A one-step Laser Process for Rapid Manufacture of Mesoscopic Perovskite Solar Cells Prepared Under High Relative Humidity

DOI:

[10.1039/C8SE00043C](https://doi.org/10.1039/C8SE00043C)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Chen, Q., Mokhtar, M. Z., Ke, J. C-R., Thomas, A., Hadi, A., Whittaker, E., Curioni, M., & Liu, Z. (2018). A one-step Laser Process for Rapid Manufacture of Mesoscopic Perovskite Solar Cells Prepared Under High Relative Humidity. *Sustainable Energy & Fuels*. <https://doi.org/10.1039/C8SE00043C>

Published in:

Sustainable Energy & Fuels

Citing this paper

Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version.

General rights

Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy

If you believe that this document breaches copyright please refer to the University of Manchester's Takedown Procedures [<http://man.ac.uk/04Y6Bo>] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.

A one-step Laser Process for Rapid Manufacture of Mesoscopic Perovskite Solar Cells Prepared Under High Relative Humidity

*Qian Chen[†], Muhamad Z. Mokhtar[†], Jack Chun-Ren Ke^{‡§}, Andrew G. Thomas^{†‡}, Aseel Hadi[†],
Eric Whittaker[‡], Michele Curioni[†] and Zhu Liu^{*†}*

[†]School of Materials, The University of Manchester, Manchester, M13 9PL, UK

[‡]Photon Science Institute, The University of Manchester, Manchester, M13 9PL, UK.

[§]School of Physics and Astronomy, the University of Manchester, Manchester M13 9PL, UK

Corresponding Author

Zhu Liu

Tel.: 0044 1613064845

*E-mail: zhu.liu@manchester.ac.uk

Abstract

Mesoscopic perovskite solar cells (PSCs) containing a TiO₂ mesoporous structure and a compact TiO₂ film have reached the highest power conversion efficiency (PCE) and excellent stability among various PSC structures. However, conventional fabrication of the mesoscopic structure requires high-temperature heating processes that are considerably time-consuming. Current methods also make it difficult to fabricate integrated or multifunctional devices on the same substrate. Laser processing offers an opportunity to develop a rapid, localized and precise treatment without damaging the substrate or surrounding materials. Here, we demonstrate a rapid and localized one-step fiber laser process to generate both mesoporous and compact TiO₂ films on tin-doped indium oxide (ITO) glass. The average PCE obtained for the PSCs by laser irradiation for 1 min, prepared under a high relative humidity of 60% by a one-step deposition method, is equivalent to that by furnace treatment for 2 h. A fundamental understanding of the laser sintering mechanism using a fiber laser with a wavelength of 1070 nm has also been established. The use of the fiber laser with a wall-plug efficiency of over 40% offers an economically feasible, industrially viable solution to the challenge of rapid fabrication of mesoscopic PSCs and integration of multifunctional devices. In addition, it opens a novel route to manufacture tandem, patterned or aesthetic solar cells in the future.

Keywords: laser; perovskite solar cell; one-step; rapid manufacture; integration

1. Introduction

The utilization of solar energy, particularly photovoltaic (PV) technology, has been considered as a promising solution to tackle the major challenge of the finite supply of fossil fuels and global environmental issues.^[1] Recently, perovskite solar cells (PSCs) have become one of the hottest topics in the field of PV research due to their rapid increases of power conversion efficiency (PCE) beyond 22% and relatively low fabrication cost.^[2–5] Up to date, mesoscopic PSCs comprising of TiO₂ mesoporous structure on a compact TiO₂ film have achieved highest efficiency and excellent stability among the various structures.^[6,7] It has been proved that the use of such TiO₂ mesoporous scaffolds contributes to improved charge collection efficiency, less hysteresis and better resistivity to moisture.^[8–10]

However, fabrication of the TiO₂ mesoscopic PSCs requires high temperature processes (>450°C) and is extremely time consuming.^[4,10] Formation of the mesoporous and compact TiO₂ films is also performed in a two-step process. Preparation of the TiO₂ mesoporous structure is carried out in a furnace at 450-550°C for 30 min to remove the organic binders and achieve sufficient interconnection between the TiO₂ nanoparticles, while formation of the compact film also requires a temperature above 450°C to transform the TiO₂ from an amorphous phase to crystalline form.^[4] These long high-temperature processes prevent the high throughput of PSCs, use of flexible substrates,^[11] e.g. plastic substrate; and at such temperatures, even glass substrates with large areas could bend irregularly.^[12] More importantly, an integral high-temperature heating process by conventional methods also prevents integrating of multifunctional devices on the same substrate.^[12] Currently, a number of alternative heating sources have been explored to replace conventional furnace sintering for fabrication of TiO₂ mesoporous structures, including UV-irradiation,^[13] near infrared (NIR) heating,^[14] flame annealing^[15] and UV-ozone treatment.^[16]

Lasers, as a state-of-the-art manufacturing tool, enable a local, precise, selective, flexible, non-contact, highly automated, low-cost and scalable fabrication process.^[17] They have been used in a number of PSC applications, including laser-assisted growth of perovskite films,^[18,19] laser-assisted deposition of NiO electrode and compact TiO₂ films.^[20,21] Moreover, in order to scale-up PSC modules for commercialization, laser scribing has been successfully used on isolating transparent conductive oxide (TCO) and other layers of the PSCs with minimal dead areas.^[22–24]

For laser heat treatment, laser sintering with various wavelengths and pulse widths has been studied in order to form TiO₂ mesoporous structure for dye sensitized solar cells (DSSCs).^[12,25,26] Compared to conventional furnace or other annealing methods, laser sintering with Nd:YAG lasers shows significant benefits. It allows the integration of DSSCs with different devices on the same substrates, which otherwise could be damaged by furnace sintering.^[17] Its local sintering feature can prevent the glass bending induced by conventional heating methods.^[12] It also allows the fabrication of TiO₂ mesoporous structure on plastic substrates for DSSCs.^[25,26] To date, to the best of our knowledge, no work has been reported on the use of laser heat treatment for generation of both mesoporous and compact TiO₂ films on TCO-coated glass in one-step.

In this work, we aim to develop a one-step, rapid fabrication technique to generate both mesoporous and compact TiO₂ films on ITO-glass using a fiber laser with 1070 nm wavelength and millisecond pulse width, without thermally damaging the ITO or the glass substrate. Compared to Nd:YAG lasers with wall-plug efficiencies of 2-3%,^[12] used in the studies described above, fiber lasers show a dramatically increased wall-plug efficiency of over 40%. In addition, the millisecond pulse width selected for this work is believed to be essential to produce efficient mesoscopic perovskite solar cells through effective sintering mechanisms for TiO₂ mesoporous structure.

2. Results and discussion

Figure 1a illustrates the laser process schematically. Initially, the titanium diisopropoxide bis(acetylacetonate) in 1-butanol and diluted 18 NRT TiO₂ paste was spin-coated on the pre-cleaned ITO-glass and dried on the hotplate as described in Experimental Section. When the laser beam irradiated on the sample surface, the TiO₂ paste containing TiO₂ nanoparticles and the organic binders absorbed the laser beam partially, but a significant amount of the laser beam penetrated through the TiO₂ paste, reaching the amorphous compact TiO₂ film and the ITO. It was confirmed by the UV-visible spectra as presented in **Figure 1b**.

To gain insight into the one-step laser process, various samples as described in Fig. 1c were irradiated with the fiber laser beam under the same processing conditions of 107 W cm⁻² for 60 s, along with temperature monitoring by an IR thermal camera. In order to form an efficient necking of the TiO₂ nanoparticles by furnace heating, sintering temperature of at least 450°C is normally required.^[27] As shown in **Figure 1c**, the bare glass showed a peak temperature of 433°C due to its low photo-thermal conversion.^[18,28] For the ITO-glass, the peak temperature was boosted to 584°C due to the photon-induced excitation of the free charge carriers in ITO resulting in instantaneous local heating.^[28] Adding a thin amorphous compact TiO₂ film (50 nm) on ITO-glass did not increase the peak temperature. Spin-coating a layer of TiO₂ paste (150 nm) resulted in a peak temperature of 595°C, due to stronger laser beam absorption of the TiO₂ paste as evidence in **Figure 1b**. This implied that the sintering of the TiO₂ paste and the crystallization of the compact TiO₂ film were the result of the direct absorption of the laser beam by TiO₂ paste, and a sufficient rise of the temperature due to the contribution from the ITO film also enhanced sintering effect and potentially improved adhesion of the compact TiO₂ films to the ITO film.

The temperature distribution obtained by the IR thermal camera as shown by the orange area in **Figure 1c** was uniform across the whole sample surface (2 cm × 1.5 cm), demonstrating a

unique feature of the fiber laser process developed in this work. Unlike the commonly used laser spot size of tens of micrometers and the use of a raster scanning to cover entire sample surfaces through overlapping laser tracks for DSSCs,^[12,17] the laser beam was defocused to achieve a spot size of 6.9 cm² (i.e. 2.96 cm in diameter) in this work. A photograph of the laser processing set-up is shown in **Figure S1**. The large size of the laser beam offers a unique capability of rapid processing of PSCs to achieve a sintering process without rastering, which overcomes various drawbacks caused by overlapping laser beam tracks, such as re-heating, and reduces processing time in a much simplified manner suitable for practical applications. Although the laser spot size was set to be larger than the sample area of 3 cm², a mask with customized area or shape could be applied to achieve local sintering of specific area or shape of samples without damaging surrounding areas.

Based on the calculation reported by Mincuzzi *et al.* on the use of a Nd:YAG laser for DSSCs, processing time (t_p) of 122 h by a raster laser processing with an average power of 7 W was required, in comparison of 50 h and 6.25 h by a hot-plate and furnace process for sintering of 1 m² mesoporous TiO₂ film.^[12] Under the existing laser processing condition in this work, i.e. power density, pulse width and beam dimension, both mesoporous and compact TiO₂ films can be locally fabricated on 1 m² ITO-glass in only 5.56 h (180 cm² h⁻¹). Therefore, this new laser process offers a significant improvement compared to the previously laser work on DSSCs. In addition, the previous work showed that the embodied energy for a Nd:YAG laser with wall plug efficiency of 3.5% was lower than that of the hot plate, oven and furnace.^[12] The fiber laser used in this work has wall-plug efficiency of over 40%. Therefore, the fiber laser process is believed to have a greater potential for industrial applications, than processing using other types of lasers.^[12,17,26]

Fig. 1 (a) Schematic representation of laser processing, (b) absorption of ITO-glass and various dried films on the ITO-glass, (c) temperature profiles of various substrates during laser irradiation of 60 s at 107 W cm^{-2} and temperature distribution of the laser irradiated area recorded with an IR thermal camera.

In the laser process, there are three critical temperatures required to achieve a successful sintering/crystallization of the TiO_2 films. For deposited TiO_2 paste, a temperature of at least 280°C is required to vaporize the organic binder, and $\sim 450^\circ\text{C}$ is needed for necking of the TiO_2 nanoparticles to take place.^[29] For the amorphous compact TiO_2 film, a temperature of 450°C is essential for crystallization of amorphous TiO_2 to occur. **Figure 2a** presents a comparison of the Raman spectra for the compact TiO_2 film obtained by the furnace-, laser-

treatment at 107 W cm^{-2} and with no treatment. Both the furnace- and laser-treated compact TiO_2 films exhibit the peaks at 144 cm^{-1} (Eg)*, 399 cm^{-1} (B1g)*, 519 cm^{-1} (B1g)*, and 639 cm^{-1} (Eg)*, corresponding to anatase TiO_2 with tetragonal symmetry.^[30] This indicates that the laser processing successfully achieved the crystallization of the amorphous compact TiO_2 film with no phase transformation to rutile. X-ray diffraction (XRD) patterns of the laser-treated amorphous TiO_2 compact film in **Figure 2b** show the peak at 25.3° corresponding to (101) anatase phase, as further evidence for crystallization induced by the laser irradiation. Crystallinity of the TiO_2 compact film is essential for high performance of PSCs due to the improved charge transport ability and electrical conductivity compared to amorphous phase.^[31]

Figure 2. (a) Raman spectra of untreated, furnace- and laser-treated compact TiO_2 films at 107 W cm^{-2} , (b) X-ray diffraction patterns of ITO glass, untreated, furnace- and laser-treated compact TiO_2 films at 107 W cm^{-2} .

Raman spectra, shown in **Figure 3a**, were also used to verify the complete removal of the organic binder within the TiO_2 paste sintered by the furnace and the laser. The ethyl cellulose organic binder gives rise to Raman peaks at 2876 cm^{-1} , 2934 cm^{-1} and 2976 cm^{-1} which were completely removed after sintering.^[13] Full removal of the organic binder is essential for efficient pore filling and improved electrical conductivity of TiO_2 mesoporous structures.^[14]

Figure 3a also shows that no phase transformation of the anatase TiO_2 nanoparticles by laser

sintering, which is further confirmed by the XRD patterns in **Figure 3b**. All the samples show the peaks at 25.3° , 48.2° and 55.1° corresponding to anatase planes at (101), (200) and (211).^[32]

Fig. 3 (a) Raman spectra of untreated, furnace- and laser-treated TiO_2 mesoporous structures at 107 W cm^{-2} , (b) X-ray diffraction patterns of ITO-glass, untreated, furnace- and laser-treated TiO_2 mesoporous structures at 107 W cm^{-2} .

Figures 4a, b and c show high-resolution SEM images of the surfaces of the TiO_2 mesoporous structures under different conditions. The TiO_2 nanoparticles in the untreated film (**Figure 4a**) were discrete, while the TiO_2 mesoporous structure treated by the laser at 107 W cm^{-2} (**Figure 4c**) and furnace (**Figure 4b**) clearly revealed necking of the TiO_2 nanoparticles and consequently increasing in the particle size due to the high temperature sintering. Efficient necking of the nanoparticles is essential to increase the diffusion length of the electrons for high performance PSCs.^[27]

Fig. 4 SEM images of top views of (a) untreated, (b) furnace- and (c) laser-treated TiO₂ mesoporous structures at 107 W cm⁻² (scale bar: 100 nm).

The fiber laser process has several advantages over other alternative processes. For example, a recent publication demonstrated an interesting method of using a near infrared (NIR) light to fabricate mp-TiO₂/mp-ZrO₂/Carbon structure based perovskite solar cells with a PCE of 11% within only 30 s.^[14] Indeed, the NIR processing is a promising method for rapid manufacturing perovskite solar cells and shows higher throughput than the laser process presented in this work. However, cracking along the standard laser patterned lines (isolating the FTO and glass) with a thickness of 1.4 mm in width was reported due to the large thermal stress induced by the significant temperature different between the FTO and glass during the rapid NIR process.^[14] Therefore, a thinner isolation line of 0.05 mm was applied to reduce the thermal stress between the glass and FTO during the NIR irradiation. A similar issue was also observed when the fiber laser in continuous-wave mode and shorter irradiating time was applied by the authors. In this work, the formation of cracking was resolved by selecting the pulse-mode with

a duty cycle of 100 ms ON/50 ms OFF under the same laser power density. The use of pulsed mode could prolong the period of time for thermal conduction between the glass and ITO, resulting in the reduction of temperature difference between the two layers compared to the continuous mode. Therefore, we have achieved the process without damaging the glass with a laser isolation line up to 2.15 mm. A schematic representation of laser-patterned ITO on glass is shown in **Figure S2**. We believe that the fibre laser process with the selective pulse widths is a safer approach to conductive oxide coated glass substrate and could be applied to more circumstances for fabrication of PSCs such as aesthetic, patterned or customized cells with different patterned ITO or FTO layer.

In order to determine the quality of the prepared mesoporous and compact TiO₂ films with regards to use in PSCs, prototype cells were fabricated. A cross-sectional view of the PSCs fabricated under a relative humidity around 60% based on a configuration of ITO/cp-TiO₂/mp-TiO₂/perovskite/spiro-OMeTAD/Ag is shown in **Figure S3**. It has been well documented that a high humidity environment is particularly detrimental to the most commonly used lead-halide based perovskites CH₃NH₃PbI₃ and CH₃NH₃PbI_{3-x}Cl_x for solar cell applications.^[33,34] An average PCE of 11% achieved in the glove box was reduced to 0.35% in the fabrication environment with humidity over 60%.^[35] To achieve a high PCE, preparation of PSCs is mainly carried out in highly controlled inert atmosphere.^[36] The use of inert atmosphere is cost-ineffective which limits the mass-production and applications of PSCs. Although highly efficient PSCs with the PCEs up to 18% have been recently reported by a two-step deposition method at high relative humidity around 70%, their work also indicated that the device performance by a one-step deposition method was badly affected by the moisture due to the uncontrollable crystallization process in the high humidity condition^[37].

In this work, we have adapted the methods reported by Troughton, J. et al. and Ke, W. et al.,^[36,38] using a one-step deposition method with a molar ratio of 1:1 of PbI₂ to CH₃NH₃I and

adding 5% $\text{Pb}(\text{SCN})_2$ into the precursor to prepare the perovskite precursor and ethyl acetate as an antisolvent in ambient air with a relative humidity around 60%. It was reported that the use of ethyl acetate as an anti-solvent contributed to a better protection of the MAI- PbI_2 -DMSO intermediate phase during the spin-coating process under the high relative condition, compared to other antisolvents such as chlorobenzene, toluene or diethyl ether,^[36] so that an improved photovoltaic performance was achieved due to a better quality of the perovskite layer with less pinholes, defects and variation of the grain sizes treated by ethyl acetate compared to other antisolvents.^[36] In addition, a small amount of $\text{Pb}(\text{SCN})_2$ additive was also reported to contribute to the increase of grain size of perovskite layer thus an improved photovoltaic performance.^[38]

Figure 5a shows the J-V curves under simulated solar irradiation of AM 1.5 G (100 mW cm^{-2}) of the PSCs fabricated with mesoscopic structures treated by the laser at different power densities, compared to a cell where the TiO_2 films were treated in a furnace. It was found that increasing the laser power densities from 86 W cm^{-2} to 107 W cm^{-2} remarkably improved the PCE from 4.5% to 8.8%. Increasing the power density also led to an increase in recorded temperature on the TiO_2 surfaces from 513°C to 595°C as shown in **Figure 5b**. Following irradiation by the laser pulse the sample was found to remain at a temperature, $T > 450^\circ\text{C}$ for 18.9 s and 39.5 s and $T > 280^\circ\text{C}$ for 66.3 s and 82.9 s for the 86 W cm^{-2} and 107 W cm^{-2} pulses, respectively. Since Raman spectra showed that the organic binders were completely removed, and crystallization of the compact TiO_2 films occurred for all three laser conditions as shown in **Figure S4** and **S5**, the difference in PCEs is believed to be related to the difference in the degree of interconnections between the TiO_2 nanoparticles. As shown in **Figure S6**, at the higher laser power density, more efficient necking of TiO_2 nanoparticles was achieved supporting the correlation between necking and higher PCEs. This is assumed to be linked to longer diffusion lengths of the electrons and fewer recombination reactions.^[39] However, with

a further increase of the laser power density to 115 W cm^{-2} , it started to show the signs of superficial melting of the glass which could adversely affect the performance of the devices.

Figure 5. (a) Current density-voltage (J-V) curves of perovskite solar cells produced by 2 h furnace treatment and laser-treated for 1 min with various power densities under standard AM 1.5G condition, (b) Temperature profiles of ITO glass coated with amorphous compact TiO_2 film and TiO_2 paste during laser irradiation of 60 s at 86 and 107 W cm^{-2} .

Table 1. Summary of photovoltaic parameters of the perovskite solar cells produced by laser and furnace sintering process at relative humidity around 60% with a one-step deposition method. Average photovoltaic parameters were calculated based on 6 cells performance.

Treatment	V_{oc} [mV]	J_{sc} [mA cm^{-2}]	FF [%]	PCE best [%]	PCE average [%]	R_s [$\Omega \text{ cm}^2$]
Laser	904 ± 23	18.2 ± 1.6	50.3 ± 5.8	8.8	8.2 ± 0.5	15.94
Furnace	960 ± 12	18.6 ± 0.4	45.6 ± 2.3	8.9	8.1 ± 0.5	20.11

Table 1 shows that a maximum PCE of 8.8%, with an average value of 8.2%, was achieved by the optimized laser processing condition of 107 W cm^{-2} . This was comparable to the maximum PCE of 8.9% with an average value of 8.1% from the furnace process within experimental error. J-V curves with forward and reverse scans for both furnace- and laser-treated samples are shown in **Figure S7a and b**. It is evident that the J-V curve with forward and reverse scans for the laser-treated sample (**Figure S7b**) presented a lower hysteresis than that for the furnace-treated (**Figure S7a**). This could be the result from the smoother and compact TiO_2 film with better uniformity and less pinholes fabricated by the laser process (**Figure 6b**) compared with that by the furnace (**Figure 6a**). A better quality of the compact TiO_2 film is beneficial for a better transport of electrons from the mesoporous TiO_2 film infiltrated with the perovskite to the compact film and ITO layer.^[40] The photovoltaic performance of the solar cells were relatively stable even with different scan rates as shown in **Figure S8**. This could, to some extent, indicate that the steady-state power output of the solar cell was relatively close to the J-V measurement.^[41] The PCEs obtained in in this work with a one-step deposition method at high relative humidity around 60% were comparable to several recent publications with one-step or even two-step deposition methods. Three examples can be given as follows: 1) a two-step method with best PCE of 8.38% at 60% humidity.^[42] 2) a one-step method with a best PCE of 8.08% and an average PCE of 6.68% at humidity around 40%.^[43] 3) an average PCE of 8.3% by spray cast method at humidity around 55%.^[44] A detailed chart with more recent publications with the comparable PCEs to our work is shown in **Table S1**.

Figure 6. SEM images of top views of (a) furnace- and (b) laser-treated compact TiO₂ films at 107 W cm⁻² (scale bar: 100 nm)

Another important observation shown in **Table 1** is the difference in fill factors. The PSCs treated at the optimized laser condition show a higher average fill factor of 50.3% than the furnace-treated with an average of 45.6%. This is more likely to be associated with the observation in Figure 6, where the laser-treated TiO₂ film exhibited better uniformity and less pinholes than the furnace-treated one. The smoother compact TiO₂ film could contribute to the improved interfacial structure between the compact film and mesoporous film infiltrated with perovskite, thus reduce the recombination sites and increase the charge transport at the interface resulting in an increase of the fill factor.^[45,46] Since the laser-treated TiO₂ film showed less pinholes and defects, it may also contribute to a better conductivity of the compact film.^[40] This is in agreement with the results obtained in our work which the PSCs with the laser-treated had a lower overall series resistance of 15.94 Ω cm² compared to 20.11 Ω cm² by the furnace-treated. In addition, it has been reported that the resistivity of ITO increases significantly when a heating process at a temperature above 450°C is applied for over 20 min.^[47] Therefore, we believe that another reason for higher series resistance of the furnace-treated devices was the heating process at >450°C for more than 1 h, leading to degradation of the conductivity of the ITO layer. Compared to furnace processes, the heating period for laser process over 450°C was only 39.5 s which caused less degradation of the ITO layer thus also contribute to a lower overall series resistance. The average V_{oc} of furnace-sintered devices (960±12 mV), on the

other hand, was higher than that of the laser-sintered devices (904 ± 23 mV). This could be attributed to a small amount of Ti^{3+} present in the furnace-sintered TiO_2 mesoporous structure, arising from surface O-vacancies.^[48] No Ti^{3+} was observed in the laser-sintered TiO_2 mesoporous structure as shown in the Ti 2p XPS spectra in **Figure 7**. It has been shown that the electronic defects existed within the TiO_2 lattice can be passivated by a small amount of Ti^{3+} ,^[49] thus resulting a higher V_{oc} for the furnace-sintered TiO_2 mesoporous structure than that of the laser sintered.

Figure 7. High resolution XPS spectra of (a) Ti 2p and (b) O 1s core levels recorded from the surfaces of the furnace and laser sintered mesoporous TiO_2 films at 107 W cm^{-2} .

3. Conclusion

In summary, we have demonstrated a rapid and localized fabrication technique to generate both mesoporous and compact TiO_2 films in one-step for use in perovskite solar cells using a pulsed fiber laser with a wavelength of 1070 nm. With a stationary irradiation of 1 min at the optimized laser power density, crystallization of the amorphous compact TiO_2 film, complete removal of the organic binders and necking of the TiO_2 nanoparticles in the mesoporous structure have been successfully achieved. This laser process offers the advantages of localized, a significant reduction of processing time (from 2 h to 1 min), an increase in fill factor and

decrease of series resistance, over the furnace treatment. In a high relative humidity up to 60%, an average PCE of 8.2% was achieved in prototype cells using the laser sintered semiconducting oxide support, identical to that produced using a furnace sintering approach. The fiber laser sintering mechanism has also been revealed through the thermal analysis combined with the UV absorption measurements for each individual layer involved in photoanode structure of the PSCs. The use of the fiber laser with over 40% wall-plug efficiency opens a promising avenue for rapid fabrication of mesoporous and multi-layered metal oxide scaffold perovskite solar cells, as well as the potential for perovskite, dye- and quantum-dot sensitized solar cells fabricated in the form of integrated, multifunctional, tandem, patterned or aesthetic devices.

4. Experimental Section

Mesoscopic structure fabrication: ITO-glass substrate (Ossila, $20 \Omega \text{ sq}^{-1}$) was cleaned in sequence with 2% Hellmanex solution in deionized water, acetone, deionized water and then treated by UV-ozone for 15 min. A compact TiO_2 layer was prepared by spin coating 0.1 M titanium diisopropoxide bis(acetylacetonate) (75 wt % in isopropanol, Sigma-Aldrich) solution in 1-butanol (Sigma-Aldrich) at 3000 rpm for 40 s on the ITO-glass and dried at 125°C for 10 min. Then, the same process was repeated with 0.3 M titanium diisopropoxide solution in 1-butanol. The ITO-glass with TiO_2 precursor was sintered in a furnace with 30 min ramping from room temperature to 500°C and kept at 500°C for 30 min, followed by natural cooling for 3 hours. Next, Diluted TiO_2 paste (Dyesol, 18NR-T) in ethanol at 1:4 by weight was spin-coated on the compact TiO_2 layer at 4500 rpm for 30 s. The film was dried at 125°C for 10 min and then the same process for sintering compact layer was repeated.

One-step laser fabrication of mesoscopic structure: After the spin coating of 0.1 M and 0.3 M compact titanium diisopropoxide in 1-butanol and drying at 125°C for 10 min, diluted TiO_2 paste was spin-coated and dried at the same condition. The substrate was then placed on a

ceramic plate on the laser work station. An IPG Fiber laser was employed for the sintering process. The laser beam with uniform power density distribution at 86, 100, 107 W cm⁻² was applied. A pulse width of 100 ms with 50 ms of interval was used. The duration of laser irradiation on the substrate was set to be 1 min. After the laser sintering process, the substrate was cooled down for 90 s to complete the fabrication process.

Solar cell fabrication: To prepare the perovskite layer, 300 mg PbI₂ (99.9%, Sigma-Aldrich), 104 mg CH₃NH₃I (98%, Sigma-Aldrich) and 10 mg Pb(SCN)₂ (99.9%, Sigma-Aldrich) was mixed in 600 mg N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich) and 150 mg Dimethyl Sulfoxide (DMSO, 99.9%, Sigma-Aldrich). The precursor was stirred at room temperature in ambient air for 1 hour. The precursor was spin-coated on the TiO₂ mesoporous structure at 4000 rpm for 30 s and 0.2 ml of ethyl acetate (99.8%, Sigma-Aldrich) was dripped on the substrate at 8 to 9 s after the starting of the spin coating process. The film was then heated at 70°C for 1 min and 100°C for 10 min to obtain a CH₃NH₃PbI₃ film. To prepare a 2,2',7,7'-tetrakis(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD, 98%, Sigma-Aldrich) solution, 40 mg of spiro-OMeTAD was mixed with 10 µl bis(trifluoromethane) sulfonamide lithium salt solution (520 mg/ml in acetonitrile) and 15 µl 4-tert-butyl pyridine in 0.5 ml chlorobenzene (99.8%, Sigma-Aldrich). The spiro-OMeTAD solution was spin-coated on perovskite layer at 3000 rpm for 30 s. Finally, 80 nm of Ag was deposited by using thermal evaporator. The average relative humidity in the lab was measured around 70%. A dehumidifier was used to keep a relative humidity of 60% during the entire fabrication process.

Material and Device Characterization: Morphology of TiO₂ mesoporous structures and cross-sectional view of the PSC device was characterized by FEG-SEM (ultra 55, Carl Zeiss). A Renishaw Raman Spectroscope with 514 nm excitation Ar⁺ laser was used to characterize the crystallization of compact TiO₂ films and binder evaporation of TiO₂ mesoporous structure. A

Bruker D8 Advance diffractometer (Cu-K α) was used to characterize the phase transformation of compact and mesoporous TiO₂ films. The surface chemistry of the TiO₂ mesoporous structure was characterized by an X-ray Photoelectron Spectroscopy (XPS, Kratos Axis Ultra). The absorption spectrum of ITO-glass and TiO₂ paste on ITO-glass was measured by an UV–vis spectrophotometer (Shimadzu UV-2401PC). Current density–voltage (J–V) characteristics were measured by a solar simulator (Class AAA, Oriel) with one sun (100 mW cm⁻²) under 1.5G air mass calibrated by NREL certified cell and a Keithley 2420 source meter. A square aperture mask with an area of 0.024 cm² was used to define the active area. All characterization was performed in an ambient environment with a relative humidity around 60%.

Acknowledgements

The authors would like to thank Mr. Damian Crosby and Dr. Wei Guo in Laser Processing Research Centre (LPRC) in The University of Manchester for their technical support on laser operations.

Conflict of Interest

There are no conflicts of interest to declare.

References

- [1] L. K. Ono, N.-G. Park, K. Zhu, W. Huang, Y. Qi, *ACS Energy Lett.* **2017**, 2 (8), 1749-1751
- [2] H. S. Jung, N. G. Park, Perovskite solar cells: From materials to devices. *Small* **2015**, 11, 10–25.
- [3] J. Jean, P. R. Brown, R. L. Jaffe, T. Buonassisi, V. Bulović, *Energy Environ. Sci.* **2015**, 8, 1200.
- [4] Q. Jiang, L. Zhang, H. Wang, X. Yang, J. Meng, H. Liu, Z. Yin, J. Wu, X. Zhang, J. You, *Nat. Energy* **2016**, 2, 16177.
- [5] M. L. Petrus, J. Schlipf, C. Li, T. P. Gujar, N. Giesbrecht, P. Müller-Buschbaum, M.

- Thelakkat, T. Bein, S. Hüttner, P. Docampo, Capturing the Sun: A Review of the Challenges and Perspectives of Perovskite Solar Cells. *Adv. Energy Mater.* 2017, 7, 1700264.
- [6] N.-G. Park, M. Grätzel, T. Miyasaka, K. Zhu, K. Emery, *Nat. Energy* **2016**, 1, 16152.
- [7] G. Grancini, C. Roldán-Carmona, I. Zimmermann, E. Mosconi, X. Lee, D. Martineau, S. Narbey, F. Oswald, F. De Angelis, M. Graetzel, M. K. Nazeeruddin, *Nat. Commun.* **2017**, 8, 15684.
- [8] Y. Shi, Y. Xing, Y. Li, Q. Dong, K. Wang, Y. Du, X. Bai, S. Wang, Z. Chen, T. Ma, *J. Phys. Chem. C* 2015, 119, 15868–15873
- [9] H. S. Kim, N.-G. Park, *J. Phys. Chem. Lett.* 2014, 5, 2927–2934.
- [10] J. Yang, K. M. Fransishyn, T. L. Kelly, *Chem. Mater.* **2016**, 28, 7344.
- [11] F. Di Giacomo, A. Fakharuddin, R. Jose, T. M. Brown, *Energy Environ. Sci.* **2016**, 9, 3007.
- [12] G. Mincuzzi, M. Schulz-Ruhtenberg, L. Vesce, A. Reale, A. Di Carlo, A. Gillner, T. M. Brown, *Prog. Photovoltaics Res. Appl.* **2014**, 22, 308.
- [13] F. Di Giacomo, V. Zardetto, A. D’Epifanio, S. Pescetelli, F. Matteocci, S. Razza, A. Di Carlo, S. Licoccia, W. M. M. Kessels, M. Creatore, T. M. Brown, *Adv. Energy Mater.* 2015, 5, 1401808
- [14] J. Baker, K. Hooper, S. Meroni, A. Pockett, J. McGettrick, Z. Wei, R. Escalante, G. Oskam, M. Carnie, T. Watson, *J. Mater. Chem. A* 2017, 5, 18643–18650
- [15] J. K. Kim, S. U. Chai, Y. Cho, L. Cai, S. J. Kim, S. Park, J. H. Park, X. Zheng, *Small* 2017, 13, 1702260
- [16] B. Feleki, G. Bex, R. Andriessen, Y. Galagan, F. Di Giacomo, *Mater. Today Commun.* 2017, 13, 232–240.
- [17] G. Mincuzzi, L. Vesce, A. Reale, A. Di Carlo, T. M. Brown, *Appl. Phys. Lett.* 2009,

- [18] M. P. Arciniegas, A. Castelli, S. Piazza, S. Dogan, L. Ceseracciu, R. Krahne, M. Duocastella, L. Manna, *Adv. Funct. Mater.* 2017, 27, 1701613
- [19] F. Li, W. Zhu, C. Bao, T. Yu, Y. Wang, X. Zhou, Z. Zou, *Chem. Commun.* 2016,52, 5394-5397.
- [20] J. H. Park, J. Seo, S. Park, S. S. Shin, Y. C. Kim, N. J. Jeon, H. W. Shin, T. K. Ahn, J. H. Noh, S. C. Yoon, C. S. Hwang, S. Il Seok, *Adv. Mater.* **2015**, 27, 4013.
- [21] B. Yang, M. Mahjouri-Samani, C. M. Rouleau, D. B. Geohegan, K. Xiao, *Phys. Chem. Chem. Phys.* 2016,18, 27067-27072.
- [22] G. D. Spyropoulos, C. O. Ramirez Quiroz, M. Salvador, Y. Hou, N. Gasparini, P. Schweizer, J. Adams, P. Kubis, N. Li, E. Spiecker, T. Ameri, H.-J. Egelhaaf, C. J. Brabec, *Energy Environ. Sci.* **2016**, 9, 2302.
- [23] S. J. Moon, J. H. Yum, L. Lofgren, A. Walter, L. Sansonnens, M. Benkhaira, S. Nicolay, J. Bailat, C. Ballif, *IEEE J. Photovoltaics* **2015**, 5, 1087.
- [24] A. Fakharuddin, F. Di Giacomo, A. L. Palma, F. Matteocci, I. Ahmed, S. Razza, A. D'Epifanio, S. Licoccia, J. Ismail, A. Di Carlo, T. M. Brown, R. Jose, *ACS Nano* **2015**, 9, 8420.
- [25] H. Kim, R. C. Y. Auyeung, M. Ollinger, G. P. Kushto, Z. H. Kafafi and A. Piqué, *Appl. Phys. A*, 2006, 83, 73–76.
- [26] H. Pan, S. H. Ko, N. Misra, C. P. Grigoropoulos, *Appl. Phys. Lett.* **2009**, 94.
- [27] S. Nakade, M. Matsuda, S. Kambe, Y. Saito, T. Kitamura, T. Sakata, Y. Wada, H. Mori, S. Yanagida, *J. Phys. Chem. B* **2002**, 106, 10004.
- [28] T. Jeon, H. M. Jin, S. H. Lee, J. M. Lee, H. Il Park, M. K. Kim, K. J. Lee, B. Shin, S. O. Kim, *ACS Nano* **2016**, 10, 7907.
- [29] E. C. Muniz, M. S. G??es, J. J. Silva, J. A. Varela, E. Joanni, R. Parra, P. R. Bueno,

- Ceram. Int.* **2011**, *37*, 1017.
- [30] L. Stagi, C. M. Carbonaro, R. Corpino, D. Chiriu, P. C. Ricci, *Phys. Status Solidi Basic Res.* **2015**, *252*, 124.
- [31] G. Yang, H. Tao, P. Qin, W. Ke, G. Fang, *J. Mater. Chem. A* **2016**, *4*, 3970.
- [32] S. Sathasivam, D. S. Bhachu, Y. Lu, N. Chadwick, S. A. Althabaiti, A. O. Alyoubi, S. N. Basahel, C. J. Carmalt, I. P. Parkin, *Sci. Rep.* **2015**, *5*, 10952.
- [33] Q. Tai, P. You, H. Sang, Z. Liu, C. Hu, H. L. W. Chan, F. Yan, *Nat. Commun.* **2016**, *7*, 11105.
- [34] J. Chun-Ren Ke, A. S. Walton, D. J. Lewis, A. Tedstone, P. O'Brien, A. G. Thomas, W. R. Flavell, *Chem. Commun.* **2017**, *53*, 5231.
- [35] Z. Yang, C. C. Chueh, F. Zuo, J. H. Kim, P. W. Liang, A. K. Y. Jen, *Adv. Energy Mater.* **2015**, *5*.
- [36] J. Troughton, K. Hooper, T. M. Watson, *Nano Energy* **2015**, *5*, 1500328.
- [37] Y. Cheng, X. Xu, Y. Xie, H.-W. Li, J. Qing, C. Ma, C.-S. Lee, F. So, S.-W. Tsang, *Sol. RRL* **2017**, 1700097.
- [38] W. Ke, C. Xiao, C. Wang, B. Saparov, H. S. Duan, D. Zhao, Z. Xiao, P. Schulz, S. P. Harvey, W. Liao, W. Meng, Y. Yu, A. J. Cimaroli, C. S. Jiang, K. Zhu, M. Al-Jassim, G. Fang, D. B. Mitzi, Y. Yan, *Adv. Mater.* **2016**, *28*, 5214.
- [39] D. Zhao, T. Peng, L. Lu, P. Cai, P. Jiang, Z. Bian, *J. Phys. Chem. C* **2008**, *112*, 8486.
- [40] C. Huang, C. Liu, Y. Di, W. Li, F. Liu, L. Jiang, J. Li, X. Hao, H. Huang, *ACS Appl. Mater. Interfaces* **2016**, acsami.6b00846.
- [41] J. A. Christians, J. S. Manser, P. V. Kamat, Best practices in perovskite solar cell efficiency measurements. Avoiding the error of Making Bad Cells Look Good. *J. Phys. Chem. Lett.* **2016**, *8*, 8520–8526.
- [42] G. Murugadoss, H. Kanda, S. Tanaka, H. Nishino, S. Ito, H. Imahoric, T. Umeyama, *J.*

Power Sources **2016**, *307*, 891.

- [43] S. Prathapani, V. More, S. Bohm, P. Bhargava, A. Yella, S. Mallick, *Appl. Mater. Today* **2017**, *7*, 112–119.
- [44] D. K. Mohamad, J. Griffin, C. Bracher, A. T. Barrows, D. G. Lidzey, *Adv. Energy Mater.* 2016, *6*, 1600994.
- [45] B. Conings, L. Baeten, T. Jacobs, R. Dera, J. D’Haen, J. Manca, H. G. Boyen, *APL Mater.* 2014, *2*, 081505
- [46] Z. Liu, Q. Chen, Z. Hong, H. Zhou, X. Xu, N. De Marco, P. Sun, Z. Zhao, Y.-B. Cheng and Y. Yang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 11076–11083.
- [47] W. L. Hsu, Y. H. Pai, F. S. Meng, C. W. Liu, G. R. Lin, *Appl. Phys. Lett.* 2009, *94*, 231906
- [48] M. J. Jackman, A. G. Thomas, C. Muryn, *J. Phys. Chem. C* **2015**, *119*, 13682.
- [49] F. Giordano, A. Abate, J. Pablo, C. Baena, M. Saliba, T. Matsui, S. H. Im, S. M. Zakeeruddin, M. K. Nazeeruddin, A. Hagfeldt, M. Graetzel, *Nat. Commun.* **2016**, *7*, 10379.

Table of contents

A one-step laser process is applied to fabricate mesoporous and compact TiO_2 films in 1 min for perovskite solar cells.