Mesoporous SnO2 electron selective contact enables UV-stable perovskite solar cells

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ABSTRACT
Perovskite solar cells are a promising new technology for large scale energy applications. The current major challenge for commercialization is increasing the device lifetime under real working conditions. State-of-the-art perovskite solar cells are prepared using TiO2 as electron selective contact. In sealed devices, however, a reversible UV light activated performance degradation mechanism was observed. In this study, it is demonstrated that replacing TiO2 with a SnO2 electron selective contact enables stable perovskite solar cells working under UV light in an inert atmosphere. Contrary to previous reports on SnO2 based perovskite solar cells, it is shown that a mesoporous electron selective contact is required to achieve UV stable perovskite solar cells.

1. Introduction
The power conversion efficiency (PCE) of perovskite solar cells (PSCs) has in recent years rapidly increased from 3.8% [1-3] to more than 22%, now rivaling the efficiency of market reference silicon solar cells [4]. Having passed this first hurdle, it is now becoming more important to increase the stability of PSCs to pass the industry standards, i.e. a PCE loss of less than 0.5% per year over a life span of 25 years [5]. More robust perovskites [6], metal contacts [7] and hole transporting materials [8] have been demonstrated to be quite effective to enhance the lifetime of PSCs, even though device stability is still far from industrial standards [8]. A major loss in PCE was found to be caused by a rapid degradation in the performance of TiO2-based devices caused by the exposure to UV light [9], which is the most common device configuration in state-of-the-art PSCs. This performance degradation arises from the desorption of O2− that passivates deep electronic traps caused by oxygen vacancies in the TiO2 lattice [8]. Although this effect can be significantly reduced by doping [10,11], attempts have been made to replace TiO2 altogether [12,13]. One promising alternative inorganic material for electron selective layers (ESL) is SnO2. Due to the wider bandgap, SnO2 absorbs less UV light and is thus more robust than TiO2 under sunlight [14]. In addition, the bulk electron mobility in SnO2 is two orders of magnitude higher than that of TiO2 [15], and electron injection from perovskite into SnO2 has been shown to be more efficient than into TiO2 [16]. SnO2 has been successfully implemented on lab scale as ESL in low-temperature processed planar PCSs, yielding a stabilized PCE of more than 19.5% [16-19]. However, the rapid and poorly controlled perovskite crystallization makes it difficult to scale up planar PSCs for industrial application. A porous ESL can overcome this problem by changing the surface wettability [20] to achieve uniform perovskite coverage over large areas [21,22]. A porous ESL has also been shown to be beneficial for electron extraction [20]. It is thus of interest to develop a mesoporous SnO2 (m-SnO2) ESL for the industrial production of stable and efficient PSCs. So far, the highest reported PCE for solution processed, high temperature sintered m-SnO2 based PSCs has only been 6.5% (not-stabilized) [23]. PSCs employing low temperature m-SnO2 deposition, however, have reached a PCE of 12% (not-stabilized) [22]. The deposition of a thin conformal coating of TiO2 onto high temperature sintered m-SnO2 has been reported to increase the PCE to 11.9% (not-stabilized) [24]. The addition of TiO2, however, defeats the purpose of using SnO2 as a potentially more stable alternative.

In this study we show that m-SnO2 PSCs are more stable than planar SnO2 and m-TiO2 PSCs during maximum power point tracking under continuous full sunlight illumination (no UV filtering) in an inert atmosphere. A significant hurdle, however, is the low open circuit
voltage ($V_{oc}$) and fill factor (FF) of m-SnO$_2$ compared to planar SnO$_2$ and m-TiO$_2$ PSCs. We show that the origin of this behavior is the poor electron selectivity of m-SnO$_2$ as processed at high temperature atop of fluorine doped tin oxide (FTO) as transparent conductive oxide (TCO) electrode. We have investigated two possible causes; cracking of the ESL upon heating, or fluorine migration [25]. Our data suggests that, at high temperature, fluorine migrates from FTO into SnO$_2$, doped the ESL to an extent where charge selectivity is compromised and recombination is increased. To circumvent this problem we prepared m-SnO$_2$ PSCs using aluminum doped zinc oxide (AZO) as TCO. Moreover, AZO has good conductivity (sheet resistance $< 10/\Omega$) and is low-cost, composed of abundant materials, easy to etch and has a high transmittance in the near-IR region [26]. Using this alternative TCO, a strong increase in PCE and a remarkable stability of m-SnO$_2$ based PSCs were achieved.

2. Experimental

2.1. Material characterization

Scanning electron microscopy was carried out on a Tescan MIRA 3 LMH with a field emission source operated at an acceleration voltage of 10 kV. Pore size was calculated using ImageJ. X-ray diffraction was measured using a Rigaku Ultima IV with a Cu Kα source.

2.2. Cyclic voltammetry

Electrochemical experiments were carried out using a Metrohm PGSTAT302N Autolab. A Ag/AgCl reference electrode was used in an aqueous electrolyte solution containing 0.5 M KCl (0.5 M), K$_2$Fe(CN)$_6$ (0.5 mM) and K$_3$Fe(CN)$_6$ (0.5 mM) [24]. Cyclic voltammograms were collected at a scan rate of 50 mV/s.

2.3. Solar cell preparation

Fluorine doped tin oxide coated glass slides (Sigma-Aldrich, ~7/3) and aluminum doped zinc oxide coated glass slides (Zhuhai Kaivo Optoelectronic Technology Co., < 10/3) were cleaned by sonication in 2% Hellmanex soap solution for 15 min. After rinsing with deionized water and ethanol the substrates were again sonicated with isopropanol and rinsed with acetone. The substrates were treated with UV-ozone for 5 min and a 30 nm thick SnO$_2$ ESL was deposited by spray pyrolysis at 450 °C from a precursor solution of butyltin trichloride (250 mM) in anhydrous ethanol [14]. Mesoporous SnO$_2$ electrodes were synthesized using a structure directing block-copolymer [27]. A tin oxide precursor sol was prepared by dissolving poly(1,4-isoprene-ethylene) (25 mg, Polymer Source, Mn: PIp(50000)-PEO(12000), Mw/Mn: 3.7) in tetrahydrofuran (1 ml), after which tin(IV) chloride pentahydrate was added (80 mg) and stirred for 30 min. The resulting solution was spin-coated (4000 rpm, 10 s) onto the substrate. The films were annealed on a programmable hotplate (2000 W, Harry Gestigkeit GmbH) using a 45 min ramp to 450 °C followed by a dwell time of 30 min to remove the block-copolymer template and crystallize SnO$_2$. Perovskite and HTM were deposited according to the literature [28,29]. Perovskite films were deposited from a precursor solution containing FAI (1 M), PbI$_2$ (1.1 M), MABr (0.2 M), PbBr$_2$ (0.2 M) and CsI (0.075 M) in anhydrous DMF:DMSO 4:1 (v:v). The perovskite solution was spin-coated in a two-step program at 1000 and 5000 rpm for 10 and 20 s respectively. During the second step, 100 µL of chlorobenzene was poured onto the spinning substrate 5 s prior the end of the program. The substrates were then annealed at 100 °C for 1 h in a nitrogen glove box. Subsequently, the substrates were cooled down for a few minutes and a spiroOMeTAD (Luminescence Technology) solution (70 mM in chlorobenzene) doped with bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI, Aldrich), tris(2-(1H- pyrazol-1-yl)-4-tert-butylyridine)-cobalt(III)tris(bis(tri- uoromethylsulfonyl)imide) (FK209, Dynemo) and 4-tert-butylpyridine (TBp, Aldrich) was spun at 4000 rpm for 20 s. The molar ratios of additives for spiroOMeTAD were: 0.5, 0.03 and 3.3 for Li-TFSI, FK209 and TBp, respectively. Finally, 60 nm of gold was thermally evaporated under high vacuum on top of the device. Dye sensitized solar cells were fabricated by employing Z907-dye as light absorber instead of perovskite [14].

2.4. Optoelectronic measurements

For photovoltaic measurements, a solar simulator from ABET Technologies (Model 11016 Sun 2000) with a xenon arc lamp was used and the solar cell response was recorded using a Metrohm PGSTAT302N Autolab. The intensity of the solar simulator was calibrated to 100 mW/cm$^2$ using a silicon reference cell from ReRa Solutions (K55 filtered). J-V-curves were measured in reverse bias (from high to low voltages), at a scan rate of 10 mV/s. For dark currents a scan rate of 25 mV/s was used. The active area of the cells was 0.148 cm$^2$ and cells measured two days after their preparation. Maximum power point tracking was used to perform stability experiments in a nitrogen filled glovebox. The measurements were done on devices stored in dry ambient air for 1 month and were brought into the nitrogen atmosphere just before the start of the measurements. Intensity modulated photovoltage spectroscopy (IMVS) was performed according to the procedure described in literature, using a white light LED driver at different light intensities and a Metrohm PGSTAT302N Autolab [30].

3. Results and discussion

3.1. Characterization of compact SnO$_2$

3.1.1. Scanning electron microscopy

AZO (Fig. 1a) and FTO (Fig. 1b) electrodes were coated with a thin compact ESL of SnO$_2$ by spray pyrolysis at 450 °C. On AZO, the ESL, consisting of densely packed particles, is clearly visible and therefore it is likely that this layer grows heteroepitaxially (Fig. 1c). In contrast, the ESL appears to have grown epitaxially on FTO and no distinct layer can be distinguished (Fig. 1d).

3.1.2. Cyclic voltammetry

To test the surface coverage and rectifying behavior of the SnO$_2$ ESL, cyclic voltammetry was performed in an aqueous solution of Fe(CN)$_6^{3−/4−}$ for both FTO (Fig. 2a) and AZO (Fig. 2b) substrates, onto which a SnO$_2$ ESL was deposited by spray pyrolysis at 450 °C. SnO$_2$ behaves like an electrochemically silent dielectric material against the Fe(CN)$_6^{3−/4−}$ redox couple [31]. The charge-transfer reaction is therefore assumed to occur exclusively at the bare TCO surface. The effective TCO surface area in contact with the electrolyte can be determined by dividing the peak current of the ESL covered substrate by the peak current of the bare TCO substrate [31], yielding an effective uncovered FTO area of 60%. In contrast, the ESL covered AZO substrate exhibited an effective uncovered AZO area of < 1%.

The poor apparent effective coverage of the SnO$_2$ ESL on FTO may have two causes; (i) thermal stresses could cause cracks/pores upon cooling and/or heating, (ii) fluorine migration from FTO to the SnO$_2$ ESL, making the two layers electronically equivalent. The first option is highly unlikely since the FTO and SnO$_2$ lattice constants match, while the wurzite/cassiterite interface of the AZO/SnO$_2$ junction has a much higher lattice mismatch, which should cause a much larger strain [32]. This implies that SnO$_2$ on AZO should be more prone to cracking than SnO$_2$ on FTO, in contrast to our observation. Indeed, SEM micrographs show a conformal SnO$_2$ ESL on FTO and no evidence of (Fig. 1). Fluorine migration in SnO$_2$ has however been previously shown, at annealing temperatures similar to this study [25,33] and would explain the observed effects, since fluorine migration renders SnO$_2$ electronically equivalent to FTO and thereby results in a loss in electron
Fig. 1. SEM micrographs of (a) AZO, (b) FTO, (c) SnO$_2$ ESL on AZO and (d) SnO$_2$ ESL on FTO.

Fig. 2. Cyclic voltammograms of (a) a bare FTO electrode and FTO covered by a spray coated SnO$_2$ ESL, (b) a bare AZO electrode and AZO covered by a spray coated SnO$_2$ ESL. The scan rate was 50 mV/s and the electrolyte solution consisted of 0.5 mM K$_4$Fe(CN)$_6$ +0.5 mM K$_3$Fe(CN)$_6$ in 0.5 M aqueous KCl. (c) The minimal and maximal dark current of one batch (8 devices) of FTO and AZO based PSCs. (d) Electron lifetimes of DSSCs employing FTO and AZO as TCO as determined by IMVS.
selectivity.

3.1.3. Dark current-voltage scan

The poor electron selectivity of SnO$_2$ on FTO also becomes clear from the current-voltage scan under dark conditions of a complete PSC. The presence of a large dark current is an indication that the ESL is not effectively preventing the TCO from contacting the photoactive or hole transporting layers. Fig. 2c shows the minimal and maximal dark currents for a single batch of PSCs (8 devices). AZO based PSCs show a narrow dark-current distribution and overall low dark currents. On the other hand, FTO based PSCs exhibit a large variation in the dark current, with high overall values.

3.1.4. Intensity modulated photovoltage spectroscopy

The effect of the electron selectivity of SnO$_2$ coated TCO can be investigated by IMVS (Fig. 2d). Because of the overlap of the perovskite and metal oxide signals [11], dye sensitized solar cells (DSSCs) were used instead. From this measurement it becomes apparent that electron lifetimes are 2–3 times longer for DSSCs employing AZO as TCO, compared to DSSCs employing FTO as TCO, showing that recombination can be reduced by using AZO instead of FTO.

3.2. Characterization of m-SnO$_2$

m-SnO$_2$ electrodes were synthesized via block-copolymer assisted self-assembly [27]. The resulting films show a homogeneous coverage of the mesoporous material with a pore size of approximately 60 nm (Fig. 3a). X-ray diffraction (XRD) showed the formation of rutile SnO$_2$ (Fig. 3b). The average particle size was 10.9 ± 1.0 nm, calculated using the Scherrer equation [34].

3.3. Photovoltaic performance

The SEM micrograph in Fig. 4a shows the cross section of a photovoltaic device employing a ~100 nm thick layer of mesoporous SnO$_2$. A top-view SEM micrograph of the perovskite film is shown in S1. The photocurrent-voltage ($J$-$V$) curves of the PSCs measured under AM1.5 simulated solar light (100 mW/cm$^2$) illumination are shown in Fig. 4b. The photovoltaic parameters extracted from the $J$-$V$ curves; the open-circuit potential ($V_{oc}$), short-circuit current ($J_{sc}$), fill factor (FF), power conversion efficiency of the backward scan (PCE BW), power conversion of the forward scan (PCE FW) and the stabilized power output efficiency after 300 s are shown in Table 1. Incident photon conversion efficiency (IPCE) spectra are shown in S2. $J_{sc}$ values are in agreement with those extracted from $J$-$V$ curves. Since the PCE of PSCs is dependent on the way the device is measured (light and bias preconditioning, voltage scan speed and direction), additional measurements are required to verify the obtained PCE for device operation under realistic conditions [35]. By performing maximum power point tracking, a PCE value can be determined that accurately represents the efficiency of a device under real-world conditions. Device parameters clearly show a superior performance for AZO based devices owing to higher $V_{oc}$ and FF, resulting in an increase in stabilized PCE from 8.7% for FTO to 11.6% for AZO based PSCs (averages of 8 devices). An increase in $V_{oc}$ and FF is indicative of improved electron selectivity and reduced recombination at the ESL/perovskite interface, as was shown by IMVS measurements. Therefore, by replacing FTO with AZO it is possible to achieve an effective m-SnO$_2$ ESL.

3.4. Stability of PSCs

Planar SnO$_2$ and m-TiO$_2$ electrodes were prepared as previously reported [16], m-SnO$_2$ electrodes were prepared as described above. PSCs prepared with these electrodes were exposed to AM1.5 simulated solar light (100 mW/cm$^2$) illumination while tracking the maximum power point for 10 h in a nitrogen atmosphere. UV-induced degradation is a rapid degradation process, manifesting itself in the first 1–2 h of operation [9–11], so any UV-induced degradation should be evident in the 10 h testing period. To exclude an effect from the TCO, all device configurations were fabricated using FTO. The result of this maximum power point tracking is shown in Fig. 5. Initial power output ($t=0$), maximum power output (max) and final power output ($t=10$ h) are shown in Table 2, as well as the final power output divided by the maximum power output. The SnO$_2$-based devices show a remarkable increase over the first 1–2 h. Previous work has shown that this can be attributed to improved electron injection from the absorber into SnO$_2$, by an increase in the relative density of acceptor states as a result of a conduction band shift, induced by charging of the SnO$_2$ and a rearrangement of charge species at the absorber-SnO$_2$ interface [25,36]. On the other hand, m-TiO$_2$ shows a rapid decay during the first hour. It is known that defects in TiO$_2$ can be passivated by the adsorption of atmospheric oxygen. Under the influence of UV-light oxygen desorbs, leading to a rapid decrease in performance in oxygen free conditions [11], as is observed here. Fig. 5 shows that this is not the case for SnO$_2$-based PSCs, presumably because of the wider bandgap of SnO$_2$ compared to TiO$_2$. Another observation is that the mesoporous device power output reaches a plateau after these initial rapid changes, whereas the planar SnO$_2$ keeps steadily decreasing. The mesoporous network has been reported to inhibit the degradation or phase segregation of the perovskite by providing mechanical and chemical stability, inhibiting the penetration of harmful substances such as moisture, oxygen [22], or gold [7] into the perovskite layer. To rule out the possibility of a bad electron selective contact causing the decrease in performance of the planar SnO$_2$ PSCs it was verified that $J$-
curves collected in the dark before and after the stability test were unchanged (S3). Overall, Fig. 5 shows superior stability for m-SnO2 under these conditions, combining the UV-stability of SnO2 with the mechanical and chemical stability of a mesoporous scaffold. This proves the importance of developing efficient m-SnO2 based PSCs.

### 4. Conclusion

Highly efficient m-SnO2-based PSCs are important because of their increased stability compared to m-TiO2 and planar SnO2 PSCs. Using FTO covered by SnO2 is however problematic because of the migration of fluorine into the SnO2, severely decreasing the electron selectivity of the ESL, as evidenced by cyclic voltammetry and dark current leakage. AZO is a viable alternative. Reduced recombination resulted in higher $V_{oc}$ and FF values, leading to an increase in stabilized PCE from 8.7% to 11.6% (champion 13.1%), an increase of ~25%. This is an important step towards UV-stable PSCs.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2016.10.055.

### References
