Impact of Mesoporous Titania-Perovskite Interface on the Performance of Hybrid Organic-Inorganic Perovskite Solar Cells

Mojtaba Abd-Jalebi*‡, M. Ibrahim Dar*§, Aditya Sadhanala‡, Satyaprasad P. Senanayak‡, Fabrizio Giordano§, Shaik Mohammed Zakeeruddin§, Michael Grätzel§, Richard H. Friend*‡

‡ Cavendish Laboratory, JJ Thomson Avenue, Cambridge CB3 0HE, United Kingdom.

§ Laboratory of Photonics and Interfaces, Swiss Federal Institute of Technology (EPFL), Station 6, Lausanne, CH 1015, Switzerland.

* ma571@cam.ac.uk, ibrahim.dar@epfl.ch, rhf10@cam.ac.uk,
We report on the optimization of the interfacial properties of titania in mesoscopic CH$_3$NH$_3$PbI$_3$ solar cells. Modification of the mesoporous-TiO$_2$ film by TiCl$_4$ treatment substantially reduced the surface traps, as evident from sharpness of the absorption edge with a significant reduction in Urbach energy (320 meV to 140 meV) determined from photothermal deflection spectroscopy and lead to an order of magnitude enhancement in the bulk electron mobility and corresponding decrease in the transport activation energy (170 meV to 90 meV) within a device. After optimization of the photoanode-perovskite interface using various sizes of TiO$_2$ nanoparticles, the best photovoltaic efficiency of 16.3% was achieved with the mesoporous-TiO$_2$ composed of 36 nm sized nanoparticles. The improvement in device performance can be attributed to the enhanced charge collection efficiency that is driven by improved charge transport in the mesoporous TiO$_2$ layer. Also, the decreased recombination at the TiO$_2$-perovskite interface and better perovskite coverage play an important role.

**Keywords:** Perovskite solar cell; TiCl$_4$ post treatment; mp-TiO$_2$; energetic disorder; nanoparticle size; interface
Recent developments in using hybrid organic-inorganic perovskites as light absorbers have raised the power conversion efficiency (PCE) of solid state mesoscopic solar cells above 20% level\textsuperscript{1-3}. Such an impressive efficiency was achieved due to desired properties including a high absorption coefficient, an ideal/tuneable band-gap and long carrier diffusion lengths as well as photon recycling capability of hybrid organic-inorganic perovskite materials\textsuperscript{4-10}. A typical mesoscopic perovskite solar cell (PSC) contains a blocking TiO\textsubscript{2} (bl-TiO\textsubscript{2}) layer, mesoporous TiO\textsubscript{2} (mp-TiO\textsubscript{2}), hybrid organic-inorganic perovskite sensitizers, hole transporting material (HTM) and counter electrode (e.g. Au) as the key components. The mp-TiO\textsubscript{2} layer in a typical dye-sensitized solar cell (DSSC) plays three major roles; provides a scaffold to increase the surface area of the absorber layer, act as a hole blocker, and transports photogenerated electron from the sensitized surface to the front contact\textsuperscript{11}. Therefore, the active surface area which has a direct link with particle size of mesoporous material is a key parameter in DSSC\textsuperscript{12}. However, Lee et al. have shown that hybrid organic-inorganic perovskite absorber can transport photogenerated electron to the conductive substrate itself\textsuperscript{13}. On the other hand, it is reported that employing the mesoporous TiO\textsubscript{2} layer substantially reduces the hysteresis behaviour of PSC\textsuperscript{14}. In addition, it is widely recognized that the interface between the absorber layer and the carrier transport layers, as well as the inherent carrier transporting properties of the layers are also important. An ideal carrier transport material is expected to possess a suitable energy level, high conductivity, and low surface recombination rate. Several materials have been investigated as electron transport layers (ETL) such as TiO\textsubscript{2}, ZnO and phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM)\textsuperscript{15-18}. Among all of them, TiO\textsubscript{2} arguably is the most commonly used ETL has delivered the best photovoltaic...
performance in PSC thus far. To improve the performance of mesoscopic solar cells, further investigation is needed to engineer the mp-TiO$_2$-perovskite interface. In this study, we explored the effect of TiCl$_4$ post-treatment of mp-TiO$_2$ on the optical behaviour and the level of electronic disorder using space charge limited current (SCLC) technique and photothermal deflection absorption spectroscopy (PDS) and correlated our findings with the photovoltaic behaviour of the fabricated PSC. We further extended the study by investigating the effect of the titania nanoparticle size on the charge transport, recombination properties, optical behaviour and the photovoltaic performance of PSC. For a comparative analysis, we synthesized two alkaline TiO$_2$ pastes (NP36 and NP50) and compared them with commercial 18NRT dyesol TiO$_2$ nanoparticles. Finally, based on our new findings, we suggest the main criteria for the mp-TiO$_2$ in acting as an ideal electron transport layer for achieving the high efficiency in PSCs.

We used a typical structure of PSC which consists of spray coated titania compact layer on fluorine-doped tin oxide (FTO) coated glass, spin-coated mp-TiO$_2$, sequential two-step spin-coated CH$_3$NH$_3$PbI$_3$ perovskite, spiro OMETAD as a hole transport layer and back contact of thermally evaporated gold layer. It is notable a capping layer of perovskite is formed on top of the mp-TiO$_2$ layer (Figure S1). We optimized the thickness of mp-TiO$_2$ which is a key parameter to achieve high PCE (see details in supporting information).

In DSSC, TiCl$_4$-treatment of mp-TiO$_2$ electrode prior to the device fabrication improves the performance of the photovoltaic devices, because of several phenomena, such as an increase in the electron injection rate, a retardation of the electron–hole recombination and/or an increase in the dye loading. However, the exact mechanism of the improvement is not clearly understood.
Herein, we investigated the effect of TiCl₄-treatment on the morphology and absorption of 36 nm sized mp-TiO₂ as well as on the device performance (Table 1). SEM images of the pristine and treated mp-TiO₂ showed that a very thin layer of compact titania covered the surface of TiO₂ nanoparticles (Figure 1a, b). Upon TiCl₄ treatment, the photovoltaic devices exhibit an increase in the open circuit voltage ($V_{oc}$) by 50 mV, in addition to the marginal improvement in the short circuit current ($J_{sc}$) and fill factor (FF) which gets reflected in the overall efficiencies of the PSC (16.1%). It is notable that the coverage and morphology of perovskite capping layer has not altered upon this treatment (Figure S2).

Based on the PDS measurements (Figure 1c), TiCl₄ treatment significantly reduced the sub-bandgap absorption and increased the density of states near the titania band-edge that has been shown to improve the mobility in metal oxides and could potentially improve the charge transport within the mp-layer in a solar cell configuration²⁴,²⁵. In a PDS spectra, the slope of the absorption at the band edge defines the Urbach energy ($E_u$), and provides a measure for the degree of energetic disorder of a material²⁶,²⁷. The estimated Urbach energy for the pristine and TiCl₄ post treated titania, along with the respective fitting errors (Figure S7), are 320 and 140.

Table 1. Summary of the photovoltaic parameters extracted from J–V measurements under simulated AM1.5G irradiation and electron mobility along with activation energy and the corresponding errors for devices (batch of 20 devices) based on 300nm thick mp-TiO₂ without (pristine) and with TiCl₄ post-treatment.

<table>
<thead>
<tr>
<th>Type of device</th>
<th>$J_{sc}$ (mA cm⁻²)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>$\mu_e$ (cm²/Vs)</th>
<th>$E_A$ (meV)</th>
</tr>
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<tr>
<td>Pristine</td>
<td>21.36±0.3</td>
<td>970±12</td>
<td>0.70±0.02</td>
<td>15.2±0.3</td>
<td>0.002±0.001</td>
<td>170±15</td>
</tr>
<tr>
<td>TiCl₄ post-treated</td>
<td>22.12±0.1</td>
<td>1020±10</td>
<td>0.71±0.01</td>
<td>16.1±0.2</td>
<td>0.03±0.006</td>
<td>95±9</td>
</tr>
</tbody>
</table>
Figure 1. (a) Top view SEM images of pristine mp-TiO$_2$ film and (b) with TiCl$_4$ post-treatment. (c) The PDS absorbance spectra of mp-TiO$_2$ films, pristine and TiCl$_4$ post-treated. The inset shows the corresponding Urbach energies. (d) Effect of TiCl$_4$ treatment on Electron mobility and activation energy in the fabricated device.

Furthermore, a direct estimation of the disorder is obtained from a measure of the activation energy ($E_A^e$) acquired from the temperature-dependent bulk transport measurements. Based on this measurement on electron-only devices FTO/TiO$_2$ (treated or untreated)/Perovskite/Al, we estimated the electron mobility ($\mu_{SCL}^e$) $\sim$ 0.002 cm$^2$.V$^{-1}$.s$^{-1}$ for pristine devices which increases to around 0.03 cm$^2$.V$^{-1}$.s$^{-1}$ upon the treatment (Table1). Correspondingly, the $E_A^e$ decreases from 170 meV to 95 meV for TiCl$_4$-treated mp-TiO$_2$ based PSC (Figure 1d). This enhancement in the electron mobility in addition to passivation of trap states at the perovskite–titania interface which considerably minimizes the recombination of the charge carriers and enhances
charge transport can then be correlated to the enhanced $V_{oc}$, $J_{sc}$ and the overall PCE of devices.  

To further understand the role of the titania interlayer on the photovoltaic performance, we investigated three different particle sizes of mp-TiO$_2$ using two synthesised titania with 36 nm (NP36) and 50 nm (NP50) sized nanoparticles based on the reported procedure and the commercial 18NRT dyesol titania paste. The aspects of these titania pastes and structural characterization of the deposited films are provided in the supporting information.

PDS of different sized mp-TiO$_2$ films shows that the sub-bandgap absorption is lower for both NP36 and NP50 compare to 18NRT and the estimated $E_u$ is the lowest for NP36 (140 meV) representative of the lowest level of electronic disorder (Figure 2a). To extract further information on the light-induced charge injection/separation, we performed time-resolved photoluminescence (PL) decay measurements on the CH$_3$NH$_3$PbI$_3$ deposited on different mp-TiO$_2$ films (Figure 2b). Using standard biexponential fits (Figure S13), the PL decay of the infiltrated perovskite in 18NRT, NP36 and NP50 films exhibits a time-constant of $\tau_1 = 1.06$ ns, 4.49 ns and 6.76 ns, respectively. It is evident that the temporal decay of PL intensity become faster, as the nanoparticle size of the TiO$_2$ reduces.

The PL decay of the aforementioned films arises from quenching of the PL intensity (Figure S14) because of the following two reasons; first, radiative relaxation of excited electrons back to the ground state of perovskite, second, electron injection from the conduction band of perovskite into the conduction band of titania. Because the radiative relaxation back to the ground state of perovskite occurs at a certain inherent rate that corresponds to the PL decay rate of the bare CH$_3$NH$_3$PbI$_3$ shown in Figure 2b, the acceleration of the PL decay rate with the reduction of the titania
Figure 2. (a) The PDS absorption spectra of different mp-TiO$_2$ films. The inset shows the corresponding Urbach energies for all the titania films. The error bar is defined by the s.d in fitting the Urbach tail (Figure S12). (b) Fluorescence decay kinetics measured at 780 nm upon excitation at 407 nm with fluence of 0.7 nJ.cm$^{-2}$ for perovskite films deposited on different mp-TiO$_2$ layers. (c) $I$–$V$ characteristics of electron only devices (FTO/TiO$_2$/Perovskite/AL), utilized for estimating the SCLC electron mobility. (d) The trends in the PCE and $E_A^e$ for PSC based on different sized mp-titania layers.

nanoparticle size in the TiO$_2$/CH$_3$NH$_3$PbI$_3$ films indicates more efficient injection of electrons from the perovskite to TiO$_2$. Therefore, we can infer that, as the size of TiO$_2$ nanoparticles become smaller, the electron injection from perovskite to TiO$_2$ becomes more efficient.

It is well established that not only the precursor compositions of perovskite$^{30,31}$ but also the substrate can influence the growth and formation of perovskite films$^{32,33}$. 


Top-view SEM images of perovskite capping layer on mp-TiO$_2$ shows that NP36 has the best coverage as the titania layer is fully covered by perovskite crystals while in both 18NRT and NP50, we observe some pinholes in between the perovskite grains (Figure S15).

In order to investigate the effect of modification of TiO$_2$ layer on the electron transport behavior, we fabricated electron only (FTO/TiO$_2$/Perovskite/Al) devices for SCLC measurement (see details in supporting information$^{34}$). Remarkably, our transport measurements indicate a clear trend where the $\mu_{SCL}^e$ and $E_A^e$ were altered upon modification of mp-TiO$_2$ (Table 2, Figure 2c, d). Electron mobility as high as ($\mu_{SCL}^e = 0.03$ cm$^2$.V$^{-1}$.s$^{-1}$ and the lowest activation energy of 95 meV was obtained for NP36 based devices (Figure S16). Therefore, the disorder in the perovskite is strongly affected by the layer on which it is deposited$^{35}$. The observed enhancement in the $\mu_{SCL}^e$ and the decrease in $E_A^e$ is expected to improve the $J_{sc}$ and decrease the recombination which could enhance the $V_{oc}$ resulting in an overall improvement in the PCE.

Hence, as a next step, photoanodes based on different sized mp-TiO$_2$ were used to explore particle size effect on the photovoltaic performance of PSC (Table 2 and

<table>
<thead>
<tr>
<th>Type of device</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>$\mu_e$ (cm$^2$.V$^{-1}$.s$^{-1}$)</th>
<th>$E_A^e$ (meV)</th>
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<tr>
<td>18NRT</td>
<td>21.32</td>
<td>965</td>
<td>0.673</td>
<td>13.8</td>
<td>0.01±0.008</td>
<td>135±13</td>
</tr>
<tr>
<td>NP36</td>
<td>22.23</td>
<td>1029</td>
<td>0.709</td>
<td>16.3</td>
<td>0.03±0.005</td>
<td>95±9</td>
</tr>
<tr>
<td>NP50</td>
<td>21.63</td>
<td>948</td>
<td>0.711</td>
<td>14.6</td>
<td>0.008±0.003</td>
<td>115±11</td>
</tr>
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</table>
Figure 3. (a) Current-voltage characteristics measured under standard 1 sun conditions (AM 1.5 G, 100 mW.cm \(^{-2}\)) (solid lines) and dark conditions (dashed lines) (b) External quantum efficiency (EQE) spectra as a function of the wavelength of monochromatic light for the perovskite solar cells obtained from different mp-TiO\(_2\) nanoparticles.

Figure 3a). The statistics of the photovoltaic parameters follow the same trend as the best performing devices (Figure S18). As the diameter of the particles increases from 18 nm to 36 nm, the average J\(_{sc}\) rises from 21.1 mA.cm\(^{-2}\) to 22.3 mA.cm\(^{-2}\). This trend in J\(_{sc}\) can be attributed to the narrow tunnels in the 18 nm TiO\(_2\) mesoscopic framework in which the perovskite cannot infiltrate till the bottom of the TiO\(_2\) layer easily. However, in the NP36, the improved pore filling caused by a larger pore size leads to an enhancement of the J\(_{sc}\). This is consistent with UV-Vis absorption spectra, which shows a higher absorption above the band edge for the perovskite deposited on NP36 compare to 18NRT (Figure S19). Further increase of the TiO\(_2\) particle size to 50 nm causes a slight decline in the photocurrent density which may be ascribed to the pronounced scattering properties of larger titania nanoparticles (Figure S8) as well as the reduction of the porosity which minimizes the amount of perovskite in the mesoscopic TiO\(_2\) framework. The enhancement in current densities of PSC based on
different size of mp-TiO₂ nanoparticles are supported by the improvement in the external quantum efficiency (EQE) spectra shown in Figure 3b.

As shown in Table 2, the FF increases from 0.67 to 0.71 when the size of TiO₂ nanoparticle’s increases from 18 nm to 36 nm and remains the same for NP50, which might be attributed to the reduction in the electron transport resistance of the TiO₂ mesoscopic structure and better filling of the perovskite. In addition, the average value of V₀c climbed from 970 mV to 1029 mV by changing the TiO₂ average particle size from 18 nm to 36 nm. Our observations indicate that NP36 exhibit the optimum pore size for efficient infiltration of the perovskite into the mp-TiO₂ (Figure S15), the highest electron mobility and the lowest disorder in the interface with perovskite which result in the enhancement of V₀c, Jsc and a maximum PCE of 16.3%.

Based on the J-V characteristic of the devices under dark, the dark current onset begins at around 600 mV for the NP50 while it shifts to ~650 and ~750 mV for 18NRT and NP36, respectively (Figure 3a). On forward biasing, the recombination of the photogenerated electrons at the interfaces between FTO or TiO₂ and HTM is a potential source of dark current. Here, the recombination at the TiO₂-HTM interface for NP50 might be due to the weak coverage of the pores with perovskite that dominates and leads to lower V₀c while the effect of recombination from the FTO-HTM interface is negligible due to the complete coverage of FTO by a compact TiO₂ layer.

To study the charge transfer and recombination processes in a PSC based on various sized mp-TiO₂, we performed intensity modulated photovoltage spectroscopy (IMVS) shown in Figure 4a. The electron recombination time constant (τᵣ) as a function of titania particle size, which is calculated using \( \tauᵣ = \frac{1}{2\pi f_r} \), where \( f_r \) is the characteristic frequency minimum of an IMVS curve. The increased \( \tauᵣ \) from 18NRT to NP36
Figure 4. (a) Comparison of $\tau_r$ for the PSC based on different sized mp-titania layers. (b) The trends in the $R_{rec}$ and $C_{cont}$ for PSCs based on various mp-TiO$_2$ layers.

suggests a reduction of the electron recombination process in the PSC. This could be attributed to two factors: firstly, the lowest electronic disorder at the TiO$_2$-perovskite interface, secondly, the improved blocking effect of perovskite overlayer for NP36, which showed the best perovskite coverage, and potentially helps in reducing the electron-hole recombination between TiO$_2$ and HTM. However, when the size of TiO$_2$ nanoparticles is further increased (NP50), higher disorder in the titania layer increases the number of trap sites in the device structure eventually leading to a possibility of electron-hole recombination and hence $\tau_r$ decreases$^{36}$.

To further understand the transport mechanism, we utilize electrochemical impedance spectroscopy (EIS) on PSC fabricated with different mp-TiO$_2$ layers. The EIS measurement was performed on the complete photovoltaic devices operating under illumination and open circuit conditions (Figure S21). The EIS spectra were fitted with an appropriate equivalent circuit to estimate parameters related to the charge recombination and polarization relaxation of the perovskite layers (see details in supporting information). Based on the fitting of the equivalent circuit to the EIS data, we obtain the recombination resistance to be maximum for NP36 which is consistent
with the trend of higher $J_{sc}$ magnitude (Figure 4b). Correspondingly, the large area in the EIS of the NP50 can be correlated to higher series resistance which is in agreement with the lower $J_{sc}$ magnitude. Differences in the trend of $V_{oc}$, $J_{sc}$ and FF of the PSC with the parameters of the EIS spectra arises due to the preliminary level of the equivalent circuit utilized for the fitting.

In general, the observation of higher value of $J_{sc}$ in a photovoltaic device can be related to a range of factors. This includes enhanced transport in the active layer which supports lower recombination and enhanced charge collection at the adjacent contacts. Since we compare photovoltaic devices with identical active layer fabricated under the same conditions, the differences originating from the charge transport in the active layer can be completely ignored. Hence, the variation in the $R_{rec}$ can be attributed to the collection efficiency of the interface. Similarly, the enhancement of the $C_{cont}$ for a particular photovoltaic cell based on NP36 directly correlates with the enhancement of the $V_{oc}$.

In summary, we have systematically studied the different parameters to explore the influence of TiO$_2$-perovskite interface for mesoscopic perovskite solar cells. We showed that the TiCl$_4$ post treatment of the mp-TiO$_2$ film prior to device fabrication passivate the titania surfaces, increases the density of states and reduces the disorder level which significantly enhances the open circuit voltage (~50mV) and the device performance. Furthermore, different sized TiO$_2$ nanoparticles were applied as electron acceptors in the mesoscopic PSC. The particle size effect of TiO$_2$ nanoparticles on the photovoltaic performance of PSC was investigated which not only influences the contact between the perovskite crystal-TiO$_2$, but also significantly affects the charge transfer kinetics at the TiO$_2$-perovskite interface and the overall disorder of the perovskite layer for charge transport. We observe that the particle size of 36 nm is
optimum for obtaining the best performance solar cells with consistent and reproducible PSC of 16.3%. Based on transport, spectroscopic and photovoltaic measurements, we conclude that the mp-TiO₂ interlayer should have the least energetic disorder, optimum particle and pore size in order to enhance the homogeneous growth of perovskite over-layer and optimum charge transport properties to realise high efficiency in mesoscopic perovskite solar cells.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: ma571@cam.ac.uk, ibrahim.dar@epfl.ch, rhf10@cam.ac.uk*

**Notes**

The authors declare no competing financial interest.

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**ASSOCIATED CONTENT**

**Supporting Information**

Experimental procedures, cross sectional and top view SEM images, optimization of the thickness of mp-TiO₂, the aspects and structural characterization of different mp-TiO₂ pastes and films, data fitting of Urbach energy for PDS measurement, fitting curves for fluorescence decay kinetics measurement, details of SCLC and EIS characterisations and statistics for photovoltaic measurements are provided.
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