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Epitaxial 1D Electron Transport Layers for High-Performance Perovskite Solar Cells

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We demonstrate high-performance perovskite solar cells with excellent electron transport properties using a one-dimensional (1D) electron transport layer (ETL). The 1D array-based ETL is comprised of 1D SnO2 nanowires (NWs) array grown on a F:SnO2 transparent conducting oxide substrate and rutile TiO2 nanoshells epitaxially grown on the surface of the 1D SnO2 NWs. The optimized devices show more than 95% internal quantum yield at 750 nm, and a power conversion efficiency (PCE) of 14.2%. The high quantum yield is attributed to dramatically enhanced electron transport in the epitaxial TiO2 layer, compared to that in conventional nanoparticle-based mesoporous TiO2 (mp-TiO2) layers. In addition, the open space in the 1D array-based ETL increases the prevalence of uniform TiO2/perovskite junctions, leading to reproducible device performance with a high fill factor. This work offers a method to achieve reproducible, high-efficiency perovskite solar cells with high-speed electron transport.

Introduction

Emerging perovskite solar cells, using organometallic halides with perovskite crystal structures as light-absorbing materials, attract great attention for their continuous renewal of world-record power conversion efficiency (PCE) achievements, as well as for the economically viable processes for their fabrication.1-2 Recent high-PCE perovskite solar cells have n-i-p junction structures mainly comprising a hole transport layer (HTL; spiro-OMeTAD or poly-arylamine, representatively),3,4 perovskite light-absorbing layer (CH3NH3PbX3, where X = I, and X' = Cl or Br),5,6 and electron transport layer (ETL; TiO2 or ZnO, representatively).7-10 The highest PCE reported from this type of perovskite solar cell is 20.2%.11 The n-i-p junction-type perovskite solar cells can be classified by their ETL structures: pillared structures with CH3NH3PbI3, and planar structures with CH3NH3PbI3Clx, depending on the charge-transport ability of the light-absorbing materials.12 Usually, oxide nanoparticle (NP)-based mesoporous (mp) layers are used for the ETL of pillared structures. The main reason for using the mp-ETL is the short electron diffusion length (Le) ~ 100 nm of CH3NH3PbI3, of which film thickness is not sufficient for the full absorption of incident solar light. Therefore, the electron transport ability of the mp-ETL is very important in the pillared structure cells, to redeem the poor electron transport property of LAL. The mp-ETL plays two other roles: an extractor of electrons from the perovskite layer and a scaffolding to support the large volume of the perovskite layer. To optimize these two roles, all the pores in the mp-ETL layer should be filled with perovskite material; otherwise, the device performance would be degraded by low shunt resistance due to the direct contact of the ETL and HTL, large series resistance of the device due to longer electron/hole path,13-15 recombination at the exposed surfaces of the ETL and light absorbing perovskite layer, and low amount of perovskite materials.13,16 However, it is very hard to perfectly fill the labyrinthine pore network of the mp-ETL.17 From this perspective, a single-crystalline or highly oriented 1D array-based ETL (1D-ETL) is promising because of its excellent charge transport properties and open-pore structure, in contrast with those of conventional mp-ETLs.8-10,17-19 A recent work reported 1D ZnO-ETL-based perovskite solar cells in which relatively sparsely packed ZnO nanowires (NWs) with small diameter (24.1 nm) and length (600 nm) are employed.8 This thin and short ZnO NWs-based perovskite solar cells exhibit higher PCE, 14.35%,8 than the former large-size 1D ZnO-based perovskite solar cells (PCE < 12%).7,18,20,21 On the other hand, 1D TiO2-ETL-based perovskite solar cells show lower PCE (13.45%,22 the best) than the recent 1D ZnO-based devices, although reverse in the mp-ETL-based perovskite solar cells; the best PCE for mp-TiO2 is 20.2%,11 while that of mp-ZnO is 15.7%.23 This inconsistency is understood to result from insufficient light absorption, owing to densely packed large-
diameter 1D TiO$_2$ which might reduce the available space for light-absorbing material. In case of single-crystalline TiO$_2$ nanowires (NWs) grown on conductive substrates, it seems so far difficult to simultaneously have a low packing density, and small diameter (a few tens of nm) and length (a few hundreds of nm), in spite of a number of works on it.\textsuperscript{28-32}

In this work, we demonstrate a high-PCE (14.2\%) perovskite solar cell based on 1D-ETL structures, comprising TiO$_2$ nanoshell/SnO$_2$ NWs. Single-crystalline rutile-structured SnO$_2$ NWs were grown on a F:SnO$_2$ (FTO) transparent conducting oxide (TCO) substrate via a vapor-liquid-solid (VLS) reaction, and TiO$_2$ nanoshells were epitaxially grown on the surface of the SnO$_2$ NWs via plasma-enhanced atomic layer deposition (PEALD). Owing to the ultrathin (20 nm) and short (300 nm) SnO$_2$ NWs, the SnO$_2$/FTO shows nearly the same transmittance as bare FTO for all wavelengths. Optimized TiO$_2$/SnO$_2$ NW-based perovskite solar cells exhibit more than 95\% absorbed photon-to-current conversion efficiency (APCE) at 750 nm, and based perovskite solar cells exhibit more than 95\% absorbed photon-to-current conversion efficiency (APCE) at 750 nm, and for application in perovskite solar cells. The axial direction, i.e., its longitudinal direction, is [101] of rutile structure as shown in Figure 1b and 1c, consistent with the preferred crystal growth direction of rutile SnO$_2$\textsuperscript{35,36}. Although some kinked NWs and non-uniform contrasts appear in the NWs, the selected-area electron diffraction (SAED) patterns obtained from many other places show the same axial direction of rutile [101], indicating the single-crystallinity of the SnO$_2$ NWs. Figure 1d shows the UV/vis transmittance spectra of bare FTO and SnO$_2$ NWs/FTO. Notably, the bare FTO substrate and the SnO$_2$ NW/FTO exhibit similar transmittance at over 400 nm of wavelength, which can be attributed to the large band gap of SnO$_2$ (3.7 eV) and the sparse packed, thin and short NWs.

**Results and Discussion**

Figure 1. (a) Cross-sectional FE-SEM image of synthesized SnO$_2$ NW arrays on FTO substrate. (b) TEM image of a typical SnO$_2$ NW (inset: SAED pattern). (c) High-resolution TEM (HRTEM) lattice image of the SnO$_2$ NW with [-101] zone axis (inset: FFT pattern), and (d) UV-vis transmittance spectrum for bare FTO and SnO$_2$ NW/FTO.

Figure 1a and 1b show microstructure of the synthesized SnO$_2$ NWs, taken with a field-emission scanning electron microscope (FESEM) and a transmission electron microscope (TEM). NWs are compactly grown on the FTO substrate. Most of the NWs possess a small degree of kinked features, and are mostly straight, typical of VLS-grown SnO$_2$ NWs.\textsuperscript{33,34} The length and diameter of the SnO$_2$ NWs can be controlled from 100 to 2000 nm and from 5 to 20 nm, respectively, by adjusting the reaction time, temperature, and oxygen flow rate. The optimized length and thickness were found to be 300 nm and 20 nm, respectively, for application in perovskite solar cells. The axial direction, i.e., its longitudinal direction, is [101] of rutile structure as shown in Figure 1b and 1c, consistent with the preferred crystal growth direction of rutile SnO$_2$.\textsuperscript{35,36} Although some kinked NWs and non-uniform contrasts appear in the NWs, the selected-area electron diffraction (SAED) patterns obtained from many other places show the same axial direction of rutile [101], indicating the single-crystallinity of the SnO$_2$ NWs. Figure 1d shows the UV/vis transmittance spectra of bare FTO and SnO$_2$ NWs/FTO. Notably, the bare FTO substrate and the SnO$_2$ NW/FTO exhibit similar transmittance at over 400 nm of wavelength, which can be attributed to the large band gap of SnO$_2$ (3.7 eV) and the sparse packed, thin and short NWs.

Figure 2a and 2b show the morphology and lattice image of the TiO$_2$ nanoshell-coated SnO$_2$ NWs. TiO$_2$ layers deposited via ALD show smooth surfaces, uniform thicknesses and no cracks. The thickness of the TiO$_2$ nanoshell is tunable by the number of deposition cycles, with a deposition rate of 0.5 Å per cycle. The device performance was optimal with a 20 nm-thick TiO$_2$ nanoshell. Figure 2c-f shows scanning transmission electron microscopy (STEM) images and elemental mapping of Ti, O, and Sn, which clearly show the SnO$_2$ core and TiO$_2$ shell. The crystal structure of the TiO$_2$ nanoshell is rutile, confirmed by Raman spectroscopy (Figure 2b) and SAED (Figure 2b inset) analyses. Substrate-dependent phase formation in ALD-grown TiO$_2$ has been reported frequently. For example, we reported the formation of the anatase phase on ITO NWs using the same process,\textsuperscript{9} while other groups observed rutile phase on rutile substrates with similar lattice parameters, such as SnO$_2$ and RuO$_2$, as the nucleation of the rutile phase can be more energetically stable than that of the anatase phase.\textsuperscript{38-41}
Interestingly, the fast Fourier transformed (FFT) patterns show exact matches in crystal directions of the TiO$_2$ nanoshell and the SnO$_2$ core. The HRTEM lattice image obtained from the TiO$_2$/SnO$_2$ interface (Figure 2b) also shows continuous lattice fringes across the interface. Both the SnO$_2$ core and TiO$_2$ shell have (101) planes parallel to the axial direction, and (010) planes aligned radially. This confirms the epitaxial formation of the TiO$_2$ shell as illustrated in Figure 2g.

![Figure 3](image-url)  
**Figure 3.** $J$-$V$ curves of TiO$_2$ NP-based mp-ETL and TiO$_2$/SnO$_2$ NW-based 1D-ETL perovskite solar cells.

![Figure 4](image-url)  
**Figure 4.** (a) LHE, (b) IPCE, and (c) APCE spectra of the TiO$_2$ NP-based mp-ETL and the TiO$_2$/SnO$_2$ NW-based 1D-ETL perovskite solar cells.

The relatively low $J_{sc}$ can be understood as a result of the low light absorption property of the 1D-ETL cells. Figure 4a shows the light harvesting efficiency (LHE) of the ETL layers, calculated using the optical absorbance (A) and reflectance (R) shown in Figure S3, ESI†, as follows:

$$LHE = 1 - (1 - 10^{-4A})$$  \hspace{1cm} \text{(1)}

Because the optical transmittance of SnO$_2$ NW/FTO is comparable to that of bare FTO, the low LHE of the 1D-ETL is attributed to small amount of the perovskite absorber material. Assuming hexagonally closed packed cylindrical nanowires,$^{17,43}$ the packing factor (PF), which is nanowire volume divided by geometric volume, is calculated to be $\sim$0.9.

On the other hand, PF of hexagonally closed packed spherical NPs is 0.74, which is the general fraction of volume in a hexagonal crystal structure. Therefore, the pore volume fraction of NP based ETL can be higher than NW based ETL. Considering that the thickness of perovskite/ETL layers are almost same for the both mp and 1D-ETL devices (see Figure S2, ESI†), the small absorber amount might be due to small pore volume of the 1D-ETL. The low LHE resulted in low external quantum yield (i.e. incident photon to current efficiency, IPCE) of 1D-ETL device, as shown in Figure 4b. The mp-ETL cell exhibits a slightly higher IPCE than the 1D-ETL cell especially in the wavelength range of 500 to 700 nm. However, it should be noted that, at long wavelengths (>700 nm), both cells show similar IPCE, in spite of the large
difference in LHE. To compare the internal quantum yields of the cells, the absorbed photon-to-current efficiency (APCE) was obtained from the IPCE and LHE as follows:

\[
APCE = \frac{IPCE}{LHE}
\]

(2)

**Figure 4c** shows that the APCE of the 1D-ETL reaches nearly 100% at the wavelength of 750 nm, implying the excellent electron-collection efficiency of 1D-ETL in longer wavelength regime.

The charge collection properties of the cells were investigated by measuring the electron diffusion coefficient, \(D_n = \frac{\tau_n}{t}\), where \(t\) is thickness of the ETL layer and \(\tau_n\) is the characteristic time constant of electron transport. **Figure 5** shows the 1D-ETL cell’s \(D_n\) being about one order of magnitude greater than that of the mp-ETL cell, which is responsible for the extremely high internal quantum yield of the 1D-ETL cell. Several studies have reported faster electron transport in 1D-based dye-sensitized solar cells (DSSCs) compared to NP-based DSSCs while in perovskite solar cells \(D_n\) values for 1D versus NP structures have rarely been compared. We demonstrate here the enhanced electron transport in epitaxial 1D-ETL over that in NP-based mp-ETL. Therefore, it can be considered that the fast electron transport of the 1D-ETL compensates the IPCE, thus PCE, of the device, despite of its lower LHE than mp-ETL.

**Figure 5.** Electron diffusion coefficient of the TiO\(_2\) NP-based mp-ETL perovskite solar cell, compared to the TiO\(_2\)/SnO\(_2\) NW-based 1D-ETL perovskite solar cells.

**Figure 6.** The extracted properties of the best performing cell among the surface treated TiO\(_2\)/SnO\(_2\) NW-based 1D-ETL perovskite solar cells.

**Figure 6** shows the \(J-V\) curve of the best 1D-ETL cell, optimized by controlling the TiO\(_2\)/perovskite interfaces via TiCl\(_4\) treatment. This cell exhibited PCE of 14.2%. The highly improved device performance is attributed to the TiCl\(_4\) treatment which is well-known to modify the TiO\(_2\) surface by increasing interconnection at the perovskite/TiO\(_2\) interface and reducing the trap states of the TiO\(_2\) surface. We note that the high \(V_{oc}\) of 1.02 V, in spite of the lower conduction band edge of SnO\(_2\) than that of TiO\(_2\) by as much as 500 meV, might be resulted from the passivation of recombination owing to the ALD TiO\(_2\) thin layer, because SnO\(_2\) layer without any passivation layer, such as TiO\(_2\) or PbI\(_2\), is known to exhibit very low \(V_{oc}\) as also confirmed by our bare SnO\(_2\) NW-based ETL PSC (Figure S4, ESI).

**Conclusions**

In summary, we demonstrated a 1D TiO\(_2\)-based perovskite solar cell which exhibits relatively high PCE, 14.2%, compared to other 1D-based perovskite solar cells. The 1D ETL layer is comprised of single-crystalline SnO\(_2\) NWs as cores and epitaxial TiO\(_2\) nanolayers as shells. The epitaxial TiO\(_2\) rutile nanoshell enhanced electron transport compared to the conventional NP-based mp-ETL, which resulted in extremely high internal quantum yield more than 95% at around 750 nm of wavelength. Additionally, the open-pore structure led to excellent pore-filling with the perovskite material, considered to be the origin of the higher FF of the 1D-ETL cells compared to that of the mp-ETL cells. The optimized TiO\(_2\)/SnO\(_2\) NW-based perovskite solar cell exhibited a high PCE of 14.2%, which is the best performance yet reported for 1D TiO\(_2\) ETL-based perovskite solar cells.

**Experimental**

**Preparation of electron transport layer**

SnO\(_2\) NWs were synthesized via the VLS reaction using a vapor transport method. Au seeds as the catalyst were coated over FTO substrate by using an ion beam coater. To grow SnO\(_2\) nanowires, the Au/FTO substrate and tin powder were placed at the center of the tube furnace with some distance, under 700 °C in vacuum (1.0 mTorr) for 1.5 hr. Oxygen gas was flowed with a rate of 20 sccm into the tube furnace during the growth of SnO\(_2\) NWs.

As the SnO\(_2\) itself is not suitable for the ETL of perovskite solar cells because of its low conduction band edge (~-4.5 eV), TiO\(_2\) nanoshell layer was employed for the ETL. TiO\(_2\) nanoshell layers were deposited on the prepared SnO\(_2\) NWs by using ALD method with the help of O\(_2\) plasma, under 1.0 Torr of basial pressure at 300 °C. After the deposition, TiO\(_2\)/SnO\(_2\) NWs were annealed at 500 °C in air for 1h to achieve high crystallinity of TiO\(_2\). We tested various thicknesses of TiO\(_2\)
nanoshells, and optimized the shell thickness of ~20 nm for efficient perovskite solar cells.

To compare the photovoltaic performance, TiO$_2$ NP-based mp-ETL was prepared following the methods reported previously.$^{56}$ First, compact TiO$_2$ layer was deposited on FTO substrate. A titanium disopropoxide bis(acetylacetonate) solution (in 1-butanol, 0.15 M) was coated on an FTO substrate, and dried at 120 °C for 10 min. Then 0.3 M titanium disopropoxide bis(acetylacetonate) solution was coated onto the substrate using the same method. After then the substrate was annealed at 500 °C for 15 min. After cooling to room temperature, the substrate was immersed in TiCl$_4$ solution (aqueous, 0.05 M) for 30 min at 70 °C. Then the substrates were rinsed with deionized (DI) water several times, and annealed at 500 °C for 15 min. Second, TiO$_2$ mesoporous layer was formed on the prepared substrate, using TiO$_2$ NPs (~20 nm, 18NRT)-based paste purchased from Dyesol$^{TM}$. A diluted paste (in ethanol, 1:3.5 wt%) was spin-coated onto the TiCl$_4$-treated substrate, and then annealed at 500 °C in air for 45 min.

Fabrication of Perovskite Solar Cells

The light absorbing perovskite layer was coated on the prepared ETL by the sequential deposition of PbI$_2$ and methyl ammonium iodide (MAI, CH$_3$NH$_3$I).$^{56}$ MAI was prepared according to the reported procedure.$^2$ 30 mL of hydriodic acid (57 wt% in water) was stirred on a round bottom flask with 27.8 mL of methylamine (40% in methanol) at 0 °C for 2 hr. Then, the solution was evaporated to precipitate the MAI. The MAI was washed three times in diethyl ether, and dried at 60 °C in vacuum oven for 6 hr. The prepared ETLs were coated with a PbI$_2$ solution (1.0 M, in dimethylformamide), and dried at 70 °C. Then, they were dipped in an MAI solution (10 mg·mL$^{-1}$, in 2-propanol) for 60 sec, rinsed with 2-propanol, and dried at 70 °C for 30 min. HTL was deposited on the perovskite layer by spin-coating (4000 rpm, 40 sec) spiro-OMeTAD (2,2′,7,7′-tetrakis-(N,N-diphenylamino)-9,9′-spirofluorene)-based solution. The solution was prepared by dissolving spiro-OMeTAD (72 mg) in chlorobenzene (1 mL), with adding 4-tert-butylylpyridine (28.8 μL) and lithium-bis(trifluoro-methanesulphonyl)imide salt (17.6 μL, 520 mg·mL$^{-1}$ in acetonitrile). Finally, 80 nm-thick Ag electrodes were deposited on HTM layers via using thermal evaporation.

Device Characterization

Microstructures of the 1D-ETLs and devices were analyzed by using a field-emission scanning electron microscopy (FESEM, JSM-7600F, JEOL) and HR-TEM (JEM-2100F, JEOL). Optical transmittance and absorbance of the materials were measured by using an UV/vis spectrometer (PerkinElmer). Crystal structures were analyzed by using Raman spectroscopy (WITec alpha 300M), and SAED combined with the HRTEM. Photovoltaic performances were evaluated using a potentiostat (CHI660, CHI instrument), under the global AM 1.5 condition simulated by a solar simulator (Oriel Sol 3A class AAA, Newport). Active cell area was 0.14 cm$^2$. Photocurrent density–voltage ($J-V$) curves were collected with 0.05 V·sec$^{-1}$ of scan rate. Time constant for photo-generated electron transport ($	au_e$) was measured using a transient photocurrent–voltage spectroscopy setup, which is described elsewhere.$^{56}$ The incident photon-to-current conversion efficiency (IPCE) was measured using a monochromatic light grating system (PV Measurements).

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$^+$ Electronic Supplementary Information (ESI) available: Histograms of the parameters, UV-vis absorption spectrum and the cross-sectional FE-SEM image of the TiO$_2$ NP based mp-ETL cell, TiO$_2$/SnO$_2$ NWs based 1D-ETL perovskite solar cells and exposure FTO at grown SnO$_2$ NWs on FTO substrate. See DOI: 10.1039/b000000x/

6 J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, S. I. Seok, Nano Lett., 2013, 13, 1764.