

INTERFACE ENGINEERING OF MESOSCOPIC HYBRID ORGANIC-INORGANIC PEROVSKITE SOLAR CELLS

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1) Context / Study motivation

We report on the optimization of the interfacial properties of titania in mesoscopic CH₃NH₃PbI₃ perovskite solar cells (PSCs). Modification of the mesoporous titania (mp-TiO₂) film by TiCl₄ treatment substantially reduced the surface traps, as is evident from the sharpness of the absorption edge with a significant reduction in Urbach energy (from 320 to 140 meV) determined from photothermal deflection spectroscopy, and led to an order of magnitude enhancement in the bulk electron mobility and corresponding decrease in the transport activation energy (from 170 to 90 meV) within a device. After optimization of the photoanode-perovskite interface using various sizes of TiO₂ nanoparticles, the best photovoltaic efficiency of 16.3% was achieved with the mesoporous TiO₂ 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 TiO₂ layer. Also, the decreased recombination at the TiO₂-perovskite interface and better perovskite coverage play important roles.

2) Description of approach and techniques

We used a typical structure of PSCs that consists of a spraycoated titania compact layer on fluorine-doped tin oxide (FTO)-coated glass, spin-coated mp-TiO₂, sequential two-step spin-coated CH₃NH₃PbI₃ perovskite, spiro-OMETAD as a hole transport layer, and back contact of a thermally evaporated gold layer^[1,2]. We then investigated the effect of TiCl₄ post treatment on the morphology and absorption of 36 nm sized mp-TiO₂ as well as on the device performance. To further understand the role of the titania interlayer on the photovoltaic performance, we investigated three different particle sizes of mp-TiO₂ using two synthesized titania with 36 nm (NP36) and 50 nm (NP50) sized nanoparticles and the commercial 18NRT dyesol titania paste. We then implemented a range of characterization techniques such as photothermal deflection spectroscopy (PDS), space charge limited current (SCLC), intensity-modulated photovoltage spectroscopy (IMVS) and electrochemical impedance spectroscopy (EIS) to investigate the effect of mp-TiO₂ modification on the absorption properties of Titana and charge transfer kinetics at the TiO₂-perovskite interface as well the photovoltaic performance of

perovskite devices.

3) Results / Conclusions / Perspectives

Upon TiCl₄ treatment, the sub-band gap absorption significantly reduced and the density of states near the titania band edge increased, which has been shown to improve the mobility in metal oxides and could potentially improve the charge transport within the mesoporous layer in a solar cell configuration^[3] (Figure 1a). Furthermore, significant reduction in the activation energy for electron transport within a device (E^A_e) acquired from the temperature-dependent bulk transport measurements^[4] as well as an order of magnitude increase in the electron mobility is achieved for the TiCl₄ treated sample (Figure 1b). In addition, the standard J-V measurements (Table 1) of 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%).

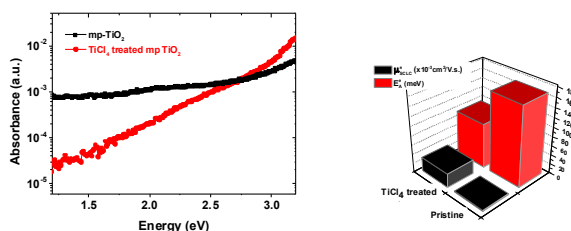


Figure 1. (a) PDS absorbance spectra of mp-TiO₂ films, pristine and TiCl₄ post-treated. (b) Effect of TiCl₄ treatment on the electron mobility and activation energy in the fabricated device.

Table 1. Summary of the Photovoltaic Parameters Extracted from J-V Measurements for Devices (Batch of 20 Devices) Based on 300 nm Thick mp-TiO₂ without (Pristine) and with TiCl₄ Post-Treatment.

Type of device	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	PCE (%)
Pristine	21.36±0.3	970±12	0.70±0.02	15.2±0.3
TiCl ₄ post-treated	22.12±0.1	1020±10	0.71±0.01	16.1±0.2

To extract further information on the light-induced charge injection/separation, we performed time-resolved photoluminescence (PL) decay measurements on the $\text{CH}_3\text{NH}_3\text{PbI}_3$ deposited on different sized mp-TiO₂ films (Figure 2). It is evident that the temporal decay of PL intensity becomes faster as the nanoparticle size of the TiO₂ reduces which is correspond to more efficient injection of electrons from the perovskite to TiO₂ with smaller particle sizes.

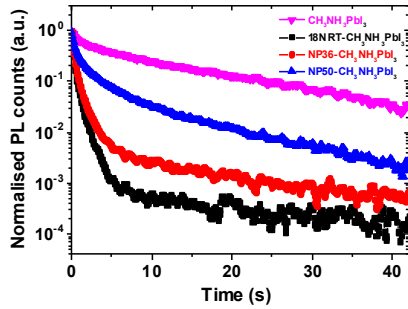


Figure 2. Fluorescence decay kinetics measured at 780 nm upon excitation at 407 nm with fluence of 0.7 nJ cm^{-2} for perovskite films deposited on different mp-TiO₂ layers.

In the next step, we studied photovoltaic behavior of PSCs having photoanodes with different sized mp-TiO₂ (Table 2). As the diameter of the particles increases from 18 to 36 nm, the average J_{sc} rises from 21.1 to 22.3 mA cm^{-2} . This trend in J_{sc} can be attributed to the narrow tunnels in the 18 nm TiO₂ mesoscopic framework in which the perovskite cannot infiltrate into the bottom of the TiO₂ layer easily. However, in the NP36, the improved pore filling caused by a larger pore size leads to an enhancement of the J_{sc} . Further increase of the TiO₂ 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 as well as the reduction of the porosity, which minimizes the amount of perovskite in the mesoscopic TiO₂ framework.

Table 2. Summary of the Photovoltaic Parameters Derived from J - V Measurements for the PSCs Based on Different Sized mp-TiO₂.

Type of device	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	PCE (%)
18NRT	21.32	965	0.673	13.8
NP36	22.23	1029	0.709	16.3
NP50	21.63	948	0.711	14.6

To study the charge transfer and recombination processes in a PSC based on various sized mp-TiO₂ layers, we performed intensity-modulated photovoltage spectroscopy (IMVS), shown in Figure 3. The increased The electron recombination time constant (τ_r) from 18NRT to NP36 suggests a reduction of the electron recombination process in the PSC. However, when the size of TiO₂ 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 a decrease in τ_r .

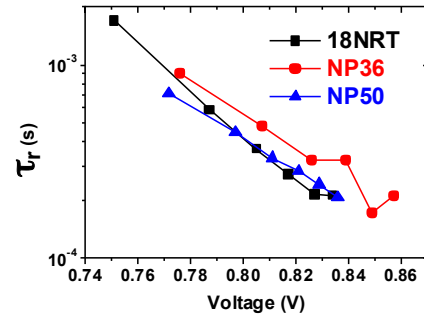


Figure 3. Comparison of τ_r for the PSC based on different sized mp-titania layers.

To further understand the transport mechanism, we utilize electrochemical impedance spectroscopy (EIS) on PSC fabricated with different mp-TiO₂ layers (Figure 4). On the basis of the fitting of the equivalent circuit to the EIS data, we found the recombination resistance (R_{rec}) to be maximum for NP36, which is consistent with the trend of higher J_{sc} magnitude. Correspondingly, the large area in the EIS of the NP50 can be correlated with higher series resistance, which is in agreement with the lower J_{sc} magnitude.

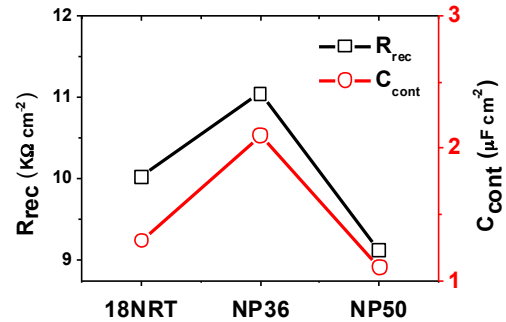


Figure 4. Trends in the R_{rec} and C_{cont} for PSCs based on various mp-TiO₂ layers.

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