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Jingsong Sun
Monash University

Alexander Pascoe
Monash University

Steffen Meyer
Monash University

Qijie Wu
University of Wollongong, qw988@uowmail.edu.au

Enrico Della Gaspera
Royal Melbourne Institute of Technology

See next page for additional authors

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Abstract

The fabrication of high efficiency perovskite solar cells at larger scales will rely on the optimized deposition conditions of every layer using scalable methodologies. Most current perovskite devices that employ the archetypal TiO₂ hole blocking layer utilise a simple air-brush approach. This approach is not scalable as it results in significant layer inhomogeneity across larger devices areas. To overcome this inherent limitation, in this work we use ultrasonic spray deposition as an alternative approach for the TiO₂ deposition. Focusing on identical reaction chemistries as for air-brush, namely bis(isopropoxide)-bis(acetylacetonate) titanium (IV) based solutions, we find that under optimized conditions smooth TiO₂ layers can be readily deposited over scalable areas on fluorine doped tin oxide. Using these layers at electron transport layers within diodes and perovskite solar cell devices, we develop effective benchmarks that predict the effectiveness of the underlying charge transport layer. This enables for the standardisation of the electron transport properties within any batch of solar cells, thus providing a readily accessible pathway towards enhancing reproducibility of fabricated devices. Under these optimized conditions, methylammonium lead halide photovoltaic devices readily possessing efficiencies of >16% are achieved. Importantly, the mean batch efficiency of devices fabricated using the ultrasonic spray deposition method is significantly improved and the standard deviation is drastically narrowed. The deposition of an additional meso-porous layer is found to lead to further improvements for both of these parameters.

Keywords

spray, deposition, tio₂, electron, transport, layers, ultrasonic, reproducible, cells, high, efficiency, hybrid, perovskite, solar

Disciplines

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Authors

Jingsong Sun, Alexander Pascoe, Steffen Meyer, Qijie Wu, Enrico Della Gaspera, Sonia Raga, Tian Zhang, Andrew Nattestad, Udo Bach, Yi-Bing Cheng, and Jacek Jasieniak

Ultrasonic Spray Deposition of TiO₂ Electron Transport Layers for High Efficiency Hybrid Perovskite Solar Cells

Jingsong Sun ^{‡,1}, Alexander R. Pascoe ^{‡,1}, Steffen Meyer¹, Qijie Wu², Enrico Della Gaspera³,
Sonia R. Raga⁴, Tian Zhang⁴, Andrew Nattestad², Udo Bach⁴, Yi-Bing Cheng⁵, and Jacek J.
Jasieniak^{*1}

¹ ARC Centre of Excellence in Exciton Science, Department of Materials Science and Engineering, Monash University, Clayton, Victoria 3800, Australia

² Intelligent Polymer Research Institute (IPRI), Australian Institute for Innovative Materials (AIIM), University of Wollongong, NSW 2522, Australia

³ Applied Sciences, RMIT University, Melbourne, Victoria 3000, Australia

⁴ ARC Centre of Excellence in Exciton Science, Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia

⁵ State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

Keywords: Titania, Spray-Deposition Electron Transport Layer, Perovskite, Solar Cell.

Abstract

The fabrication of high efficiency perovskite solar cells at larger scales will rely on the optimized deposition conditions of every layer using scalable methodologies. Most current perovskite devices that employ the archetypal TiO_2 hole blocking layer utilise a simple air-brush approach. This approach is not scalable as it results in significant layer inhomogeneity across larger devices areas. To overcome this inherent limitation, in this work we use ultrasonic spray deposition as an alternative approach for the TiO_2 deposition. Focusing on identical reaction chemistries as for air-brush, namely bis(isopropoxide)-bis(acetylacetonate) titanium (IV) based solutions, we find that under optimized conditions smooth TiO_2 layers can be readily deposited over scalable areas on fluorine doped tin oxide. These are found to serve as highly effective blocking layers, with photovoltaic devices readily possessing highest efficiencies of $> 16\%$. Importantly, the mean batch efficiency of devices fabricated using the ultrasonic spray deposition method is significantly improved and the standard deviation is drastically narrowed. The deposition of an additional mesoporous layers is found to lead to further improvements for both of these parameters.

1. Introduction

Hybrid metal halide perovskites have rapidly emerged as a promising material for use in photovoltaics owing to their ease of processing and excellent optoelectronic properties.¹ Leveraging heavily from gradual advances in dye-sensitised, organic and thin-film inorganic solar cell configurations,² perovskite solar cell (PSC) efficiencies have improved at an unprecedented rate, increasing from an efficiency of only 3.8% in 2009, as reported by Kojima et al.,³ to values

that already exceed 22% for lab-scale devices.⁴ This efficiency rivals that of mature solar cells, such as multicrystalline silicon (mc-Si), cadmium telluride (CdTe) and copper-indium-gallium-selenide (CIGS) technologies. While PSC devices are still considered an early-stage technology that is yet to identify a relevant market, one of the chief attributes boasted by PSCs is the solution-based methods commonly used during device fabrication. This attribute affords the potential for mass production, which provides perovskite-based cells with an innate advantage over more established technologies. Nevertheless, PSCs require considerable challenges to be resolved around stability, toxicity and scalability before the technology can be considered as a viable alternative. Important progress has been made to address concerns of device stability⁵ and toxicity,⁶ which are prolific fields in their own right. Here, we focus on addressing a key processing challenge that impacts reproducibility and scalability of PSCs – the deposition of a high quality electron transport layer.

Electron and hole transport layers in PSCs are fundamental towards achieving high efficiency devices as they selectively block holes and electrons, respectively, to reduce interfacial recombination at the electrode interfaces. This has been demonstrated for all high efficiency planar,⁷⁻⁸ meso-porous⁹⁻¹¹ and sensitized¹² PSC architectures. Within their “normal superstrate” device configuration, that being where the electron transporting layer (ETL) is deposited on the transparent conductive electrode and the hole transporting layer (HTL) is deposited on the perovskite, almost ubiquitously TiO₂ has been used as the ETL and doped Spiro-OMeTAD (2,2',7,7'-tetrakis(*N,N*-di-*p*-meth-oxyphenylamine)-9,9-spirobifluorene) as the HTL. Both of these layers have origins in dye-sensitized solar cells (DSSCs).¹³ The selection of the Spiro-OMeTAD is largely based on its ease of deposition through a low-temperature solution-coating process. Meanwhile, TiO₂ remains the archetypal material owing to its high chemical stability,

high optical bandgap of 3.2 eV and appropriate conduction band energy of -4.2 eV vs. vacuum for minimizing voltage losses.

TiO₂ deposition has been demonstrated using spin coating,^{9, 14} atomic-layer deposition,¹⁵⁻¹⁶ spray pyrolysis,^{11, 17-18} electrodeposition,¹⁹⁻²⁰ sputtering²¹ and thermal oxidation.²²⁻²³ Of these, spray deposition is the most commonly employed approach owing to its simplicity. It involves the deposition of a suitable titanium complex, such as titanium (IV) bis(isopropoxide)-bis(acetylacetonate) (Ti(acac)₂OiPr₂) dissolved in isopropanol, onto a heated substrate at ~500 °C, which induces its thermal decomposition to form TiO₂.²⁴ This processing temperature also facilitates crystallization of the TiO₂ into the anatase phase, which provides reduced structural defects and improved electron mobilities compared to its low-temperature processed amorphous state.²⁵⁻²⁶

Conventionally, the spray deposition of TiO₂ for use as a blocking layer in solar cells has been carried out using an airbrush spray technique.²⁷ This form of “pressurized” spray, relies on a high pressure carrier gas to atomise a liquid flowing through a nozzle. The particle diameters emerging from these systems and their size distribution are related to the nozzle geometry, the physical properties of the liquid, its flow rate, the air pressure and distance between the nozzle and the substrate that is being coated.²⁸ Typical median droplet sizes of > 50 µm are common, albeit with very broad droplet size distributions due to the inherent atomization process. Importantly, the droplets are carried to the substrate within the gas stream at pressures of 100’s kPa, which causes them to have very high impact velocities with the substrate (10-100’s m/s). Practically, this is beneficial from the point of view of reducing evaporation rates of volatile droplets during the deposition process, particularly when depositing on heated substrates. However, the large distribution in droplet size can make coatings inhomogeneous and the high pressures cause

significant overspray, which necessitates high efficiency exhaust systems and increases material waste.

For these reasons, ultrasonic spray deposition systems have started to be harnessed in many applications that require homogeneous thin film coatings, such as protective coatings for steel,²⁹ transparent electrodes,³⁰ and even perovskite solar cells.³¹ Ultrasonic nozzles use a tip vibrating at a frequency f to nebulize a liquid stream into a mist of droplets. The median droplet size in this case is proportional to $f^{-2/3}$, which for typical frequencies of 20-100 kHz gives median droplets of size ~ 20 -100 μm .³² Importantly, these droplets have a narrower size distribution and 10-100 times lower impact velocities as compared to the airbrush spray approach. The lower size distributions can enable more homogeneous coatings to be prepared, which is a very lucrative aspect for the use of ultrasonic systems in thin film coatings.

In this work, we compare the airbrush and ultrasonic deposition of TiO_2 ETLs for use in methyl ammonium lead iodide (MAPbI_3) PSCs. It is found that ultrasonic deposition results in superior device performance under optimized conditions and, more importantly, yield a significant improvement in terms of device reproducibility.

2. Materials and experimental details

TiO_2 blocking layer deposition and characterization. Unless otherwise stated, all materials were purchased from either Sigma-Aldrich or Alfa Aesar, and used as received. The home-built spray system comprised a Sono-Tek 120 kHz Accumist ultrasonic spray shaping nozzle mounted to a 3-axis gantry robot, a Sonotek Selectaspray cabinet with a generator sequence controller, and a syringe pump liquid delivery system. Fluorine doped tin oxide (FTO)/glass substrates were

cleaned using a three stage sonication process in hellmanex, water and ethanol. The dense TiO₂ blocking layer was formed by the spray pyrolysis of a bis(isopropoxide)-bis(acetylacetonate)titanium(IV) (TAA) solution at 500 °C. This solution was formed by diluting TAA in isopropanol (1:19 vol). The sprayed samples were annealing for 10 mins at 500 °C in air after the completion of the spray cycle, before being cooled down to room temperature. For the mesoporous devices, an 18nm TiO₂ nanoparticle paste (JGC-C&C) was diluted in ethanol (1:8 vol) prior to spin-coating on the dense TiO₂ blocking layer at 8000 rpm for 40 s in air and then annealed at 500 °C for 30 mins.

UV-vis spectroscopy was performed using a PerkinElmer Lambda 950 UV/VIS/NIR spectrophotometer. Ellipsometric measurements were carried out on J.A. Woollam M-2000DI Spectroscopic ellipsometer with TiO₂ samples being deposited on polished silicon wafers with a natural oxide layer. Atomic Force Microscopy (AFM) measurements were performed on a Dimension Icon (Veeco).

Diode fabrication and characterization. Spiro-OMeTAD (2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9-spirobifluorene) was purchased from Luminescence Technology Corp. The spiro-OMeTAD solution was formed by mixing 40 mg of spiro-OMeTAD in 500 µL of chlorobenzene, with 7.5 µL lithium bis(trifluoromethylsulphonyl)imide in acetonitrile (500 mg mL⁻¹) and 16.88 µL 4-tert-butylpyridine as additives. This spiro-OMeTAD solution was spin-coated on the dense TiO₂ blocking layer at 3000 rpm for 30 s. An 80 nm gold layer was then evaporated onto the devices. The current-voltage response of the diodes were measured with a continuously increased voltage from 0 to 1.5 V in the dark using a Zahner Zennium electrochemical workstation (ECW IM6).

Solar cell fabrication and characterization. Fabrication of solar cell devices was carried out in a N₂ filled glovebox. The perovskite precursor solution was formed by mixing stoichiometric amounts of CH₃NH₃I and PbI₂ in a combination of dimethyl sulfoxide (DMSO) and *N*-methyl-2-pyrrolidone (NMP) (7:3 vol) to form a (46 wt%) concentration solution. 30 μ L of the perovskite precursor solution was applied to the surface of the substrate prior to spin-coating. The films were spin-coated using a two-stage process: 1000 rpm for 5 s using an acceleration of 200 rpm/s, then 6000 rpm for 50 s using an acceleration of 6000 rpm/s. A nitrogen gas flow was introduced after 20 s of the second spin-coating step and sustained for a further 20 s. The perovskite films were then annealed on a hot-plate at 100 °C for a duration of 10 mins. A spiro-OMeTAD solution was spin-coated on the perovskite film at 3000 rpm for 30 s, the same as that deposited on the diode devices. An 80 nm gold layer was then evaporated onto the devices. Current-voltage characterization was performed using a solar simulator (Oriel) fitted with a filtered 1000 W xenon lamp to replicate AM1.5, 1 kW/m² conditions. The illumination of the light source was calibrated using a silicon reference cell (Peccell Technologies) with a color filter to minimize the spectral mismatch between the calibration diode and the perovskite solar cell. The J-V response was recorded using a Keithley 2400 source meter. The solar cells were masked with a non-reflective aperture of 0.16 cm² that defined the active area of the device. Impedance spectroscopy measurements were performed under 1 sun illumination using a white LED powered by a PP210 potentiostat. A Zahner Zennium electrochemical workstation ECW IM6 was used as a frequency response analyzer.

3. Results and discussion

The thickness of TiO₂ films deposited through the spray deposition of TAA show a linearly increasing relationship with greater concentration of the precursor and the number spray cycles.³³ However, the resulting structural, optical and electronic properties of the sprayed TiO₂ films can vary significantly owing to the large number of experimental variables, such as deposition temperature, rate, spray distance and pattern, gas pressure, etc. In this work we have undertaken this optimization process using the conventionally used TAA: isopropanol solution as a drop-in replacement within an ultrasonic spray deposition system to coat 10 x 10 cm² FTO/glass substrates with TiO₂ at 500 °C. Towards this goal, we have investigated myriad of spray parameters within the defined spray pattern shown in Figure 1a. We have defined a single spray cycle as the completed deposition across all four offset spray trajectories (labelled in Figure 1a as 1-4). The optimized conditions at a flow rate of 0.5 mL/minute with a nozzle velocity of 100 mm/s were found to be: length = 12 cm, line spacing (dW) = 1.5 cm, height = 13.5 cm, and nozzle power = 1.5 W. The shaping pressure was controlled between 10 – 200 kPa, with the later being preferred for this particular spray nozzle (*vide infra*).

Figure 1b,c show the digital photographs of TiO₂ film sprayed on a silicon wafer using a typical hand nebuliser at ~350 kPa and our ultrasonic spray system at a shaping pressure of ~200 kPa, respectively. For both samples, the spray nozzle was fixed at 13.5 cm above the substrates and 6 mL of spray precursor solution was used to do the coating. Ellipsometric mapping of these samples, as measured over 0.4 x 0.4 cm² areas, are shown in Figure 1d,e, respectively. It is evident from both the optical images and ellipsometric mapping that the ultrasonic process facilitates TiO₂

film deposition of an enhanced homogeneity, particularly at the mm scale. Analysing the ellipsometric maps more closely shows that the TiO₂ deposited by the hand nebulizer results in a mean thickness deviation of up to $\pm 15\%$, while for the ultrasonic process it was $< \pm 5\%$. This is clear evidence of the superior coating properties offered by the ultrasonic deposition process, and is directly related to the improved droplet distribution.

In addition to homogeneity, the thickness of the TiO₂ needs to be precisely controlled to ensure optimised charge blocking layer characteristics. For simplicity, from hereon we define the TiO₂ layers deposited on the original FTO coated glass at different cycles as T_x, where x denotes the number of TiO₂ deposition cycles. The thickness (t) of these layers was measured by depositing reference samples on a silicon wafer substrate with a native oxide layer and then using spectroscopic ellipsometry (Figure S1). This approach was chosen because attempts to measure the thickness directly on FTO glass through SEM was deemed inconclusive due to a low contrast between the FTO and TiO₂ layers (Figure S2). From these measurements the functional correlation between T_x and t under the above deposition conditions was determined to be $t \text{ (nm)} = 5.9 T_x$.

The effectiveness of TiO₂ as a blocking layer depends on its hole blocking, electron collection and shunting properties. To analyse the effectiveness of these processes, Au/Spiro-OMeTAD/TiO₂/FTO diodes were fabricated using different thicknesses of ultrasonically sprayed TiO₂. The corresponding J–V curves of these diodes are shown in Figure 2a. For completeness we have also included the J–V curve of Au/Spiro-OMeTAD/FTO structure, even though this is not a diode. Consistent with the standard Shockley one-diode formalism, three regimes can be clearly identified: (i) at low voltages ($< \sim 0.3\text{V}$) the devices exhibit Ohmic behavior due to residual shunting, (ii) at intermediate voltages a clear turn-on behavior is seen, which is characteristics of the junction ideality factor, temperature and saturation current, and (iii) at higher voltages the

current saturates to series resistance limits. The extracted parameters from fits of the diodes to the Schockley diode formalism are included in Table 1. The ideality factors show a slight variation across the samples, with a general trend of being at ~ 3 . This suggests that for all the diodes the carrier recombination is likely to be interface or deep-level defect limited.³⁵⁻³⁶ These trends cannot be reliably compared to solar cells because the interfaces and dominant charge transport mechanisms in such devices are entirely different compared to these diodes. We note that the series resistances extracted here are evidently limited by the electrodes and the rectifying junction, and not reflective of the TiO₂ layers, which should have seen progressive increase with increasing T_x . A comparison between the shunt resistances provides the most direct measure of the TiO₂ homogeneity and effectiveness as a charge blocking interface, although it is hard to determine what an appropriate value should be without a qualitative comparison to a complete solar cell. Such a qualitative comparison has been made by Peng and co-workers for dye-sensitised solar cells by simply considering the currents at 0.4V and 0.8V for identical diodes made here, but using hand-spray approach for the TiO₂. Those values are plotted in Figure 2b, with the authors finding a current density of 0.01 mA cm⁻² (0.1 mA cm⁻²) at 0.4V (0.8V) being sufficiently low to yield good blocking properties. We include the equivalent current densities from our diodes for comparison in this figure. It can be observed that the required current densities are achieved at T_2 , which is equivalent to only 12 nm. This represents a TiO₂ film that is 80 % thinner than those reported by Peng and co-workers, indicating a higher quality deposition process using the ultrasonic method. Further inspection of the diodes fits indicates that a progressive reduction in J_0 parameter is observed with increasing T_x . This should yield a greater turn-on voltage and, subsequently, higher open circuit voltages in functional solar cells.

To validate these charge blocking properties, planar MAPbI₃ PSCs were fabricated using the TiO₂ films as ETLs (Figure 3a). The resulting photovoltaic parameters are summarized in Figure 3b. These show comparable median open circuit voltages (V_{oc}) of ~1050 mV and FFs of ~0.72 across all T_x . This expected trend arises due to the similar interface chemistry between the TiO₂ and perovskite layers. Of all the parameters, the short-circuit current density (J_{sc}) shows the largest deviation with a peak value at T_4 of 22.4 mA cm⁻². A progressive reduction is observed at higher T_x and at T_2 . This trend can be partly understood from the diode measurements, which show that T_4 has a 20-fold greater shunt resistance than T_2 . Within the device, for the T_2 sample, a low R_{sh} would result in a higher hole surface recombination at the FTO, yielding the lower photocurrent. Meanwhile, at the higher T_x , an enhancement of the electron recombination is expected due to an accumulation of electrons at the interface within the perovskite arising from the poor electron transport properties of TiO₂.³⁴ These factors result in the PSCs with T_4 possessing the most optimal hole blocking and electron transport properties, yielding the highest PCEs. Notably, this correlation allows us to identify that a shunt resistance of ~75 k Ω cm² for a FTO/TiO₂/Spiro-OMeTAD/Au diode provides a good benchmark for achieving good blocking layer properties in functional solar cells.

To further investigate the performance variation of these devices, electrochemical impedance spectroscopy (EIS) measurements were conducted under illumination. Figure 4a shows the Nyquist plots for the perovskite device with T_x ETLs at 0.8V bias under the 1 sun illumination. The equivalent circuit used for fitting the EIS data is shown in Figure 4b. It consists of a recombination resistance (R_{Rec}) component, a constant phase element (CPE) element and a series resistance (R_s) contribution. We find that the series resistances of T_2 to T_6 devices are comparable at ~1.9 Ω cm², but that the T_{10} device shows an increased series resistance of 2.8 Ω cm² (see Figure

4a (inset)) This confirms that the TiO_2 layer is indeed having an impact on the total series resistance, but it is significant only at the larger thicknesses. In Figure 4c we show the R_{Rec} versus applied voltage. The recombination resistance shows an increase from T_2 to T_4 devices and then subsequently drops for the T_{10} device. As higher R_{Rec} correlates to reduced carrier recombination within a device,³⁷ the above results confirm that the T_4 devices provide a TiO_2 -perovskite interface with the most favourable charge extraction characteristics as well as optimum blocking of the FTO recombination pathways. We summarize the above findings through a schematic of the proposed carrier extraction and recombination mechanisms at the TiO_2 -perovskite for different T_x in Figure 4d.

Noting that PSC exhibit the hysteresis, in Figure 5a we show typical forward and reverse J-V curves of planar PSC using T_4 . The reverse scan shows a PCE of 17.5%, with $V_{\text{oc}}=1048$ mV, $J_{\text{sc}}=23.2$ mA cm^{-2} and FF=0.72, while the forward scan shows a decrease in FF to 0.55, which leads to a lower PCE of 13.1%. The steady-state output of this PSC was measured using a voltage of 850 mV at maximum power output for 300s, where the efficiency stabilized to ~16.3%, as shown in Figure 5b.

The above PSCs were fabricated using TiO_2 at a nozzle shaping higher pressure of 200kPa; however, as we now show, this high gas pressure is a very important factor for achieving such high efficiency PSCs. In Figure 6a,b, digital images of T_4 sprayed TiO_2 on silicon wafer are shown for 10 kPa and 200 kPa shaping pressures, respectively. Close inspection of these images demonstrate that the higher pressure facilitates a slightly more macroscopically homogeneous TiO_2 film. This is further validated through spectroscopic ellipsometry thickness mapping, which shows slightly larger features on the surface of the 10 kPa sample (Figure 6c) and an overall standard deviation in thickness of 0.7 nm compared to only 0.4 nm for the 200 kPa (figure 6d). More prominent

structural variations are observed at the microscopic level across these samples, with atomic force microscopy (AFM) topographic images shown in Figure 6c,d for the 10 kPa and 200 kPa samples, respectively. It is evident that the surfaces of the 10 kPa sample possess significant nanoscale perturbations compared to the 200 kPa sample (Figure 6g,h).

Evidently, the low pressure deposition conditions cause larger TiO₂ coating variations compared to the higher pressure deposition both at the macro and micro levels. This observation is likely to arise directly from the lower droplet and impact velocities, which are critical parameters for depositing volatile droplets onto high-temperature substrates. If the droplets being deposited prematurely evaporate to a point where decomposition is occurring during the droplet flight and/or they do not coalesce on the substrate following impact, then an inhomogenous coating will be observed.³⁸ Fortunately, the TAA solution thermalizes relatively slowly compared to the carrier solvent (IPA), which makes variations moderate and prevents dry powder deposition under our experimental conditions, but noticeable differences are observed nonetheless because this balance isn't achieved at the lower shaping pressure.

To understand the relative impact of these structural variations using ultrasonic spray deposition to that for TiO₂ deposited through the traditional hand-spray system, we have fabricated batches of PSCs using the entire 100 cm² TiO₂ coated FTO/Glass substrates cut to 1.25 x 2 cm² sizes. The extracted device characteristics of these samples without any sample discrimination within a batch are shown in Figure 7. A comparison between the planar device characteristics of hand-spray, 10 kPa and 200 kPa samples clearly indicates the superior performance of the 200 kPa ultrasonic deposited TiO₂ across all device characteristics. Importantly, the hand-spray samples exhibit a relatively high median efficiency of 14.5%, but have a large device performance spread with a standard deviation of 4.6%. In comparison, the 200 kPa sample exhibit a median efficiency of

15.6%, albeit with a drastically reduced standard deviation of 1.5%. This indicates that the hand-spray can provide high quality blocking layers suitable for high-efficiency PSCs, but due to homogeneity problems, there are many poor performing devices. Somewhat surprisingly, the 10 kPa samples showed the lowest mean performance characteristics, but had comparable standard deviations to the 200 kPa. This confirms that the slight differences in macroscopic inhomogeneity of the TiO₂ do not perturb the sample reproducibility over the 100 cm² deposition scale; however, the topographic variations at the microscopic scale evidently yield poorer hole blocking properties.

To understand if higher levels of reproducibility and device performance could be achieved, we further deposited ~150 nm thick mesoporous layers of TiO₂ on top of 200 kPa sprayed T₄ layers prior to the deposition of the perovskite layers. These were deposited by spin-casting using a commercial ink tailored for this deposition approach. This is consistent with the prospects of manufacturing such devices, for which the meso-porous layers would likely be printed, whilst very thin transport layers would in fact be spray deposited. As has been previously suggested, the mesoporous scaffold reduces shunting pathways and enhances electron extraction within perovskite devices.³⁹ The device characteristics of the mesoporous PSC devices fabricated here are also shown in Figure 7. It is evident that the presence of the mesoporous layer has a favourable effect on all device characteristics, particularly J_{sc} and FF, with the median efficiency being 17.4%. This represents a 12% relative enhancement compared to the planar device (see in Table 2). Importantly, these enhancements are accompanied by drastic reductions to the absolute standard deviations of all the parameters, with that for efficiency being a remarkable 0.5%. This is direct evidence that the mesoporous layer further assists in creating a more macroscopically homogeneous ETL with more favourable charge extraction properties within this PSC configuration.

4. Conclusions

In this work we have compared the effectiveness of TiO₂ layers deposited through the conventional hand-spray and ultrasonic methods as suitable electron transport layers in perovskite solar cells. It was found that hand-spray deposition of TiO₂ yields coatings with a macroscopic mean thickness deviation of up to $\pm 15\%$. This deviation could be significantly reduced to less than $\pm 5\%$ using ultrasonic deposition. However, this was only achieved when the shaping pressure used during the deposition was high (200 kPa). In comparison, the films deposited at lower pressures (10 kPa) exhibited slightly larger thickness variations and were significantly more inhomogeneous at the microscopic level. These structural variations had a significant effect on the performance of methyl ammonium lead iodide perovskite solar cells, with devices featuring TiO₂ deposited using the high shaping pressure ultrasonic approach yielding the highest median efficiency of 15.6%, followed by hand-spray at 14.5%, and finally low shaping pressure ultrasonic method at 11.8%. Importantly, the ultrasonic method yielded devices with a 300% reduction in standard deviation of efficiency compared to the hand-spray, which can be directly correlated to the macroscopic homogeneity of the TiO₂ layers. The inclusion of a mesoporous TiO₂ nanoparticle scaffold onto the high shaping pressure TiO₂ layers was found to enhance the mean efficiency to 17.4% and remarkably provide a further 300% reduction to its standard deviation. These results indicate that the ultrasonic spray method is a suitable approach to fabricating high quality and reproducible TiO₂ electron transporting layers for PSC, provided that high deposition pressures are used. Coupling this deposition approach to additional mesoporous layers provides further efficiency and reproducibility benefits, which are important factors towards larger area perovskite device fabrication.

FIGURES

Figure 1. Schematic diagram of the ultrasonic spray deposition approach used in this work (a). Digital photographs and relative thickness maps derived from spectroscopic ellipsometry of marked areas in the micrographs of TiO₂ sprayed on silicon wafers by a conventional hand nebulizer (b, d) and through ultrasonic spray deposition (c, e).

Figure 2. J-V curves of TiO₂ layers for increased spraying cycles of FTO/TiO₂/Spiro-OMeTED/Au diodes (a) and specific current values at selected voltages of 0.4 and 0.8V (b). The dashed lines at 0.1 and 0.01 mA cm⁻² represent the minimum proposed current density requirements at 0.4 and 0.8 V, respectively, for this diode to exhibit sufficient blocking characteristics to be suitable in solar cells, as identified by Peng et al.³⁴

Figure 3. Structural model of perovskite solar cells (a) and summarized parameters of devices using TiO₂ layers sprayed by increased cycles (b).

Figure 4. Nyquist plot of perovskite device with T_x ETL at a bias of 0.8 V under 1 sun illumination (a) using the equivalent circuit model (b), recombination resistance (R_{rec}) as the function of the applied voltage at 1 sun illumination (c) and schematic of the proposed carrier extraction and recombination mechanisms at different TiO₂-perovskite interface (d).

Figure 5. J-V curves (a) and steady state output curves (b) of perovskite solar cell using TiO₂ layers sprayed by 4 cycles from forward and reverse scan.

Figure 6. Digital photographs (a, b), spectroscopic ellipsometer thickness maps relative to the median thickness (c, d), 3-dimensional (e, f) and line (g, h) AFM profiles of ultrasonic spray-deposited TiO₂ films on silicon wafers with a 10 kPa (top) and 200 kPa (bottom) shaping gas pressure, respectively.

Figure 7. Summary of the perovskite solar cell V_{oc} s, J_{sc} s, FFs and PCEs (represented in a, b, c and d, respectively) using TiO₂ made by hand-spray, ultrasonic spray with low pressure shaping gas, ultrasonic spray with high pressure shaping gas with and without mesoporous TiO₂ layer.

TABLES

Table 1. Fitted devices parameters of TiO₂/Spiro-OMeTAD diodes using a Schokley model.

T_x	R_s (Ω cm²)	R_{sh} (kΩ cm²)	J₀ (mA cm⁻²)	n
2	7.97	4	1.22×10^{-5}	3.68
4	8.47	43	1.04×10^{-9}	2.58
6	7.81	115	1.11×10^{-9}	2.72
10	10.67	667	2.86×10^{-9}	2.94

Table 2. Mean and medium parameters for PSC devices using different TiO₂ ETLs.

Samples	J_{sc} (mA cm⁻²)	V_{oc} (mV)	FF	PCE (%)
Hand-spray	17.95±(5.13)	988.20±(64.55)	0.61±(0.09)	11.43±(4.56)
	21.08	1009.00	0.64	14.49
Ultrasonic spray	19.23±(2.13)	960.28±(45.70)	0.62±(0.06)	11.76±(1.61)
(10kPa)	20.21	971.50	0.61	11.73
Ultrasonic spray	21.52±(0.97)	1027.75±(14.02)	0.67±(0.03)	15.14±(1.54)
(200kPa, planar)	21.68	1032.00	0.68	15.56
Ultrasonic spray	23.16±(0.59)	1047.65±(7.56)	0.71±(0.03)	17.16±(0.55)
(200kPa, meso)	23.34	1046.50	0.71	17.35

Supporting Information

The Supporting Information provides thickness maps derived from spectroscopic ellipsometry of TiO₂ sprayed on silicon wafers and SEM analysis of TiO₂ deposited with different cycle number on FTO.

Author Information

Corresponding Author

*Corresponding author: Jacek.Jasieniak@monash.edu

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

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