Solid-State Solar Cells Based on TiO$_2$ Nanowires and CH$_3$NH$_3$PbI$_3$ Perovskite

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Abstract: Perovskite inorganic-organic solar cells are fabricated as a sandwich structure of mesostructured TiO$_2$ as electron transport layer (ETL), CH$_3$NH$_3$PbI$_3$ as active material layer (AML), and Spiro-OMeTAD as hole transport layer (HTL). The crystallinity, structural morphology, and thickness of TiO$_2$ layer play a crucial role to improve the overall device performance. The randomly distributed one dimensional (1D) TiO$_2$ nanowires (TNWs) provide excellent light trapping with open voids for active filling of visible light absorber compared to bulk TiO$_2$. Solid-state photovoltaic devices based on randomly distributed TNWs and CH$_3$NH$_3$PbI$_3$ are fabricated with high open circuit voltage $V_{oc}$ of 0.91 V, with conversion efficiency (CE) of 7.4%. Mott-Schottky analysis leads to very high built-in potential ($V_{bi}$) ranging from 0.89 to 0.96 V which indicate that there is no depletion layer voltage modulation in the perovskite solar cells fabricated with TNWs of different lengths. Moreover, finite-difference time-domain (FDTD) analysis revealed larger fraction of photo-generated charges due to light trapping and distribution due to field convergence via guided modes, and improved light trapping capability at the interface of TNWs/CH$_3$NH$_3$PbI$_3$ compared to bulk TiO$_2$.

Keywords: perovskite; TiO$_2$ nanowires; electron transport layer; finite-difference time-domain

1. Introduction

Recently, photovoltaics based on solid-state hybrids with inorganic nanostructures and organic conducting materials have been evolved as promising next generation solar cells. They provide additional route of nanofabrication integration with organic electronics [1,2]. In these hybrid integration, very thin active material layer(s) (AMLs) based on molecular organic/inorganic dyes [1,3], or quantum dots [4–7], are typically utilized between the interface of inorganic electron transport layer(s) (ETLs) and the organic hole transport layer(s) (HTLs), which enhance the conversion efficiency (CE). The light excitation produces electron-hole pairs in the AMLs, assists separation of photo-generated carriers, and injects electrons into ETLs and holes into the HTLs, which subsequently collect to the respective electrodes. Therefore, these interfaces of AMLs/ETLs and AMLs/HTLs play a significant role to the overall hybrid performance [2,3,8]. To optimize the light absorption and energy-level alignments in these interfaces, the optical and electronic properties of the ETLs can be varied by changing the bandgaps of the material using quantum dots [9,10], or by utilizing molecular dyes with variable LUMO-lowest-unoccupied molecular orbitals, and HOMO-highest occupied molecular orbital [11,12]. Yet, utilizing these AMLs materials to conventional mesoscopic ETLs arise problems such as ineffective electron transport in the ETLs due to partial filling of AMLs [13,14]. On the contrary, another way to achieve the energy band alignment between AMLs/ETLs is by adjusting the optoelectronic properties and structure of the ETLs by fabricating the ETLs with nanostructures, which could
improve the charge transfer and CE of the device. The perovskite material as AMLs in solar cell has recently reported the efficiency over 15% [15–17]. The rapid improvements in the efficiency during past few years suggests it as promising next generation material for solar cells. This material family is composed of CH$_3$NH$_3$PbX$_3$, where X represents I or Cl. CH$_3$NH$_3$PbI$_{3−x}$Cl$_x$ possess very high electron/hole diffusion lengths (1 μm~1.2 μm) and light harvesting capability [18,19]. Generally, perovskite solar cells are fabricated as sandwich structure of mesostructured TiO$_2$ as ETLs, CH$_3$NH$_3$PbX$_3$ as AML, and Spiro-OMeTAD [2,2′,7,7′-tetrakis(N,N-di-p-methoxy-phenyl-amine)9,9′-spirobifluorene] as HTL. The crystallinity, structural morphology, and thickness of TiO$_2$ layer play a crucial role to improve the overall device performance [20,21]. For example, the mesoporous TiO$_2$ films possesses highly convoluted porous channel which prevent filling of active materials in dye sensitized solar cells [22]. This problem also afflicts all solid-state devices based on TiO$_2$ based perovskite hybrids [23]. Specially, the family of methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) has lower electron diffusion length of 100 nm compared to CH$_3$NH$_3$PbI$_{3−x}$Cl$_x$, which is not sufficient for effective collection of charges at the anode. For example, increasing the thickness of mesoporous TiO$_2$ to above 600 nm, cause large resistance, loss of open-circuit voltage ($V_{oc}$) and poor fill factor. Therefore, the realistic approach suggests that the thickness of the TiO$_2$ should be controlled within the range of 400 nm~600 nm [16,24–26]. There have been various strategies utilized for improving the performance of TiO$_2$ [27,28]. These efforts can mainly be classified into: (1) The morphological studies based on engineering the TiO$_2$ material by fabricating different nanostructures such as nanoparticles [27], nanowires [29,30], nanosheets [31,32], and nanotubes [33], particularly to improve both charge transfer process and surface area. The high performance of nanostructure requires both high surface area and architecture to promote longer photo-generated carrier lifetime. Among nanostructures, TiO$_2$ nanoparticles (TNPs) offer highest area, while TiO$_2$ nanowires (TNWs) and nanotubes (TNTs) possess better charge separation and collection mechanism [34]. Meanwhile, it has been widely accepted that the photo-conversion efficiency of TNWs is higher than that of TNPs [35,36]. Additionally, the filling of the active AML in the voids between the TNWs can be more efficient compared to planar TiO$_2$. Such filling enables the forming of fully passivated perovskite/TiO$_2$ interface with nearly no dead volumes. The preparation of the TNWs via hydrothermal process provide controllable length to diameter ratio and self-aligned array with wire to wire spacing. Meanwhile, TNWs fabricated by this facile approach improves electron transport mechanism 200 times faster compared to mesoporous TiO$_2$ films [37].

We have developed the one-dimensional (1D) TNWs with controlled thickness and length of 0.1 μm, 0.2 μm and 0.35 μm for providing the direct path to the photo-generated electrons in the organometal halide perovskite (CH$_3$NH$_3$PbI$_3$). This nano-crystalline channel allows the filling of the CH$_3$NH$_3$PbI$_3$ in the nano-voids with large surface area, which improve the electron transport efficiency. The resulting devices reveal high $V_{oc}$ and $V_{bi}$ which indicate no voltage modulation in the perovskite solar cells by varying lengths of TNWs. In addition, Maxwell modeling of the 3-D mesh analysis using Finite-Difference Time-Domain (FDTD) suggest greater generation of charges at the interface of TNWs/CH$_3$NH$_3$PbI$_3$ compared to bulk TiO$_2$.

2. Methodology

2.1. Experimental Details

Firstly, substrate preparation was undertaken under ambient conditions. Transparent Fluorine doped Tin Oxide glass (7 Ω/□ sheet resistivity) were cleaned with 2% solution of detergent of Hellmanex diluted in deionized water, thoroughly rinsed with ethanol and acetone diluted in deionized water, and further kept in open air for drying. The hydrothermal process is utilized to fabricate the TNWs on the FTO glass. In a typical process, the autoclave with Teflon-lined stainless steel is utilized to mix the solution of Ethylene glycol (0.5 mL) and deionized water (6 mL), stirred for 5 min, then HCl (3 mL) is mixed, and the resulting mixture is stirred for another 5 min. The 220 μL of Titanium
butoxide Ti(OBu)₄ is later dropwise added in the mixture and the final solution is stirred for 10 min to obtain the clear transparent solution. FTO glass is placed inside the solution, and against the wall of Teflon with tilt of 45°. The hydrothermal synthesis was carried at 150 °C for 6 h, and later autoclave is removed and allowed to cool in air. The obtained TNWs on FTO glass were taken out of the cooled autoclave, extensively rinsed by deionized water, and kept in air for drying. The post-baking, and sintering are applied at 500 °C for 45 min in furnace to remove the residuals. The synthesis of CH₃NH₃PbI₃ absorber is carried out after utilizing the crystals of methyl iodide (CH₃NH₃I) and lead iodide (PbI₂) prepared according to the reported methods with slight modifications [38]. The prepared crystals of CH₃NH₃I are mixed with equimolar PbI₂, then dissolved in Dimethylformamide solution (~40 wt.%, anhydrous) with stirring at 60 °C for 6 h to produce CH₃NH₃PbI₃ (2.5 mM). This perovskite absorber was deposited on TNWs using spin-coating method at 3500 rpm, followed by baking at 80 °C for 30 min. During baking process, the crystallization causes the absorber film to turn from yellow color to dark brown. The hole-transporter layer (HTL) of Spiro-OMeTAD was deposited on top of perovskite by controlling the spin coating rate of 2000 rpm for 45 s. The solution of HTL was prepared using 25 µL of chlorobenzene solution that contained 26 mM lithium bis (trifluoromethylsulfonyl)imide (Li-TFSI) salt, 53 mM tert-butylpyridine (tBP), and 62 mM Spiro-OMeTAD. Further, the samples were left for drying in glove-box for 15 min. Finally, the metal mask was used for silver (Ag) electrodes which were deposited through thermal evaporation at ultra-low pressure of 10⁻⁵ mbar forming the cathode.

2.2. Characterization

The MIRA3 system by TESCAN equipped with Schottky emitter (TESCAN, Brno, Czech Republic) is used for field emission scanning electron microscope (FESEM). The photovoltaic characterization under air mass 1.5 illumination was conducted using CompactStat (±30 mA/±10 V) by HS technologies after calibration with NREL certified reference cell compliance to VLSI standards by photovoltaic Measurements, Inc. (Washington, USA) with uncertainties under standard testing conditions (STC) incident photon current efficiency (IPCE) measurement is performed after calibration with reference photodetector using Xe light source (300 W) equipped k3100 system with monochromator. IviumStat (±5 A/±10 V) by HS technologies is used for Mott-Schottky measurements. For 3D-FDTD, optical device simulations are performed using Maxwell solver by Lumerical (Vancouver, BC, Canada).

3. Results and Discussion

The layout of the solid-state perovskite device with FTO, TNWs, Perovskite, Spiro-OMeTAD, and Ag electrodes, is shown in Figure 1a. The band adjustment scheme of the device in Figure 1b shows that photo-generated electrons transfer from the perovskite to TiO₂ (subsequent the electrons are transported to the FTO) and Spiro-OMeTAD collects the holes which further transport to Ag electrodes.

Figure 2a shows top view of the TNWs uniformly fabricated on the FTO glass. The TNWs were fabricated via temperature controlled autoclaving process where the length is controlled with increasing time. The CH₃NH₃PbI₃ is deposited onto the TNWs by two steps process of spin-coating forming a compact film that penetrates deep in the gaps of nanowires with conformal coverage as shown in Figure 2b. It is worth mentioning that the CH₃NH₃PbI₃ penetrates deep in the gaps of the TNWs and empty voids fill with sensitizer. As shown in Figure 2c–e, the cross-sectional view of the three solid-state devices with variable length of the TNWs, calculated as 0.35 µm, 0.2 µm, and 0.1 µm with the average width of 50 nm, after varying the auto-clave processing time from 5 to 6 h. The minor discrepancies in the length of the nanowires were seen while keeping the batch same with similar synthesis process. It can be seen in Figure 2e that short lengths of TiO₂
(0.1 µm) increase the probability of shortening of contacts between CH$_3$NH$_3$PbI$_3$ and FTO compared to compact layers formed with longer TiO$_2$ lengths. After the conformal coating of CH$_3$NH$_3$PbI$_3$, the HTL of Spiro-OMeTAD is spin-coated and the leakage of the film to TiO$_2$ is avoided in the device. To check the influence of length of compact TNWs, perovskite devices were fabricated and electrically characterized.

Figure 1. (a) Schematic illustration of the solid-state solar cell device based on TNWs and Perovskite, (b) Energy band alignment of the device structure.

Figure 2. (a) Top rough surface of the TNWs and, (b) conformal CH$_3$NH$_3$PbI$_3$ coated TNWs, (c–e) Cross-sectional FESEM images of solid-state TNWs/Perovskite solar cells with compact TNWs lengths of 0.35 µm, 0.2 µm, and 0.1 µm. All figures have scale bar of 0.5 µm.

The typical current-density (J-V) curves with forward and reverse sweeps are shown in Figure 3a,b. The results of solid-state perovskite devices with TNWs are compared in Table 1. It is established that the performance of the devices was degraded with decreasing TNWs lengths to the extent if perovskite directly contact with the FTO in open voids. These results further emphasize the alternative approach of ultrathin TiO$_2$-passivation ETLs via atomic layer deposition on 1D TiO$_2$ for efficient perovskite solar cell applications [38,39]. While increasing the length to 0.35 µm, the fill factor and current density decreases, which ultimately reduces the efficiency to 6.13%. The highest efficiency of 7.4% were attained with relatively shorter TNWs of 0.2 µm. The performance of the reverse sweeps with dark currents in Figure 3b are shown where the devices with the compact TNWs of 0.2 µm, and 0.35 µm compared to 0.1 µm reflect consistent performance with slight change in reversed and forward bias due to change in series resistance resulting due to partial filling of perovskite and are consistent with SEM images with different length of TNWs. This is further evident in the IPCE shown in Figure 3c, where the trend continuous while TNWs of
0.2 μm utilize the short wavelength light to 60%, and 0.35 μm utilize 50% at the wavelength range between 500 nm and 700 nm. The poor J-V performance and IPCE of the shorter TNWs of 0.1 μm is due to the leakage current degrading overall performance. The further analysis of the Mott-Schottky in Figure 3d demonstrates very high and stable built-in potential of 0.89 V for 0.1 μm, 0.92 V for 0.2 μm, and 0.96 V for 0.35 μm. This indicates that irrespective of varying the TNWs lengths, there is no depletion layer voltage modulation which shows stable parasitic capacitance in the TNWs/Perovskite solar cells [40].

![Figure 2](image.png)

**Figure 2.** (a) Top rough surface of the TNWs and, (b) conformal CH₃NH₃PbI₃ coated TNWs, (c)–(e) Cross-sectional FESEM images of solid-state TNWs/Perovskite solar cells with compact TNWs lengths of 0.35 μm, 0.2 μm, and 0.1 μm. All figures have scale bar of 0.5 μm.

![Figure 3](image.png)

**Figure 3.** (a,b) J-V characteristics (forward sweep) and dark current of prepared solid state devices, (c) IPCE with the influence of changing length of the TNWs, and (d) Mott-Schottky plots to extract the $V_{bi}$ of the solid-state hybrid devices.

<table>
<thead>
<tr>
<th>Solid-State Perovskite Devices</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>CE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃NH₃PbI₃/TNWs (0.2 μm)</td>
<td>13.06 (±0.02)</td>
<td>0.91(±0.06)</td>
<td>63.2  (±0.1)</td>
<td>7.40 (±0.04)</td>
</tr>
<tr>
<td>CH₃NH₃PbI₃/TNWs (0.35 μm)</td>
<td>11.11 (±0.05)</td>
<td>0.92 (±0.03)</td>
<td>60.1  (±0.1)</td>
<td>6.13 (±0.07)</td>
</tr>
<tr>
<td>CH₃NH₃PbI₃/TNWs (0.1 μm)</td>
<td>10.66 (±0.07)</td>
<td>0.89 (±0.02)</td>
<td>61.1  (±0.1)</td>
<td>5.80 (±0.05)</td>
</tr>
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To understand the light trapping and distribution though field convergence via guided modes, FDTD simulations based on Maxwell equations are performed by considering 3-dimensional (3-D) mesh of the fabricated device geometry. While electric field distribution with normalized magnitude (0–1) were evaluated using transverse polarization by curl equations [41,42]. The cross-section of 3-D devices are shown in Figure 4 with the incident wave lengths of 350, 500, and 700 nm in z-direction. The lengths of the TNWs are taken as 0.2 μm and 0.35 μm, and further compared with the planar compact device. At 350 nm, the compact TiO₂ based devices shown in Figure 4a–c, showed that the entire electric field
uniformly distributed in layered path through perovskite and the magnitude of less than 0.8 was observed. However, in case of TNWs, the magnitude of 0.92 to 0.98 were observed with 0.2 µm and 0.35 µm devices, shown in Figures 4d–f and 4g–i, respectively. At 500 nm, the field distributions were 0.8 for planar and 1 for both TNWs based devices. At 700 nm, the field magnitude of 0.7 with planar device were observed as compared to the relatively high magnitude of 0.98 for both TNWs based devices. The high electric field in case of TNWs at lower and higher wavelengths were observed due to mainly two factors. Firstly, the reflections of the TNWs are suppressed due to randomly distributed wires along the interface of the device. The profile of such interface has graded refractive index, hence can act as antireflection layer, and improve light trapping. Therefore, incident light is directed through directional paths of TNWs. Second, the TNWs can act as guided modes that efficiently couple the incident light which later interact with the perovskite layers. This is relatively more noticeable in case of higher wavelengths of 700 nm, indicating comparatively strong modes confined in the TNWs which interact with perovskite. Besides, the electric field distributions with the bunch of neighboring TNWs/perovskite can also lead to strong intensity field’s distributions of 0.8 to 1.0 compare with 0.5 to 0.6 of compact TiO$_2$/perovskite as shown in Figure 5a,b. Hence, it can be concluded that mainly larger fractions of photo-generated charges are generated due to field convergence via guided modes and increases light trapping capability at the interface of TNWs/CH$_3$NH$_3$PbI$_3$ compared to compact layered TiO$_2$.

![Figure 4](link_to_image)

**Figure 4.** The 3D mesh of perovskite devices integrated for FDTD over the wavelengths of 350 nm, 500 nm, and 700 nm. (a–c) The planar device with TiO$_2$ presented to compare the intensity of the electric field. (d–i) The electric field distributions within the devices are compared based on the influence of changing length of the TNWs from 0.2 to 0.35 µm.
Figure 4. The 3D mesh of perovskite devices integrated for FDTD over the wavelengths of 350 nm, 500 nm, and 700 nm. (a–c) The planar device with TiO$_2$ presented to compare the intensity of the electric field. (d–i) The electric field distributions within the devices are compared based on the influence of changing length of the TNWs from 0.2 to 0.35 µm.

Figure 5. (a) The bulk TiO$_2$/Perovskite compare to (b) TNWs/Perovskite truncated interface at 700 nm.

4. Conclusions

The solid-state perovskite solar cells are fabricated with randomly distributed 1-D TNWs with active filling of CH$_3$NH$_3$PbI$_3$. The resulting device demonstrates high $V_{oc}$ of 0.91 V, with CE of 7.4%. Mott-Schottky analysis revealed high $V_{bi}$ ranging from 0.89 to 0.96 V which reflect that there is no depletion layer voltage modulation in the fabricated solar cells. FDTD analysis showed that larger fractions of photo-generated charges are generated due to field convergence within the nanowires and presence of guided modes at the interface of TNWs/CH$_3$NH$_3$PbI$_3$ compared to layered TiO$_2$. These results suggest that the 1D TNWs-based perovskite device offers utilizing thinner TiO$_2$ with larger surface areas without sacrificing the charge transport efficiency.


Funding: This work was supported by the International Collaborative Energy Technology R&D Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) (No. 20168520011370), and the Future Semiconductor Device Technology Development Program (10067739), and granted financial resource from the Ministry of Trade, Industry & Energy and Korea Semiconductor Research Consortium (KSRC), Republic of Korea.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

References


