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Rutile TiO₂ Nanowires Perovskite Solar Cells

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Abstract: Different lengths of rutile TiO₂ nanowires (NW) with wide-open space for effective material filling were used as photoanodes for perovskite solar cells. Cells with 900 nm nanowires as photoanodes exhibit current density of 22 mA/cm² and efficiency of 11.7%, exceeding the reported TiO₂ nanowire-based perovskite solar cells.

Since it was first reported in 2009, perovskite type CH₃NH₃PbI₃ solid solar cells have recently been reported with over 15% efficiency.²,³,⁴ The astounding improvements in efficiency achieved in the past few years suggests that it is a promising candidate for the next generation solar cells. This material exhibits unusual excellence in both charge transport (electron/hole diffusion lengths are about 1μm/1.2μm CH₃NH₃PbI₃Clₓ, respectively⁵), and light harvesting (1.5 × 10⁶ cm⁻¹ at 550 nm).⁶ In general, perovskite solar cells are configured as a sandwich structure. Explicitly, a mesostructuredTiO₂ layer on FTO serves as the photoanode, which is filled up with perovskite CH₃NH₃PbX₃ as PV active layer, followed by capping with a hole transport material layer (HTM) and a metal counter electrode. It is noticed that the morphology, thickness and crystallinity of the TiO₂ layers,⁷,⁸ including both the compact electron-blocking layer and the mesostructured layer,⁸,⁹ play a crucial role in the efficiency of similar solar cells. For example, in dye sensitized solar cells, mesoporous TiO₂ films often suffer from the difficulty in filling of dye molecules in the highly convoluted porous channels.¹⁰ This is also a problem with perovskite CH₃NH₃PbI₃Clₓ.¹¹ On the other hand, electron diffusion length in CH₃NH₃PbI₃ is about 100 nm,⁵ not thick enough to suffice light harvesting. For instance, when the thickness of mesoporous TiO₂ exceeds 600 nm, the electron/hole transport encounters large resistance, resulting in significant loss of open-circuit voltage (Vₒᶜ) and fill factor (FF).⁶ Thus, the optimized thickness for mesoporous TiO₂ must be controlled in range of 400 nm to 600 nm.¹²,¹³

The use of aligned array of one dimensional TiO₂ NWs as photoanode in perovskite solar cells provides a potential solution to the conflicting demands on light absorption and charge transport appeared in mesoporous photoanodes. As depicted in Figure 1, on one hand, the high electron diffusion length in the NWs facilitate/afford directed electron transport in the case of thick CH₃NH₃PbI₃ layer.¹⁵ On the other hand, if the voids between the NWs is widely open, the filling of the perovskite solution can be much efficient than the compact NWs, forming a perovskite layer with nearly no dead volumes. Indeed, perovskite solar cell with one dimensional TiO₂ NWs array has reach 4.9% efficiency in the early stage,¹⁵ and shortly, the efficiency achieved 9.4% using a rutile compact TiO₂ nano-rods structure, which is so far the highest efficiency achieved on NW-based perovskite cells.¹⁶ Both reported TiO₂ NWs used in these previous works are all prepared via hydrothermal method.

Figure 1. Schematic comparison between NWs TiO₂ and mesoporous TiO₂ photoanodes. Perovskite CH₃NH₃PbX₃ precursor and HTM filling paths were indicated in green for the nanowire photoanodes. In contrast, mesoporous photoanodes inevitably contains some dead volumes (blue parts) that are not readily accessible for the perovskite materials.

Recently, we reported a solvothermal method for the synthesis of rutile NWs with controllable length-to-diameter ratio and well-separated wire-to-wire space. We have also demonstrated that electron transport in these rutile NWs is 200 time faster than that of mesoporous rutile films.¹⁷ Herein, we apply these rutile NW arrays with different length as photoanodes in perovskite solar cells and we achieved 11.7% efficiency, which is 2% (absolution value) higher than the best perovskite solar cells using nanowire as photoanode reported in the literatures.¹⁶
spinning-coated spiro-MeOTAD (2,2’-7,7’-tetrakis(N,N-di-p-methoxyphenyl amine)-9,9’-spirobifluorene as hole transport layer. Finally, a thermally evaporated gold layer (80 nm) is deposited as the cathode.

Figure 2a, 2b, 2c and 2d are the cross-section SEM images of 400 nm, 600 nm, 900 nm and 1.2 µm NWs on FTO, respectively. It can be seen that the NWs are 30~50 nm apart from each other, providing the voids for the filling of perovskite CH₃NH₃PbI₃ precursor. The top view of the 900 nm NWs (Figure 2e) further confirms that the voids among the NWs are open and accessible. According SEM images, the density of the rutile NWs is ~90/µm². Figure 2f is the SEM topview image around the edge of the gold electrode after filling of perovskite in the voids of the TiO₂ NWs and thermal deposition of gold counter electrodes. The brighter part is the thermally deposited gold electrode in comparison to the dark part that is not coated with gold. Apparently, no NWs or open space can be observed from top, indicating a good filling of CH₃NH₃PbI₃. The cross-section SEM image the device (Figure 2g) also manifests the tight filling of the CH₃NH₃PbI₃ in the wire-to-wire voids. Energy dispersive spectrometer (EDS) also confirms the existence of CH₃NH₃PbI₃ with 3:1 atomic ratio between I and Pb (See Fig. S1 in ESI).

X-ray Diffraction (XRD) of TiO₂ rutile NWs on fluorine doped tin oxide (FTO) substrate was shown in Figure 3. Peaks from FTO are indicated by triangles. Peak (101) along with the enhanced (002) peak in the NWs suggests that the rutile crystal grows with (101) plane parallel to the FTO substrate and the NWs are oriented along the (002) direction. The high resolution transmission electron microscope (HRTEM) image (Inset Figure 3) suggests the feature of the NWs. The (110) lattice crystal plane with a fringe spacing of 0.325 nm indicates that these nanowires are rutile TiO₂.

Cells with 900 nm TiO₂ NWs as photonanodes give the best efficiency of 11.7% followed by 600 nm TiO₂ NWs and 400 nm TiO₂ NWs with efficiency of 10.8% and 9.7%, respectively. For cells using 1.2 µm TiO₂ NWs as photonanode, the efficiency encounters a significant drop to only 4.8%. In terms of photocurrent density (J_sc), it increases as the length of NWs from 400nm (18.6 mA/cm²) to 600 nm (20.4 mA/cm²), to 900nm (22.3 mA/cm²). It is worth to note that the efficiency of our 900nm TiO₂ NWs-based CH₃NH₃PbI₃ perovskite cells outperforms the best reported TiO₂ NWs-based perovskite solar cells in literature by 2% (absolute), and the enhancement is mainly contributed from the elevated J_sc in our 900 nm NWs cells(7 mA/cm² greater than the best reported cells). As the length of TiO₂ NWs reaches 1.2 µm, however, J_sc decreases significantly to only 9.3 mA/cm², leading to the large drop inefficiency to only 4.8%.
photoanodes can be evidenced by the photovoltage transient, namely, based on the devices we can prepare, it is necessary to study their procedures of perovskite layer, the thickness of the HTM layer and photocurrent of the 500 nm thick mesoporous cells is 14.3 mA/cm².

Notes: The lower shunt resistance of the cells using 1.2 µm TiO₂ NWs with respect to the best mesoporous TiO₂ P-based devices with shorter NWs than the 900 nm NWs. The series resistance of the cells using 1.2 µm TiO₂ NWs is notably greater than others due to longer transport distance in 1.2 µm wires.

For comparison, perovskite solar cells using 500 nm thick mesoporous TiO₂ as photoanode are also prepared, which is among the thickness range reported to be the optimized thickness (400 nm - 600 nm) to achieve the best efficiency for mesoporous TiO₂-based cells.²⁰ We keep all other parameters, such as the coating procedures of perovskite layer, the thickness of the HTM layer and gold layer, the exactly same as the NWs-based cells. As can be seen in Figure S2 in ESI, the V_oc of these cells is about 0.80 V, nearly the same as solar cells with TiO₂ NWs as photoanodes. However, the photocurrent of the 500 nm thick mesoporous cells is 14.3 mA/cm², about 8 mA/cm² lower than the 900 nm NWs-based cells. The efficiency is 6.8% for mesoporous TiO₂ solar cells, which is very close to the reported value (7.16%) for this thickness.

In order to understand the enhancement in J_sc found in our 900 nm-long NWs-based devices with respect to the best mesoporous TiO₂-based cells that we can prepare, it is necessary to study their respective light harvesting efficiency (LHE), i.e. external quantum yield, because J_sc depends largely on LHE. In Figure S3, it is notable that the device with 900 nm TiO₂ NWs exhibits nearly 95% LHE between 400 nm and 650 nm comparison to 80% in the device with 500 nm mesoporous TiO₂. The LHE for both devices drops after 750 nm, agreeing with literatures.¹²,²¹²²

The fast kinetics of net charge collection in 900 nm-long TiO₂ NWs photoanodes can be evidenced by the photovoltage transient, namely, the kinetic rising profile of V_oc of the devices, which reflects how rapidly the electrons and holes can be photoinduced and further transport through the internal layers (electrons from perovskite→TiO₂→FTO, and holes from perovskite→HTM→gold) in presence of the recombination of the above process.²³ Figure 5 shows that the rising time (defined as the time it takes from shutter open to 90% of the V_oc) of V_oc for the 900 nm and 1.2 µm long TiO₂ NWs-based perovskite solar cells are 17 ms and 76 ms, respectively. Note that neither the motion of the shutter (response time = 0.7 ms) from full-close to full-open nor the data acquisition rate (with the highest rate at 10 µs per data point) is the bottleneck of the above measurement, as confirmed by a commercial ultrafast silicon photodiode with a response time of 20 ns (see ESI Figure S4b). We think the slower photovoltage rising in 1.2 µm NWs is due to the recombination in the thickness that above the maximal hole diffusion length in CH₂NH₂PbI₃. Rising time of 400 nm and 600 nm long TiO₂ NWs-based perovskite solar cells are 16.7 ms and 16.9 ms, respectively, as shown in Figure S5. In contrast, rising time of a 500 nm mesoporous anatase film is much slower (see supporting information Figure S3a). This result agrees with our previous finding that electron transport in TiO₂ rutile NWs-based DSSCs is faster than that in mesoporous films.

![Figure 4. J-V curves of perovskite solar cell with 400 nm, 600 nm, 900 nm and 1.2 µm TiO₂ NWs as photon anode.](image)

Table 1: Photovoltaics performance of solar cells with 400 nm, 600 nm, 900 nm, 1.2 µm TiO₂ NWs as photoanodes.

<table>
<thead>
<tr>
<th>NW length (nm)</th>
<th>J_sc (mA/cm²)</th>
<th>V_oc (V)</th>
<th>FF</th>
<th>η (%)</th>
<th>R_sh (Ω)</th>
<th>R_s (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>18.6±0.2</td>
<td>0.85±0.03</td>
<td>0.62±0.03</td>
<td>9.7±0.1</td>
<td>1029±22</td>
<td>72±5</td>
</tr>
<tr>
<td>600</td>
<td>20.4±0.3</td>
<td>0.78±0.02</td>
<td>0.68±0.01</td>
<td>10.8±0.2</td>
<td>1012±20</td>
<td>54±8</td>
</tr>
<tr>
<td>900</td>
<td>22.3±0.1</td>
<td>0.77±0.02</td>
<td>0.68±0.01</td>
<td>11.7±0.2</td>
<td>1043±16</td>
<td>57±5</td>
</tr>
<tr>
<td>1200</td>
<td>9.3±0.2</td>
<td>0.72±0.02</td>
<td>0.71±0.03</td>
<td>4.8±0.3</td>
<td>957±21</td>
<td>114±8</td>
</tr>
</tbody>
</table>

Notes: R_sh is Shunt resistance of solar, R_s is series resistance.

The lower shunt resistance of the cells using 1.2 µm TiO₂ NWs than that of the cells using 900 nm NWs indicates a greater charge recombination, resulting in its loss in V_oc. The series resistance of the cells using 1.2 µm TiO₂ NWs is notably greater than others due to longer transport distance in 1.2 µm wires.

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Conclusions

In summary, length-controllable rutile nanowire arrays with fully accessible and wide-open inter-wire voids are synthesized and used as photoanodes in perovskite solar cells. The length of the NWs reflects a compromise between the thickness of the perovskite material and the effective charge transport in the perovskite material. Due to the high electron diffusivity in rutile nanowires, the electron transport can be effectively conducted in these rutiles nanowires, leaving holes as the majority charge carriers in the perovskite. As a result, effective charge transport can be achieved in up to 900 nm long rutile nanowires, allowing...
additional loading of the perovskite materials for higher light absorption, thus, higher attainable current density.

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Notes and references