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Rapid and low temperature processing of mesoporous TiO₂ for perovskite solar cells on flexible and rigid substrates

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Keywords: perovskite solar cell, mesoporous titanium dioxide, intense pulsed light curing, plastic substrate, low temperature sintering

Graphical abstract:

Research highlights:

- Binder-containing and binder-free TiO₂ pastes were characterized.
- 15 % PCE with a processing time of 2 ms on glass (binder-free TiO₂).
- The shelf life stability exceeded 1000 hours.
- 12 % PCE with a processing time of 3.1 s on plastic foil (binder-free TiO₂).

Abstract

Perovskite solar cells (PSCs) have recently attracted the attention of the scientific community because of the rapid advances in their development. Most of the state-of-the-art devices contain mesoporous titanium dioxide (TiO_2) as an electron transport layer. The drawback of such TiO_2 layers is that it often needs high temperature sintering at 450-500 °C for 30 minutes, which slows down the fabrication process and is clearly not compatible with future roll-to-roll (R2R) manufacturing.

The aim of this study was to develop low temperature and rapid curing techniques for mesoporous TiO_2 thin films, which are compatible with R2R processing and heat-sensitive plastic substrates for PSCs. Several alternative annealing techniques were tested on rigid and flexible substrates, such as UV-ozone (UV/O_3) treatment, oxygen plasma treatment (O_2 plasma) and Intense Pulsed Light (IPL) sintering and compared to conventional thermal annealing. After each treatment, the mesoporous layers were characterized using Raman spectroscopy, UV-visible spectroscopy, thermogravimetric analysis and scanning electron microscopy. Low temperature sintering techniques were specifically optimized for the mesoporous TiO_2 layers and were adapted for the fabrication of PSCs. Sintering process and solar cells manufacturing were optimized for two different device architectures on glass as well as on polyethylene naphthalate (PEN) substrates. Moreover, the maximum temperature of the mesoporous TiO_2 layer during the IPL curing process was simulated to better understand the curing process. By employing IPL curing, the processing time for the mesoporous TiO_2 layer can be reduced from 30 minutes to a few seconds without significant loss in the device performance. In particular stabilized PCE of 16 % and 12 % were obtained using IPL on glass and PEN substrates respectively. This processing route paves the way for future low temperature R2R processing of mesoscopic PSC on plastic substrates.

1.1 Introduction

Perovskite solar cells (PSCs) have attracted the attention of the scientific community because of the rapid advances in their development. Over the last eight years the power conversion efficiency (PCE) of these devices increased from 2.6 % [1] up to 22.1 % [2]. Furthermore, the high theoretical efficiency limit of 31 % due to its optimal bandgap [3], the low material cost and the compatibility with roll-to-roll (R2R) manufacturing due to low temperature solution processing of the perovskite layer [4] promise a bright future for this novel solar cell family.

In order to fabricate PSCs on flexible plastic foils using R2R manufacturing, the different thin layers, namely electron transport layer (ETL), photoactive layer (PAL) and hole transport layer (HTL), are sequentially deposited and annealed (if needed) at the temperatures compatible with the plastic substrate. The state-of-the-art devices widely utilize a high temperature treated mesoporous TiO_2 ETL on glass substrates [5]. The advantage of mesoscopic structure is that the interconnected nanoparticle network enables an enhanced charge extraction from the photoactive layer due to its increased surface area [6]. Moreover, recent studies have attributed improved device stability to the usage of a mesoporous cell structure when compared to a planar equivalent [7].

Although the application of mesoporous TiO_2 layer could be beneficial for PSCs, the drawback of this layer is the use of high temperature annealing. This step removes any binder contained in the TiO_2 paste after the layer deposition and promotes necking between nanoparticles [8]. The application of organic binder (e.g.: ethyl cellulose) in the TiO_2 paste enables the tuning of the paste viscosity providing better wetting of the paste on the substrate, compatibility with screen printing, high porosity and layer uniformity for the deposited mesoporous TiO_2 film. Moreover, the presence of binder prevents the formation of cracks during the sintering and enables good adhesion to the substrate [9], resulting in uniform and homogeneous coating. In contrast to binder-containing pastes, the films coated using binder-free TiO_2 pastes does not require prolonged high temperature annealing; however, post-treatments still required to remove residuals of additives, used in different synthesis routes [10]. Moreover, the TiO_2 layer produced from binder-free formulations often exhibits lower porosity.

As a common treatment after the deposition of the TiO_2 paste, both for binder-containing and binder-free mesoporous films, is drying at 130-140 °C [11] for at least 10 minutes to remove the excess solvent. For binder-containing thin films, the drying step is followed by a calcination step at 450-500 °C [8,12–14] for approximately 30 minutes in order to remove the organic binder and to improve the electromechanical bonding between the TiO_2 nanoparticles and the substrate. Furthermore, post-treatments such as UV/ O_3 treatment [15], radio frequency oxygen (O_2), argon and nitrogen (N_2) plasma treatments can be used as additional binder removal and surface modification steps [16–18].

The selection of a suitable treatment (drying, calcination, post-treatment) for TiO_2 nanoparticle pastes in R2R processing mostly depends on the heat-sensitivity of the flexible substrate. Typically, commercial plastic substrates, e.g.: poly-ethylene terephthalate (PET) coated with indium tin oxide (ITO), yield maximum working temperature of 150 °C, and when higher thermal stability is required poly-ethylene naphthalate (PEN) can be applied up to 180 °C [19]. Unfortunately, high temperature sintering is therefore not suitable for R2R production on plastic substrates and the time consuming low-energy post treatments such as UV/ O_3 and plasma treatments for TiO_2 paste are not compatible with a high speed of R2R manufacturing. Therefore the development of a rapid non-contact and efficient sintering technique is required.

Although only a few studies have been carried out so far on low temperature curing of commercial nanocrystalline mesoporous TiO_2 for PSCs applying UV irradiation for binder-containing and binder-free TiO_2 pastes [20–22], several alternative sintering techniques were pioneered for the fabrication of Dye-sensitized Solar cells (DSSCs) to replace the high annealing temperatures for the mesoporous TiO_2 . Low temperature and non-contact curing techniques were successfully developed such as microwave sintering [23], laser sintering [24–26], near infrared sintering (NIR) [27,28] and intense pulsed light curing (IPL) [29].

NIR sintering, a non-contact large area curing technique, was successfully applied for mesoporous TiO_2 coated both on titanium foil and fluorine-doped tin oxide (FTO)/glass substrates for DSSCs [27,28]. By employing NIR sintering, the electrode (Ti or FTO) absorbs the NIR wavelengths (from 800 nm to 1500 nm) and acts as a hotplate for the mesoporous thin films above. This heating effect causes the calcination of the mesoporous TiO_2 thin films within 12.5 seconds giving comparable results to conventional annealing. Although this rapid fabrication technique can be appealing for future R2R production on metal foils (inconvenient for module fabrication [30]), the indiscriminate heating of the entire stack would damage plastic foils such as PET and PEN [19].

Similarly to NIR sintering, IPL sintering (also known as photonic flash sintering, or photonic sintering) is a non-contact, large area photonic sintering technique which employs parts of the ultraviolet (UV), visible and NIR spectrum (wavelengths from 200 nm up to 1500 nm) employing a xenon flash lamp, whereas NIR sintering employs only part of this spectrum. Compared to NIR sintering, the main advantage of this novel curing technique is that the xenon flash lamp can deliver very high energy density within milliseconds enabling high throughput R2R manufacturing. These short millisecond light pulses allow the curing of the deposited thin films selectively without damaging the heat sensitive substrate underneath. Moreover, the usage of the UV part of spectrum could promote additional surface modification and decomposition of organic and inorganic residuals [15,31,32]. IPL curing was frequently applied for organic light emitting diodes and organic solar cells for the fabrication of the top metal grids from metallic nanoparticles (e.g.: copper [33] or silver [34]). Moreover this technique was also employed for photovoltaic applications for TiO_2 electron transport layers. Hwang et al. [29] demonstrated the IPL sintering of binder-containing mesoscopic TiO_2 thin films on FTO/glass substrate for DSSCs. Similarly for PSCs, Das et al. [35] applied IPL sintering for the annealing of sol-gel prepared TiO_2 thin films on rigid and flexible substrates.

By employing IPL sintering the processing time and manufacturing costs can be significantly reduced compared to conventional thermal annealing techniques, which makes it one of the most desirable candidate for R2R manufacturing. However, most of the studies for the mesoporous TiO_2 layer sintering have been carried out for dye-sensitized solar cells, and only a very few investigation have been done in application to perovskite solar cells.

In this paper we will show how IPL curing can provide a fast and R2R compatible process to cure the TiO_2 mesoporous layer at low temperature on both glass and PEN substrates, delivering PSC with stabilized PCE up to 16 %. A benchmark with other low temperature curing process (thermal annealing, UV/ O_3 , O_2 plasma) will demonstrate how IPL sintering can provide PSCs as efficient as with the other methods while reducing the curing time from 60 minutes to a few milliseconds.

1.2 Experimental

Borosilicate glass (Corning® Eagle XG, 700 μm thickness, 30 x 30 mm^2) and pre-patterned commercial ITO/glass (Naranjo, 10 $\Omega \square^{-1}$, 30 x 30 mm^2) substrates were sequentially cleaned in an ultrasonic bath with detergent, deionized water and isopropyl alcohol (IPA). After the IPA cleaning, the wet substrates were blow-dried using a N_2 gun and treated in a PR-100 UVIKON UV-Ozone photo reactor for an additional 20 minutes to remove the organic residuals. The cleaning procedure was followed by the deposition of 50 nm compact TiO_2 layer using a Scotty e-beam evaporator (by Cryofox). For the PSC device fabrication, the edges of the substrates were masked from the TiO_2 compact layer to enable TiO_2 free ITO contacts. Then, the samples were UV/ O_3 treated for 5 minutes to improve the wettability of the surface. Mesoporous TiO_2 thin films were spin coated in air using commercial binder-containing (Dyesol 18-nrt TiO_2 diluted in ethanol with weight ratio 1:5) and binder-free (Solaronix: Ti-Nanoxide T-L/SC) pastes. The final thicknesses of the mesoporous TiO_2 layers were measured using Bruker XT Dektak profiler.

ITO/PEN substrates were prepared as described elsewhere [36]. PEN foil was laminated to a glass carrier for easy processing and device fabrication. An organic planarization layer was deposited on top of the PEN surface. In order to introduce a water and oxygen permeation barrier and to improve the adhesion between the PEN/planarization and ITO, a silicon nitride layer was deposited with a chemical vapour deposition tool. The patterned ITO bottom electrodes (135 nm thick, 60 $\Omega \square^{-1}$) were sputtered using an AJA sputter tool and patterned using photolithography. The ITO/PEN substrates were rinsed and sonicated for 10 minutes both in deionized water and isopropyl alcohol (IPA), and blow-dried with a N_2 gun. As an additional step (compared to the ITO/glass) the substrates were vacuum dried at 70 $^\circ\text{C}$ for 15 minutes in a Gallenkamp vacuum oven. The dried substrates were treated using 5 minutes UV/ O_3 treatment (2.5 min O_2 plasma treatment for the devices with IPL sintering) to remove the organic residuals. After the cleaning steps, a 50 nm compact TiO_2 layer was deposited using the same deposition technique and masking as for ITO/glass substrates. Only binder-free TiO_2 paste was used for the fabrication of ITO/PEN devices.

The different mesoporous layers, both on borosilicate glass and ITO/glass substrates, were exposed to different thermal and low temperature treatments. For moderate and high temperature curing (from 140 $^\circ\text{C}$ to 300 $^\circ\text{C}$) a conventional hot plate with an in-built thermometer was used, while for higher temperature sintering at 500 $^\circ\text{C}$ for 30 minutes (for binder containing mesoporous TiO_2 films) a Gobi oven (by Stagge) was used. Low temperature treatments were applied to the mesoporous TiO_2 layers using a UV/ O_3 reactor (PR-100 UVIKON UV-Ozone photo reactor). Moreover, O_2 plasma treatments were applied to the binder-containing mesoporous TiO_2 films using a Branson/IPC 2100 plasma system. IPL curing was applied using Pulse Forge 1300 Photonic curing system (by Novacentrix) utilizing a xenon flash lamp and an elliptic mirror (single pulse area: 75x150 mm^2 ; maximum processing area 300x150 mm^2). The energy of each pulse was measured using BX 100 Pulse Light Energy meter. In order to adapt low temperature and rapid annealing techniques for the PSC device preparation of ITO/PEN samples, binder-free mesoporous TiO_2 films were treated using UV/ O_3 and IPL sintering (tools described above).

After the different treatments of the mesoporous TiO_2 films, the samples were directly transferred to a N_2 filled glovebox and the perovskite layer was spin coated using a two-step deposition method [37]. The perovskite precursors, PbI_2 (Sigma Aldrich, 99 %) and methylammonium iodide (MAI) (Dyesol, 99 %) were dissolved in dimethylformamide (DMF): dimethylsulfoxide (DMSO) mixture with a volumetric ratio of 5:1 (Sigma Aldrich, 99 %) and in IPA (Sigma Aldrich, 99%) respectively. The concentration for PbI_2 and MAI was 430 mg ml^{-1} and 47.5 mg ml^{-1} respectively. First, the PbI_2 solution was spin coated at 2000 rpm for 40

seconds followed by the immediate deposition of the MAI solution using the same rotation speed and spinning time. The drying film was directly placed on a hotplate and annealed at 130 °C for 10 minutes. The perovskite annealing was followed by the spin coating of the HTL inside the same glovebox. For the preparation of the hole transport material ink, 80 mg of 2,20,7,70-tetrakis-(N,N-dip-methoxyphenylamin)9,9'-spirobifluorene (spiro-OMeTAD) (Lumtec, 99.9 %) was dissolved in 1 ml of chlorobenzene (Sigma Aldrich, 99.99%) and doped using 28,5 µl of 4-tert-butylpyridine (Sigma Aldrich, 99%) and 17,5 µl of 520 mg ml⁻¹ lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) (Sigma Aldrich, 99.5%) in acetonitrile (Sigma Aldrich, 99%). The samples were stored overnight in air (RH of approximately 45 %). After the air soaking of the HTL coated samples, patterned 100 nm Au back contacts were deposited using vacuum (10⁻⁶ mbar) assisted thermal evaporation. For the PSC devices the ITO bottom contacts were cleaned from the mesoporous layers using IPA before the sintering of the mesoporous TiO₂. Cleaning the ITO contacts from perovskite and doped spiro-OMeTAD layers were performed in air using a 5:1 volumetric ratio DMF: chlorobenzene solvent mixture.

The photovoltaic characteristics (Current-Voltage (J-V), maximum power point tracking (MPPT) and hysteresis J-V curves) of the devices were measured in a N₂ filled glovebox using a shadow mask with a well-defined active cell area (0.089 cm²). The solar simulator is equipped with a halogen lamp light source calibrated to simulate 100 mW cm⁻² of AM 1.5 G standard test conditions. The solar simulator was calibrated using a Silicon reference cell with a Keightley 2400. For light soaking experiments the unsealed devices were irradiated with a halogen lamp in standard test conditions in a N₂ filled glovebox. The temperature during the light soaking experiments was monitored using a resistive thermometer.

Thermogravimetric analysis (TGA) was conducted on dried (at 80 °C) binder-containing and binder-free TiO₂ paste samples using Discovery TGA Thermogravimetric Analyzer from TA Instruments. UV-visible (UV-vis) measurements were conducted using Agilent HP 8453 UV-Visible spectrometer (without integrating sphere) to measure the transmittance of the mesoporous TiO₂ coated samples. Raman spectroscopic spectra were obtained using a Raman Renishaw micro-Raman spectrometer (equipped with 1800 lines/mm diffraction grating and CCD camera). The samples were excited using an argon ion laser (514 nm) with an incident laser normal to the surface and observed at 50 times magnification (InVia Raman Microscope). Scanning electron microscopy (FEI Nova600 NanoSEM) was applied to obtain cross sectional SEM images. Finally, the optical constants of the binder-free mesoporous TiO₂ coated borosilicate glass substrate were obtained using a J.A. Woollam Co. M-2000 Spectroscopic Ellipsometer.

The simulated temperature during the IPL curing process was calculated using GenPro4 optical simulation script and COMSOL 5.2 Multiphysics software. The detailed description of the simulation process can be found in Appendix B.

1.3 Results and discussion

1.3.1 Binder-containing TiO₂ paste

As a starting point, PSC were fabricated using commercial binder-containing mesoporous TiO₂ pastes on ITO/glass substrates to compare the state-of-the-art-high temperature and low temperature processing route. After the spin coating of the TiO₂ pastes (thickness 180 nm) the samples were dried at 140 °C drying (drying) for 10 minutes. As a calcination step high temperature (HT) annealing at 500 °C and low temperature UV/O₃ treatments (1 hour) were applied separately to remove the organic binder [20]. As a post-treatment we used 20 minutes UV/O₃ treatment before the PAL deposition. In order to validate the decomposition temperatures for the high temperature treatment thermogravimetric analysis was conducted (see **Fig. A.1**).

Table 1 compares the averaged photovoltaic parameters of the perovskite employing binder-containing mesoporous TiO₂ paste. As can be seen in **Table 1**, UV/O₃ treatment gave comparable average power conversion efficiencies (PCE_{average}) to conventional HT annealing confirming the available results in the literature [20]. Moreover the stabilized PCE was always equal or higher than the one measured with a J-V scan, confirming the validity of the photovoltaic parameter measured. UV/O₃ treatment can effectively decompose the organic residuals in the layer due to the presence of ozone and to the high photocatalytic activity of anatase TiO₂.

Although one hour UV light (in our case UV/O₃) treatment can be compatible with heat-sensitive flexible substrates (as demonstrated in [20] with UV light only), the treatment time for this step is not R2R compatible. In order to find the minimum treatment time for this process, the 10 minutes of drying was followed by UV/O₃ treatments with varying treatment time (from 5 to 60 minutes) on mesoporous TiO₂ coated ITO/glass substrates. Similarly to UV/O₃ treatments, O₂ plasma treatments were also tested in the same manner on the mesoporous TiO₂. To monitor the removal of the organic binder, Raman and UV-vis spectroscopic measurements were conducted for each treatment (see **Fig. A.2/ A-D**).

The optimized low temperature treatments for the binder-containing mesoporous TiO₂ are summarized in **Fig. 1/ A and B**. As can be seen from both images 15 minutes O₂ plasma and 20 minutes UV/O₃ were sufficient in removing the binder. The intensity of the characteristic fingerprints of ethyl cellulose binder (at 2876, 2934 and 2976 cm⁻¹) [31] gradually diminished by increasing treatment times in both cases (see **Fig. A.2/ A and C**). The presence of anatase TiO₂ phase was also detected with its most intense peak at 144 cm⁻¹, making Raman spectroscopy a versatile technique to study such layers [38]. In conclusion, the treatment times of binder-containing TiO₂ for both UV/O₃ and O₂ plasma treatments could be effectively used in the laboratory scale device fabrication, but are not ideal for future mass manufacturing due to long processing time (at least 15 minutes).

To test R2R manufacture compatibility, IPL curing was utilized as a non-contact treatment with an emission spectrum ranging from approximately 220 nm to 1000 nm (see **Fig. A.3**). The IPL sintering process can be also better understood by simulating the temperature evolution in the mesoporous layers (as will be discussed later for binder-free TiO₂ paste).

Although several IPL sintering treatments were tested on binder-containing mesoporous TiO₂ films coated on ITO/glass substrates, the calcination of the layer was not complete. Even after a highly energetic treatment consisting of ten consecutive 2 milliseconds pulses with a radiant energy of 12.3 J/cm² and 0.5 Hz fire rate (see IPL (10x) in **Fig. A.4/ A and B** and in **Fig. 1/ A and B**) the ethyl cellulose binder was still present in the mesoporous layer. Binder removal did not occur, because the temperature during the IPL curing process in the

mesoporous layer did not exceed the decomposition temperature of the binder. The processing time was not adequately long to allow photocatalytic degradation of the binder promoted by the UV part of the emission spectrum of the xenon flash lamp. As it was highlighted by Di Giacomo et. al [20], the presence of the ethyl cellulose binder in high concentration in the mesoporous TiO_2 can be fatal for the performance of PSCs, because it can negatively affect the growth of the perovskite crystal within the pores. Moreover, the remaining binder could hinder the flow of electrons from the PAL to the mesoporous TiO_2 thus resulting in very low current densities.

In summary, although we found that high temperature curing can be substituted by foil compatible UV/O_3 or O_2 plasma treatments, the time required for binder decomposition is not compatible with standard R2R manufacturing. Moreover, IPL sintering was not effective for removing the ethyl cellulose binder. Therefore, the next step of the study was focused on the investigation of a binder-free TiO_2 paste.

1.3.2 Binder-free TiO_2 paste

Binder-free TiO_2 pastes could provide a better option for a processing time reduction when high throughput processing is considered. By omitting the binder, both temperature for the annealing and the treatment time for the process can be dramatically reduced. It is worth mentioning that by omitting the mesoporous layer ones can further reduce processing time and recently high efficiency above 20% have been achieved on planar TiO_x [39]; however, for the perovskite used in this study the efficiency of planar devices was lower than the mesoporous ones (see **Table A.1**). For characterizing the selected binder-free TiO_2 paste, Raman spectroscopic measurements were conducted to examine the crystallinity of nanoparticles and the presence of additives which can affect device performance and can help studying the annealing process (see **Fig. 2/ A**). Similarly to the used binder-containing paste, a pure anatase phase was detected for the TiO_2 nanoparticles. Moreover, a peak at 1048 cm^{-1} was found. This peak can be assigned to the $\nu(\text{NO})$ stretching vibration (1050 cm^{-1}) of nitrate ion [40,41] which was presumably originated from the nitric acid additive in the TiO_2 paste. According to Ricci et al. [42], nitrate ions can passivate the surface oxygen vacancies of the TiO_2 nanoparticles and their presence can be eliminated by using thermal treatment (e.g.: $80\text{ }^\circ\text{C}$ vacuum for several hours). The author suggests that by removing these surface nitrate ions, reactive sites might be formed which can play a role during the inter-particle bridging (in the presence of oxygen). Low temperature acid-catalysed chemical sintering was already successfully employed in flexible DSSCs [10].

To find a suitable annealing temperature, thermogravimetric analysis was conducted on pre-dried mesoporous TiO_2 samples. As can be seen on the **Fig. 2/ B**, the total weight loss during the measurement was 12 wt%, and approximately half of this value was related to the loss of the remaining water and ethanol content (from $80 - 100\text{ }^\circ\text{C}$). The other 6 wt% change could be linked to the loss of the decomposition of nitrate surfactant with an onset temperature at $187\text{ }^\circ\text{C}$. It is noteworthy to mention that the predicted melting point ($189\text{ }^\circ\text{C}$) and boiling point ($492\text{ }^\circ\text{C}$) of nitrate ion [43] might be in a good agreement with the observations from the TGA measurements. Additionally, isothermal TGA experiments were conducted to determine the weight loss for the pre-dried TiO_2 paste during 10 minutes at three different temperatures: $140\text{ }^\circ\text{C}$, $187\text{ }^\circ\text{C}$ and $300\text{ }^\circ\text{C}$ (namely below, equal and higher than the decomposition temperature observed in the TGA data, see **Fig. A.5**). As can be seen, the percentage during the three isothermal TGA measurements did not show a significant drop after 10 minutes. As will be shown later, this nitrate content from the TGA (together with the measured Raman intensities) might be used to give an estimate of the effectiveness of the IPL curing.

Nitrate decomposition was confirmed by Raman spectroscopy using mesoporous TiO₂ coated on borosilicate glass substrates (see **Fig. 2/ C**). The TiO₂ layers were treated 10 minutes with the temperatures equal to those applied during the isothermal TGA measurements (140 °C, 187 °C and 300 °C) and compared to a non-treated sample. Moreover, we tested the combination of 140 °C drying with 20 minutes UV/O₃ treatment applied to TiO₂ layer (called drying with UV/O₃ later), the same as we used for the binder containing paste. According to [32], applying drying with UV/O₃ treatment an improved photocatalytic activity can be achieved with anatase mesoporous TiO₂ films which can enable improved decomposition of organic and inorganic additives. As can be seen in **Fig. 2/ C**, by increasing treatment temperature the intensity of the nitrate ion peak at 1048 cm⁻¹ can be suppressed due to its decomposition. By curing the samples at 300 °C for 10 minutes, the intensity of the nitrate peak can be reduced to a low level as was observed it from the TGA measurements (approximately 2 wt% nitrate content). Furthermore, drying with UV/O₃ treatment also seems to be as effective in removing nitrate as a 187 °C treatment for 10 minutes, confirming the statements in the literature [32].

The effect of the presence of nitrate in the mesoporous TiO₂ on the performance of solar cells was investigated by applying the same treatments as discussed above. For the fabrication of these PSCs the same device architecture was utilized as for the binder-containing mesoporous TiO₂ devices. **Fig. 2/ D** summarizes the average PCEs and PCE_{MPPT} for PSCs with treated (thermal annealing and drying with UV/O₃) and non-treated mesoporous layers. It can be seen that for an improved efficiency of the solar cells, a suitable treatment for binder-free mesoporous TiO₂ is required. The devices without any treatment delivered relatively low average efficiencies (12.9 ± 1.2 %) compared to the rest of the devices. When increasing the treatment temperature of the mesoporous layer, the stabilized device efficiency (PCE_{MPPT}) shows an increasing trend, which can be correlated to the decreasing nitrate content in the mesoporous TiO₂ layer. The standard deviations of the average PCE for the UV/O₃ treated samples were significantly smaller compared to the thermal treated samples with the highest efficiencies (see **Fig. 2/ D**). A relatively low standard deviation suggests better reproducibility for the device fabrication using UV/O₃ treatment for mesoporous TiO₂. The averaged electronic characteristics of these PSCs can be found in **Table A.1** and their hysteretic J-V curves in **Fig. A.6**. It is noteworthy to point out that the devices have higher open circuit voltages (V_{oc}) when the mesoporous TiO₂ layer was exposed to UV/O₃ treatments, compared to the devices with only thermal treated mesoporous TiO₂.

Our results show that low temperature drying (140 °C) combined with UV/O₃ can be an effective method for mesoporous TiO₂ treatment, avoiding high temperatures (important for plastic substrates). However, it can be a convenient and reproducible curing process only for laboratory scale device fabrication, because the processing time (30 minutes in total) for this treatment combination is not compatible with future R2R processing.

For the IPL sintering of the binder-free mesoporous TiO₂ films, the same sintering parameters were applied as for the binder-containing mesoporous TiO₂ films (12.3 J/cm² energy pulses with a pulse length of 2 ms) on glass substrates. To calculate the absorbed energy from the emission spectra of the xenon flash lamp, the optical constants for each layer (glass, ITO, compact TiO₂ and mesoporous TiO₂) were taken into account. For simulating the IPL sintering process, we assumed excellent reflection conditions from the sample holder table by using a silver reflector in our model. This assumption could provide an upper estimate for the temperature during the sintering process. According to our simulation the estimated temperature in the mesoporous TiO₂ layer exceeds 300 °C after ten pulses (see **Fig. 3/ A**). Moreover, the mode show that the heating of the layer is due both to the high absorption of

the ITO layer (UV and IR) but also to the absorption of the mesoporous and compact TiO₂ layers (UV).

Fig. 3/ B demonstrates the change in the Raman intensity of the nitrate peak (at 1048 cm⁻¹) during the IPL sintering process. By increasing the number of pulses the presence of nitrate surface ion was gradually diminishing. Even after one pulse the intensity of the nitrate peak decreased to a level comparable to that of 10 minutes 187 °C annealing (see **Fig. 2/ C**). By using three, five and ten consecutive pulses, the Raman intensity of the nitrate peak declined to a similar value as for the glass substrate.

As a next step, the same IPL sintering settings were tested for PSC fabrication. The treatments for the mesoporous TiO₂ layers for PSCs were compared to no-treatment and drying with UV/O₃ treatment (as a reference). **Fig. 3/ C** summarizes the average values of PCEs and the PCE_{MPPT} for the best devices. As was expected from the Raman spectroscopic measurements (**Fig. 3/ A**) all the IPL cured samples yielded higher average PCEs than the devices with non-treated mesoporous layers. Furthermore, ten pulses yielded better device performances (with the smallest standard deviation in PCE) than the rest. By using ten pulses of IPL curing the treatment time was reduced by two orders of magnitude (from 1800 to 18 seconds) with an average PCE (16.2 ± 0.5 %) compared to our reference treatment (15.9 ± 0.5 %). In addition, a maximum PCE of 16.1 % can be achieved with a single pulse that corresponds to a treatment time of 2 ms which is six orders of magnitude faster than the standard process.

The averaged photovoltaic characteristics for the devices employing IPL cured mesoporous TiO₂ are summarized in **Table A.2** and their hysteretic J-V curves can be seen in **Fig. A.7**. As we observed earlier for thermal treatments of the mesoporous TiO₂, after each pulses the FF increased gradually which could be explained with the reduced series resistance and longer electron diffusion length in the mesoporous film towards the electrode. Similarly to the FF improvements, the V_{oc} seemed to show an increasing trend after each pulses of IPL curing which may be related to the decomposition of nitrate. Nitrate decomposition can be linked to the high photocatalytic activity of anatase TiO₂ (caused by UV light emitted by the xenon flash lamp) and the combination of the heating of the mesoporous layer [44].

It is noteworthy to mention that the hysteresis for J-V curves decreased with increasing number of pulses (see **Fig. A.7/ A and B**), pointing out that this treatment can promote faster charge extraction. The reduction of the hysteresis effect is most likely related to the decreasing number of nitrate surface ions which was similar to our observations for the PSC devices with thermal annealed binder-free mesoporous TiO₂.

The morphology of the non-treated and IPL cured mesoporous TiO₂ layers was examined using cross sectional SEM (see **Fig. 4/ A and B**). As can be seen the fracture surface of the non-treated mesoporous TiO₂ layer was significantly different from the one treated with ten pulses (see **Fig. 4/ A and B**). We believe that this difference could be due to the enhanced interconnection of the TiO₂ nanoparticles (as we assumed from the FFs) which could result in such brittle-like fracture surface. Moreover, after the IPL sintering of the mesoporous TiO₂ film the nanoparticles seem to be arranged in a random close packed form. Tallarek and Baranau derived the maximum packing densities for jammed polydisperse hard spheres with a minimum porosity of 36 % (monodisperse spheres) and for increasing standard deviation of the nanoparticle size the minimum porosity value decreases to lower values than for monodisperse spheres [45]. Additionally, to validate our assumptions derived from the SEM image of the IPL cured mesoporous TiO₂, the effective refractive index of the IPL cured mesoporous TiO₂ (see **Fig. A.8**) was applied to estimate the porosity. For the calculation the Maxwell-Garnett approximation [46,47] was applied (see **Eq. (A.1)**) and resulted in a void fraction of 35.8% confirming our assumptions.

To investigate the effect of the presence of nitrate in mesoporous TiO_2 on the initial PSC lifetime, shelf life experiments were carried out on unsealed devices. Three set of devices were selected for testing the shelf life stability (drying with UV/O_3 , one and ten pulses of IPL curing) and stored in the dark in N_2 atmosphere between each measurement. The presence of nitrate for all the three cases seemed to have no effect on the device stability, because even after 1300 hours the average PCE and PCE_{MPPT} remained close to their initial values (see **Fig. A.9/ A and B**). The shelf life experiments were followed by light soaking experiments, wherein the three best devices from each set were exposed to 6 hours irradiation (light soaking) using halogen light bulbs (simulating AM 1.5 G spectrum) in N_2 atmosphere. However, after exposing these devices to 6 hours of light soaking, the stabilized efficiency (PCE_{MPPT}) dropped significantly (see **Fig. A.10/ A**). This drop could not be linked only to the degradation of the spiro-OMeTAD layer because the device temperature did not exceed 45°C (see **Fig. A.10/ B**). Similarly to the observations of Nie et. al [48], the device performance (PCE_{MPPT}) recovered after overnight storage in the dark. Moreover, the stabilized efficiency of the devices containing moderate and high nitrate ion content (drying with UV/O_3 and one pulse of IPL sintering) did not recover completely as the ones with low nitrate content, showing better durability for the IPL cured PSCs.

Finally, to test that IPL sintering is compatible with future R2R processing, the same device architecture was fabricated on ITO/PEN substrates as utilized on ITO/glass substrates. For the treatment of the mesoporous TiO_2 the previously used drying with UV/O_3 treatment was applied as the reference treatment and compared to a reduced energy IPL sintering. As a comparison to ITO/glass, one pulse (2 ms) with a radiant energy of 12.3 J/cm^2 was also tested on a PEN substrate which resulted in the black discoloration of its surface. This colour change was presumably due to the degradation of PEN which might exceeded its degradation temperature. The high absorption of the ITO/PEN substrate compared to ITO/glass was linked to the higher absorption of plastic substrate (see **Fig. A.11**). Hence, the radiant energy for one pulse was reduced to 2.35 J/cm^2 by keeping the pulse length at 2 milliseconds. Moreover, by reducing the energy for one pulse, the time between two pulses can also be reduced which resulted in a total processing time of 3.1 seconds after ten pulses.

The J-V curves and the stabilized efficiencies (PCE_{MPPT}) of the best perovskite solar cells on glass and PEN substrates are compared in **Fig. 5**. Additionally, the average photovoltaic characteristics of these devices are summarized in **Table A.3**. In both cases for the ITO/PEN substrates the average J_{sc} and the FF were significantly lower compared to the same stack on glass substrates. A possible explanation for this drop is first of all related to the lower transmittance of the plastic substrates, which could result in lower short-circuit current densities. Moreover, the higher sheet resistance of the ITO bottom electrode ($60\ \Omega/\square$) on PEN substrate can explain the lower fill factors. Thus, the performance of the devices on plastic substrates drops due to obvious reasons. In addition, the IPL curing parameters for ITO/PEN substrates could be further optimized. However, the demonstrated treatment technique could serve as a starting point for future studies for perovskite solar cells utilizing cheap commercial plastic substrates. Further development could benefit from the ad-hoc fabrication of the flexible substrate in two different ways: on one hand a PET substrate will allow using higher pulse energy due to the high UV transmittance; on the other hand, using a metal electrode will enhance the heat generation with low pulse energy.

1.4 Conclusion

In summary, low temperature and rapid annealing techniques were successfully applied for binder-free mesoporous TiO_2 thin films for perovskite solar cells both on ITO/glass and ITO/PEN substrates without any loss in device performance compared to the references devices with high temperature annealed mesoporous TiO_2 . Low temperature curing techniques evaluated in this study were UV/ O_3 treatment, O_2 plasma treatment and IPL sintering.

The application of the combination of pre-drying (at 140 °C) and UV/ O_3 treatment for commercial binder-containing TiO_2 paste could replace high temperature treatments (at 500 °C) with a minimum treatment time of 20 minutes. Similarly to UV/ O_3 treatment, 15 minutes O_2 plasma treatment was as effective in removing the binder as high temperature annealing. However, both low temperature treatments are only efficient with long processing time, which is hardly compatible with future R2R production. Adaptation of IPL sintering for binder-containing TiO_2 paste was not efficient.

In contrast, a commercial binder-free TiO_2 dispersion was proven to be more promising for post-treatments with IPL curing. For this mesoporous TiO_2 film, high temperature sintering (300 °C) are still beneficial due to the presence of surface nitrate ions. According to the experiments, a high amount of nitrate in the mesoporous TiO_2 layer could negatively affect the device performance causing low FFs, increased J-V hysteresis and faster decline in the device performance under prolonged light soaking. Initially, similarly to binder-containing paste, the high temperature sintering (with PCE up to 15.5%) of binder-free mesoporous TiO_2 films was successfully replaced by a low temperature treatment combining 140 °C drying and 20 minutes UV/ O_3 without loss in the PSC performance (PCEs up to 16.4 %).

Then, in order to develop a fast R2R compatible process for the treatment of TiO_2 , IPL sintering (without any additional pre-treatment) was exploited for a binder-free mesoporous TiO_2 films. This post-treatment method has delivered an average stabilized efficiency of 16.7 % for the PSC devices fabricated on ITO/glass and stabilized efficiency of 12.3 % for the devices fabricated on ITO/PEN substrates. The achieved results are remarkable in terms of processing time, because IPL curing allowed the reduction of processing times from two to six orders of magnitude (see **Fig. 6**) enabling fast processing within seconds on ITO/glass and ITO/PEN substrates.

1.5 Acknowledgement

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1.6 References

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Tables

Table 1 Photovoltaic characteristics of the perovskite solar cells fabricated using binder-containing TiO₂ paste. The average results were obtained from 8 samples and the best cells of each substrates were selected for the maximum power point tracking (PCE_{MPPT}). The highest PCE values are shown in brackets.

Treatment of the meso. layer	PCE _{average} (%)	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	PCE _{MPPT} (%)
30 min 500 °C	12.8 ± 0.4 (13.2)	1010.2 ± 5.7	19.7 ± 0.6	67.3 ± 0.3	13.2
1 hour UV/O ₃	12.5 ± 0.4 (12.9)	1024.6 ± 9.3	19.8 ± 0.6	63.4 ± 2.5	13.7

Figures

Fig. 1 Study of different post-treatments of a binder containing mesoporous TiO₂ paste **A)** UV-vis transmittance of ITO/glass coated mesoporous TiO₂ samples. **B)** Raman spectroscopic measurements.

Fig. 2 **A)** Raman spectroscopic measurement of the dried binder-free TiO₂ paste. **B)** For TGA measurement the samples were heated from room temperature to 700 °C with a 1 °C/minute ramping. The annealing temperatures for the device fabrications are presented with triangles (labeled red: 140 °C, blue: 187 °C, brown: 300 °C). **C)** The intensity decrease of the peak of nitrate ion (at 1048 cm⁻¹). **D)** The average PCE for 8 cells for the 5 different set of devices. The maximum power point tracking efficiency (PCE_{MPPT}) is denoted by stars for each cases for the best devices.

Fig. 3 A) The simulated temperatures during the IPL curing process of the mesoporous TiO₂ layer (labeled meso-TiO₂) and the bottom of the glass substrate. **B)** Raman intensity of the stretching vibration of nitrate ion after one, five, and ten consecutive pulses (labeled IPL (1x), (3x), (5x) and (10x)) compared to no treatment. The Raman spectrum in this case was baseline corrected using cubic spline correction. **C)** Average PCEs and maximum power point tracking performances for three IPL cured devices (labeled IPL (1x), (5x) and (10x)) compared to no treatment and 140 °C drying with 20 minutes UV/O₃ treatment (labeled 140 °C + UV/O₃).

Fig. 4 The cross sectional SEM images of the mesoporous (labeled meso) TiO_2 /e-beam TiO_2 /ITO/glass: **A)** before treatment. **B)** after ten pulses of 12.3 J/cm^2 pulse energy (2 ms) pulses with a fire rate of 0.5 Hz.

Fig. 5 Photovoltaic J-V curves for our best devices on ITO/glass and ITO/PEN substrates employing binder-free mesoporous TiO_2 . The mesoporous TiO_2 scaffold was treated with 140°C drying and 20 min UV/O_3 (labeled UV/O3) or with ten pulses of IPL curing (labeled IPL) with a pulse length of 2 ms (radiant energy of 12.3 J/cm^2 for glass and 2.35 J/cm^2 for PEN).

Fig. 6 Summary of the average PCEs for the processing time reduction for all the devices with different treatment procedures: 10 min thermal annealing (labeled with the curing temperatures), 10 min drying at 140 °C with 20 minutes UV-Ozone (labeled UV/O₃) and Intense pulse light (labeled IPL) curing for different number of pulses (pulse length: 2 ms, radiant energy: 12.3 J/cm²). For ITO/PEN substrates the radiant energy was reduced to 2.35 J/cm².