh,recom}$ [Ω cm$^2$] | $n$ |
|-----------|---------------------|--------------------------|------------------|---------------------|--------------------------|-----|
| w/o PS    | 3.53 × 10$^{-7}$    | (± 2.93 × 10$^{-7}$)     | 9.53             | 266.7               | 266.7                    | 1.64|
| 1:2       | 2.55 × 10$^{-3}$    | (± 0.68 × 10$^{-3}$)     | 2.18             | 460.9               | 467.8                    | 2.98|

Dark-saturation current density ($J_0$), photogenerated current density ($J_{ph}$), series resistance ($R_s$), shunt resistance ($R_{sh}$), recombination shunt resistance ($R_{sh,recom}$), and ideality factor ($n$), respectively (AM 1.5 at 100 mW cm$^{-2}$).
decreased with the improved $R_s$ and $(R_{sh\text{recom}})^{-1}$. The similar dependence of $R_s$ and $(R_{sh\text{recom}})^{-1}$ may be from the reduced interfacial traps leading to the decreased resistance of charge transfer or recombination [49]. However, consequently from this simplistic simulation, much drastic variations of $R_s$ and $R_{sh\text{recom}}$ are correlated with the morphological engineering. This implies that besides the interfacial effects, other factors like the grain size (crystallinity) and thereby the carrier mobility which is affected by the defects or impurities at the grain boundary should be considered to explain the improvement of $R_s$ and $R_{sh\text{recom}}$, and thereby resultant boost of $\eta$ [7–9, 50].

To further increase $\eta$, blocking layer deposition method is altered from solution deposition (data in Tables 1 and 2, Fig. 4, and Additional file 1: Figure S6 and S8) to sputter deposition (Tables 3 and 4, Fig. 6, and Additional file 1: Figure S9) to ensure the compactness. Actually, the SEM images in Additional file 1: Figure S10 confirm the porous morphology by the spin-coating and rather compact structure on each FTO grain by sputtering [48, 51–53]. The modified compact blocking layer results in the enhancement of ~0.3 mA cm$^{-2}$ in $J_{sc}$, ~30 mV in $V_{oc}$, and ~0.7% in $\eta$ (both bare and PS-templated TiO$_2$), and consequently, approximately 20% increase of $\eta$ is achieved through the nanostructural control of both blocking and porous layers compared to the bare sample. The compact TiO$_2$ hole-blocking layer more effectively inhibits the direct contact between the FTO and the perovskite (preventing the back electron transfer), which is predicted as the origin of charge recombination from the one-diode model. Actually, the modified TiO$_2$ blocking layer leads to the decreased $J_0$ (recombination current) in both bare and PS cases with the slight improvement in $R_{sh\text{recom}}$, and these are correlated with the improved $V_{oc}$ and $FF$ as listed in Tables 3 and 4. The performance of the device in this study is not comparable with the state-of-the-art device due to the low $V_{oc}$, and the hysteresis problem should be resolved. However, the beneficial optical and electrical properties of perovskite are rationally correlated with the nanostructures to elucidate the origin of the enhanced $J_{sc}$. Furthermore, the principal results from the structural engineering in this work will be applicable for various photovoltaic systems utilizing other metal-oxide-based electron-selective contacts and perovskite compositions due to the simplicity of our approach. In addition, the study applying the defect control will further enhance the $V_{oc}$ in this device architecture which already shows the promising $J_{sc}$ values, potentially improving the device performance even further. As a summary, the effects of
intended pore engineering in mesoporous TiO₂ and the blocking layer are illustrated in Fig. 7.

Conclusions
In this work, the mesoscopic TiO₂ structure was facilely engineered by using a sacrificial template, and the perovskite solar cells were fabricated on nanostructure-controlled scaffolds by systematically examining the concomitant key factors of pore engineering that influence the cell performance. The enhanced efficiency by the enlarged pores was attributed to the effectively infiltrated perovskite grains that provided the beneficial light-harvesting features by the absorption enhancement. The perovskite-TiO₂ interfacial area was rationally correlated with the internal resistances of solar cell and associated with the charge transfer and recombination. Consequently, the enlarged perovskite grains with the reduced interfacial area contributed together to the internal resistances, changing direction into the efficiency improvement. The leakage current that caused the recombination was successfully resolved through the compact blocking layer, achieving further performance enhancement. We believe that this work suggests a rational nanostructural design of electron-transport layer for high optoelectronic properties in the emerging solar cells.

Additional file

Additional file 1: Figure S1. SEM images showing the TiO₂ nanostructures with the PbI₂ pre-coating and MAPbI₃(Cl) infiltration into the PS-templated TiO₂. Figure S2. The effect of PS ratio and the concentration of precursor solution on the X-ray diffraction of MAPbI₃(Cl) perovskite. Figure S3. Cross-sectional back scattered electron images exhibiting the MAPbI₃(Cl) perovskite infiltration in the porous TiO₂ layer. Figure S4. Cross-sectional elemental distributions from energy dispersive X-ray spectroscopy (SEM-EDS) showing the Sn, Ti, O, Pb, and I distributions for different porous TiO₂ scaffolds. Figure S5. Microstructures of MAPbI₃(Cl) on the TiO₂ blocking layer. Figure S6. Photovoltic parameters with the average and the standard deviation in each condition. Figure S7. Ideal one-diode model for the perovskite solar cell. Figure S8. Current density vs. bias under dark and the corresponding fitting results. Figure S9. The effect of TiO₂ blocking layer by sputter deposition on the performance of the perovskite solar cell. Figure S10. Morphology comparison by the spin-coating and sputter deposition.

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Authors’ Contributions
TH and SL carried out the overall scientific experiments and drafted the manuscript. JK (Jeonghyun Kim) conducted in optimizing the blocking layer deposition. JK (Jaewon Kim) participated in analyzing the X-ray diffraction. CK and BS helped to improve the logical flows in the manuscript. BP supervised this study and gave valuable advices of scientific logics in detail and finalized the manuscript. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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References
1. Cho H, Jeong SH, Park MH, Kim YH, Wolf C, Lee CI, Heo JH, Sadhanala A, Myoung N, Yoo S, Im SH, Friend RH, Lee TIW (2015) Overcoming the photoluminescence efficiency limitations of perovskite light-emitting diodes. Science 350:1222–1225
2. Jeon NJ, Noh JH, Kim YC, Yang WS, Ryu S, Seok SI (2014) Solvent engineering for high-performance inorganic-organic hybrid perovskite solar cells. Nat Mater 13:897–903
3. Saidaminov MI, Abdelhady AL, Murali B, Alarousu E, Burlakov VM, Peng W, Dursun I, Wang L, He Y, Maculan G, Gorkeli A, Wu T, Mohammed OF, Bakır OM (2015) High-quality bulk hybrid perovskite single crystals within minutes by inverse temperature crystallization. Nat Commun 6:7586
4. Xu J, Buin A, Ip AH, Li W, Voznyy O, Comin R, Yuan M, Jeon S, Ning Z, McDowell JJ, Kanjanaboos P, Sun J, Lan X, Quan LN, Kim DH, Hill HG, Maksymovych P, Sargent EH (2015) Perovskite–fullerene hybrid materials suppress hysteresis in planar diodes. Nat Commun 6:7081
5. Park HH, Hasley R, Sun L, Steinhann V, Jaramillo R, Hartman K, Chakraborty R, Sinersmsukakul P, Chua D, Buonassissi T, Gordon RG (2015) Co-optimization of SnS absorber and Zn(O, S) buffer materials for improved solar cells. Prog Photovolt Solar Cells 23:901–908
6. Li C, Wu Y, Poplavsky J, Pennycook TJ, Paudel N, Yin W, Haigh SJ, Doley MP, Lupini AR, Al-Jassim M, Pennycook SJ, Yan Y (2014) Grain-boundary-enhanced carrier collection in CsTe solar cells. Phy Rev Lett 112:256103
7. Tian W, Zhao C, Leng J, Cui R, Jin S (2015) Visualizing carrier diffusion in individual single-crystal organolead halide perovskite nanowires and nanowire arrays. J Am Chem Soc 137:12458–12461
8. Shi D, Adinolfi V, Comin R, Yuan M, Alarousu E, Buin A, Chen Y, Hoogland S, Rothenberger A, Katsie K, Losovyj Y, Zhang X, Dowben PA, Mohammed OF, Sargent EH, Bakır OM (2015) Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. Science 347:19–522
9. Nie W, Tsai H, Asadpour R, Blancon JC, Neukirch AJ, Gupta G, Crochet JJJ, Chhowalla M, Tretak S, Alam MA, Wang HL, Mohide AD (2015) High-efficiency solution-processed perovskite solar cells with millimeter-scale grains. Science 347:522–525
10. Yin WJ, Chen H, Shi T, Wei SH, Yan Y (2015) Origin of high electronic quality in structurally disordered CH₃NH₃PbI₃ and the passivation effect of Cl and O at grain boundaries. Adv Electron Mater 1:1500044
11. Xie FX, Zhang D, Su H, Ren X, Wong KS, Gratzel M, Choy WCH (2015) Vacuum-assisted thermal annealing of CH₃NH₃PbI₃ for highly stable and efficient perovskite solar cells. ACS Nano 9:639–646
12. Raja SR, Jung MC, Lee MV, Leyden MR, Kato Y, Qi Y (2015) Influence of air annealing on high-efficiency planar structure perovskite solar cells. Chem Mater 27:1597–1603
13. Liu J, Shirai Y, Yang X, Yue Y, Chen W, Wu Y, Islam A, Han L (2015) High-quality mixed-organic-cation perovskites from a phase-pure non-stoichiometric (2-x)PbI₂ x–PbI₂ for solar cells. Adv Mater 27:16201–16204
14. Cheng C, Lee MM, Noel NK, Hughes GM, Ball JM, Assender HE, Snaith HJ, Watt AAR (2014) Polystyrene templated porous titania arrays. Phys Status Solidi A-Appl Mat 210:255–260
15. Pham TTT, Besho T, Mathews NK, Zakeeruddin SM, Lam YM, Mhaisalkar S, Gratzel M (2012) Light scattering enhancement from sub-micrometer cavities in the photoanode for dye-sensitized solar cells. J Mater Chem 22:16201–16204
16. Cheng C, Lee MM, Noel NK, Hughes GM, Ball JM, Assender HE, Snaith HJ, Watt AAR (2014) Perovskite templated porous titania films for quantum dot heterojunction solar cells. ACS Appl Mater Inter 6:14247–14252
17. Horantner MT, Zhang W, Saibah M, Wojciechowski K, Snaith HJ (2015) Templated microstructural growth of perovskite thin films via colloidal monolayer lithography. Energy Environ Sci 8:2041–2047
18. Song X, Wang M, Xing T, Deng J, Ding J, Yang Z, Zhang X (2014) Fabrication of micro/nano-composite porous TiO$_2$ electrodes for quantum dot-sensitized solar cells. J Power Sources 253–257.

19. Hwang T, Cho D, Kim J, Kim J, Lee S, Lee B, Kim KH, Hong S, Kim C, Park B (2016) Investigation of chlorine-mediated microstructural evolution of CH$_3$NH$_3$PbI$_3$-xCl$_x$ nanorods through high optical-electronic responses. Nano Energy 25–99.

20. Kim J, Hwang T, Lee S, Lee B, Kim J, Jung GS, Nam S, Park B (2016) Solvent and intermediate phase as boosters for the perovskite transformation and solar cell performance. Sci Rep 6:25668.

21. Kim J, Choi H, Nahm C, Moon J, Kim C, Nam S, Jung DR, Park B (2011) The effect of a blocking layer on the photovoltaic performance in CdS quantum-dot sensitized solar cells. J Power Sources 196:10526–10531.

22. Heo JH, You MS, Chang MH, Yin W, Ahn TK, Lee SJ, Sung SJ, Kim DH, Im SH (2015) Hysteresis-less mesoscopic CH$_3$NH$_3$PbI$_3$ perovskite hybrid solar cells by introduction of Li-treated TiO$_2$ electrode. Nano Energy 15:530–539.

23. Lin CH, Chattopadhyay S, Hsu CW, Wu MH, Chen WC, WU CT, Tseng SC, Hwang JH, Jang IH, Pellet N, Gratzel M, Park NG (2014) Growth of CH$_3$NH$_3$PbI$_3$ perovskite nanorods in ethanol for TiO$_2$ layer. Nano Energy 14:468–487.

24. Divitini G, Cacovich S, Matteocci F, Cina L, Carlo AD, Ducati C (2016) Charge transfer in CH$_3$NH$_3$PbI$_3$ perovskite solar cells by interstitial sites in the TiO$_2$ blocking layer. J Phys Chem Lett 7:3936–3943.

25. Lee SJ, Flanagan JC, Kang J, Kim J, Shim M, Park B (2015) Integration of CdSe/CdSe$_x$Te$_{1-x}$ type-II heterojunction nanorods into hierarchically porous TiO$_2$ electrode for efficient solar energy conversion. Sci Rep 5:17472.

26. Xiao C, Yip HL, Acton O, Baek NS, Ma H, Jen AKY (2008) Interfacial modification to improve inverted polymer solar cells. Appl Phys Lett 92:303101.

27. Kang SH, Lim JW, Kim HS, Kim JY, Chung YH, Sung YE (2009) Photo and electrochemical characteristics dependent on the phase ratio of nanocolloidal structured TiO$_2$ films by magnetron sputtering technique. J Mater Chem 21:2777–2788.

28. Heiniger LP, Nazeeruddin MK, Park NG, Gratzel M (2014) Strong photocurrent amplification in perovskite solar cells with a porous TiO$_2$ blocking layer under reverse bias. J Phys Chem Lett 5:3936–3943.

29. Chen C, Cheng Y, Dai Q, Song H (2015) Radio frequency magnetron sputtering deposition of TiO$_2$ thin films and their perovskite solar cell applications. Sci Rep 5:17684.

30. Ge S, Xu H, Wang W, Cao R, Wu Y, Xu W, Zhou J, Xue F, Hong F, Xu R, Xu F, Wang L, Huang J (2016) The improvement of open circuit voltage from the sputteredITO layer for efficient perovskite solar cell. Vacuum 128:91–98.

31. Song X, Wang M, Xing T, Deng J, Ding J, Yang Z, Zhang X (2014) Fabrication of micro/nano-composite porous TiO$_2$ electrodes for quantum dot-sensitized solar cells. J Power Sources 253:17–26.

32. Manser JS, Kamar PV (2014) Band filling with free charge carriers in organometal halide perovskites. Nat Photonics 8:737–743.

33. Kamar PV, Manser JS, Kwon J, Kim J, Li S, Wang Y, Zhang P, Lee S, Wang Z, Hwang JH, Torre E, Carbone L, Gratzel M, Park NG (2016) Size-dependent transport and structural properties. Chem Mater 25:9118–9126.

34. Choi H, Hwang T, Lee S, Nam S, Kang J, Lee B, Park B (2015) The construction of tandem dye-sensitized solar cells from chemically-derived nanoporous photoelectrodes. J Power Sources 274:937–942.

35. Aitola K, Sveinbjornsson K, Correa-Baena JP, Kaskela A, Abate A, Todorov T, Gershon T, Gunawan O, Sturdevant C, Guha S (2014) Perovskite/organic solar cells. Adv Mater 21:759–773.

36. Blekinge-Rasmussen A, Lægsgaard E, Hammer B, Besenbacher F (2008) The role of interstitial sites in the TiO$_2$ blocking layer for high efficiency perovskite solar cells. J Mater Chem A 3:9179–9186.

37. Todorov T, Gershon T, Gunawan O, Sturdevant C, Guha S (2014) Perovskite/organic solar cells. Adv Mater 21:759–773.

38. Rizzo A, Calestani G, Gigli G, Angelis FD, Mosca R (2013) MAPbI$_3$xCl$_x$ mixed halide perovskite for hybrid solar cells: the role of chloride as dopant on the performance planar solar cells based on CH$_3$NH$_3$PbI$_3$-xCl$_x$ perovskites with intermediate phase as boosters for the perovskite transformation and solar cell performance. Sci Rep 6:25668.

39. MacManus-Driscoll JL, Greenham NC, Friend RH (2015) Size-dependent transport and structural properties. Chem Mater 25:9118–9126.

40. Yin WJ, Shi T, Yan Y (2014) Unusual defect physics in CH$_3$NH$_3$PbI$_3$ perovskite solar cell absorber. Appl Phys Lett 104:063903.

41. Leijtens T, Eperon GE, Barker AJ, Grancini G, Zhang W, Ball JM, Kandada ARS, Sneth HJ, Petrozza A (2016) Carrier trapping and recombination: the role of defect physics in enhancing the open circuit voltage of metal halide perovskite solar cells. Energy Environ Sci 9:3472–3481.

42. Li Z, Timkham J, Schulke P, Yang M, Kim DH, Berry J, Selliinger A, Zhu K (2016) Acid additives enhancing the conductivity of spiro-OMeTAD toward high-efficiency and hysteresis-less planar perovskite solar cells. Adv Energy Mater 6:1601451.

43. Shi T, Yan Y, Zhang W, Grancini G, Zhang W, Ball JM, Kandada ARS, Sneth HJ, Petrozza A (2016) Carrier trapping and recombination: the role of defect physics in enhancing the open circuit voltage of metal halide perovskite solar cells. Energy Environ Sci 9:3472–3481.

44. Hau SK, Yip HL, Acton O, Baek NS, Ma H, Jen AKY (2008) Interfacial modification to improve inverted polymer solar cells. Appl Phys Lett 92:303101.

45. Chen X, Yang S, Zheng YC, Chen Y, Hou Y, Yang HG (2015) Multifunctional inverse opal-like TiO$_2$ quantum dot-sensitized solar cells for efficient hybrid perovskite solar cells. Adv Sci 2:1500105.

46. Hau SK, Yip HL, Acton O, Baek NS, Ma H, Jen AKY (2008) Interfacial modification to improve inverted polymer solar cells. Appl Phys Lett 92:303101.