A Stable Aqueous SnO$_2$ Nanoparticle Dispersion for Roll-to-Roll Fabrication of Flexible Perovskite Solar Cells

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Abstract: Perovskite solar cells (PSCs) are attracting increasing commercial interest due to their potential as cost-effective, lightweight sources of solar energy. Low-cost, large-scale printing and coating processes can accelerate the development of PSCs from the laboratory to the industry. The present work demonstrates the use of microwave-assisted solvothermal processing as a new and efficient route for synthesizing crystalline SnO$_2$ nanoparticle-based aqueous dispersions having a narrow particle size distribution. The SnO$_2$ nanoparticles are analyzed in terms of their optical, structural, size, phase, and chemical properties. To validate the suitability of these dispersions for use in roll-to-roll (R2R) coating, they were applied as the electron-transport layer in PSCs, and their performance was compared with equivalent devices using a commercially available aqueous SnO$_2$ colloidal ink. The devices were fabricated under ambient laboratory conditions, and all layers were deposited at less than 150 $^\circ$C. The power conversion efficiency (PCE) of glass-based PSCs comprising a synthesized SnO$_2$ nanoparticle dispersion displayed champion levels of 20.2% compared with 18.5% for the devices using commercial SnO$_2$ inks. Flexible PSCs comprising an R2R-coated layer of synthesized SnO$_2$ nanoparticle dispersion displayed a champion PCE of 17.0%.

Keywords: perovskite solar cells; tin oxide; electron transport materials; encapsulation; stability; lifetime; and efficiency

1. Introduction

Solar cells incorporating organic-inorganic lead-halide perovskites as the light-harvesting layer have the potential to be lighter, more efficient, and cheaper than conventional silicon solar cells. This is in part due to the possibility of large-scale fabrication on flexible substrates via roll-to-roll (R2R) processes [1]. Furthermore, flexible perovskite solar cells (PSCs) are attracting strong interest for commercialization in applications other than conventional grid-scale photovoltaic (PV) power generation, such as portable electric chargers, electronic textiles, PV-integrated roofing and other building products, and auxiliary power sources for electric vehicles [2]. Continuing technical advances have led to significant improvements in the power conversion efficiency (PCE) and stability (lifetime) of PSCs, as well as a reduction in their production costs [3–5]. Further developments are multi-faceted, involving modified formulations for the perovskite light-absorbing layer, suitable surface and grain-boundary passivation layers, higher stability, and lower cost charge transport layers and electrodes [6,7]. Underlying this is a need that all advances need to be achieved using scalable deposition approaches to avoid the “spin-coating hurdle” induced by the difficulty to translate between small, spin-coated devices and those fabricated using more commercially-ready approaches. Here, we address the key challenge of developing cheap, stable, and scalable nanomaterials that can be applied using industrially-relevant coating
or printing methods to achieve electron transporting layers (ETL) suitable for efficient PSCs [7,8].

In general, nanoparticles in a colloidal system tend to reach their lowest thermodynamic energy state through particle aggregation, which can compromise the desired properties of the nanomaterials [9]. In solar applications, it is imperative to control the nanoparticle size to achieve the desired optical properties and hence increase device performance. Metal nanoparticles could offer the prospect of increasing device efficiency by reducing surface reflectance and/or increasing light-trapping, whereas it can also decrease the efficiency of solar cells due to absorption of light within the nanoparticles or by increasing reflectance of the front surface due to back-scattering. Therefore, metal nanoparticles must be suitably designed to provide the correct optical properties for a given application [10]. Organic stabilizers (usually polymers or surfactants) are often included in the reaction mixture to control the particle size distribution and enable dispersion [11]. However, the presence of these stabilizers on the surface of semiconductor nanoparticles designed for use as charge-transporting layers in electronics applications can result in electrically resistive properties of such layers [12]. To overcome this, the nanoparticles can be post-processed at elevated temperatures to remove residual organic-based stabilizers [13]. However, the temperature range available for post-processing nanomaterials is limited when coated onto a heat-sensitive polymeric substrate such as polyethylene terephthalate (PET), which is commonly used for flexible electronics and can only withstand temperatures of up to 140 °C. Furthermore, the upper-temperature limit for such polymer film substrates also precludes the use of certain semiconducting nanomaterials for the charge-transport layer. For example, titanium dioxide (TiO$_2$) nanoparticle formulations are widely used to form the ETL in laboratory-scale PSCs fabricated using glass substrates. However, the temperature required to anneal the coated TiO$_2$ nanoparticles is incompatible with processing on flexible polymeric substrates like PET [14]. Therefore, the development of stable semiconducting nanoparticle formulations that can be processed at suitably low temperatures is vital for realizing the potential commercial opportunities for PSCs using flexible polymeric substrates.

The high electron mobility, suitable energy levels, and relatively low processing temperature of tin oxide (SnO$_2$) make it an excellent candidate for the ETL material in PSCs fabricated on polymeric substrates [15]. Various methods for the synthesis of SnO$_2$ nanoparticles have been reported, including precipitation [16], sol-gel [17], hydrothermal [18], and solvothermal [19] approaches. Of these, the hydrothermal and solvothermal routes are the most widely used and are normally performed in a sealed vessel under a controlled temperature and pressure. The reaction conditions determine the morphology, particle size distribution, and crystallinity of the synthesized SnO$_2$ nanoparticles, where the properties are all highly influential on the electron-transporting properties of the coated SnO$_2$ layer in a PSC device. Controlling SnO$_2$ nanoparticle size and distribution is particularly important for achieving smooth SnO$_2$ ETLs, which is beneficial for perovskite film growth and interfacial contact between the SnO$_2$ and perovskite layers [20–22]. As a result, the trap densities at this interface and within the perovskite absorber layer are greatly reduced, leading to largely suppressed carrier recombination and improved solar cell performance [23].

Simultaneous control over average particle size, particle size distribution, shape, and phase purity is technically challenging, as these properties are highly dependent on the preparation methods and conditions adopted [24]. Recently, microwave-assisted methods have been used to enhance the reaction kinetics of hydrothermal methods, enabling more homogeneous and rapid heating, which results in a shorter synthesis time and nanoparticles having uniquely high purity, narrow distribution, and uniform morphology [25–27]. The emerging technique of microwave-assisted heating is an in situ mode of energy conversion that is fundamentally different from the heat transfer that occurs in a conventional heating process. Wang et al. synthesized flower-like SnO$_2$ nanostructures having improved electrochemical properties by controlling the synthetic conditions of the microwave-assisted solvothermal approach [28]. Komarneni’s group fabricated SnO$_2$ nanoparticles having an
average size of 5 nm and demonstrated the benefits of using microwave-assisted heating over conventional heating for the hydrothermal synthesis method [29]. Shi and Hwang discussed the significance of using microwave heating technology for the industrial-scale fabrication of nanomaterials having a narrow particle size distribution using wet-chemistry synthesis routes [30]. Our group has recently demonstrated a facile one-pot microwave-assisted “benzyl alcohol” based synthetic approach for non-aqueous SnO₂ dispersions that can routinely be applied to PSCs [31]. The synthesis method enables crystalline SnO₂ nanoparticles to be synthesized with a controlled average particle size (~6.5 nm) and can be used directly as an ink without any post-synthesis purification (i.e., one-pot synthesis). This was the first attempt at developing R2R processable non-aqueous SnO₂ ink using the microwave-assisted method.

Here we introduce a simple microwave-assisted solvothermal synthetic approach to produce a stable aqueous SnO₂ nanoparticle dispersion suitable for coating on polymeric substrates to produce flexible PSCs. In this approach, SnO₂ nanoparticles were made through a gradual dissociation of Sn₄(EDA)₄⁺ complexes under alkaline media. The ethylene diamine (EDA) present in the reaction media assists in the stabilization of smaller nanoparticles by attaching to the surface through hydrogen bonding which demonstrates excellent stability over several months’ storage at room temperature without the presence of any additional organic stabilizers. Controlling the EDA amount in the reaction mixture results in a dramatic narrowing in the particle size distribution and a concomitant reduction in average particle size to ~2 ± 1 nm. The favorable charge-transport properties of the ETL produced using the synthesized SnO₂ aqueous formulation are reflected in the superior PV performance of PSCs relative to those comprising an ETL using a commercially available aqueous SnO₂ ink. On the other hand, all the functional layers of the PSC devices fabricated in this work, except the evaporated metal electrode, were deposited under ambient laboratory conditions. Furthermore, the aqueous SnO₂ nanoparticle dispersion developed in the present work was successfully coated onto the polymeric substrate that meets the criteria for practical pilot-scale R2R production. In our previous work, we achieved a record device efficiency of 17.4 % for flexible PSCs [32]. Therefore, the results presented here show a PCE closer to the best-reported efficiency so far for flexible PSCs with an R2R-processed ETL layer (17%), further highlighting the viability of our synthesized SnO₂ ink for achieving high-efficiency printed PSCs.

2. Experimental

2.1. SnO₂ Nanoparticle Dispersion

An aqueous solution of SnCl₄ was prepared by dissolving 0.68 g of tin (IV) chloride pentahydrate (SnCl₄·5H₂O, 98%, Alfa Aesar Co., Lancashire, UK) in 20 mL of an EtOH/H₂O mixture (50% v/v). Ethylenediamine (EDA, H₂NCH₂CH₂NH₂, 99% Aldrich Co., Lancashire, UK) was added dropwise (0.1 mL) into the solution at room temperature under stirring, after which stirring was continued for 2 h. This “precursor solution” was then filtered (Minisart filter, pore size 0.45 μm) before transfer into the microwave reaction vial, which was then sealed using a headspace cap soon after purging with N₂ for 2 min. The sealed vial was transferred to a microwave reactor cavity (Biotage® Initiator Classic, 400 W, Uppsala, Sweden), and the reaction was carried out at 100 °C for 30 min. After the reaction was completed, the milky suspension was centrifuged at 7000 rotations per minute (rpm) for 5 min, and removed the supernatant. The resulting precipitate was washed first with de-ionized water and then with ethanol. In each wash cycle, the wet paste was separated by centrifuging at 7000 rpm for 5 min. The SnO₂ colloidal dispersion used for spin-coating or slot-die coating was prepared by re-dispersing 2.2 g of the wet precipitate (solid loading ~4 w/w%) in 10 mL of an aqueous solution of 0.12 M KOH.
2.2. Perovskite Solar Cell Fabrication

2.2.1. Glass Device Fabrication

The PSCs were constructed by coating the ETL onto ITO-coated glass (ITO-glass) substrates using synthesized or commercial SnO\(_2\) inks. A suspension of commercial SnO\(_2\) ink (15 w/w\% SnO\(_2\) colloidal dispersion in H\(_2\)O, Alfa Aesar Co.) was prepared by dilution with water (1:6.2 v/v). The SnO\(_2\) weight percentages of synthesized and commercial dispersions were ca. 3.5% and 2.1%, respectively.

The SnO\(_2\) layer was fabricated on an ITO-glass substrate by spin-coating at a speed of 4000 rpm for 30 s (70 µL) and then annealed at 150 °C for 15 min. Prior to the perovskite coating, the SnO\(_2\) layer was treated with UV for 10 min. 1.25 M perovskite (FA\(_{0.91}\)Cs\(_{0.09}\)PbI\(_3\)) ink was made by dissolving PbI\(_2\) (1.25 M), FAI (1.13 M), and CsI (0.11 M) in 1 mL of DMF:DMSO (9:1 v/v%). MACl (23 mol% with respect to the PbI\(_2\)) was added to the above ink; then, the solution was stirred at 65 °C for 2 h in a nitrogen-filled glovebox. The perovskite layer on the SnO\(_2\) layer was fabricated using the ink (80 µL) by spin-coating at two steps (1000 rpm for 10 s and then at 3000 rpm for 5 s) followed by nitrogen blowing for 10 s (100 L min\(^{-1}\)). Then the film was immediately annealed at 160 °C for 10 min. The hole transporting Spiro-OMeTAD layer was prepared by using ink made by dissolving 72.66 mg of Spiro-OMeTAD in 1 mL of CB with the addition of 18 µL from the LiTFSI stock solution (520 mg LiTFSI in 1 mL acetonitrile), 30 µL 4-tertbutylpyridine, and 29 µL from the FK209 stock solution (300 mg FK209 in 1 mL acetonitrile). Using the ink (70 µL), the Spiro-OMeTAD layer was coated on the perovskite layer by spin-coating at 2000 rpm for 30 s. All the layers were coated under ambient conditions. Finally, a gold top-electrode (80 nm) was thermally evaporated under a high vacuum to fabricate the working PSC with an active area of 0.2 cm\(^2\).

Encapsulated ITO-glass based PSC devices consisted of a cover glass (HanaAMT) with a recess in the middle to accommodate a 10 mm × 15 mm piece of desiccant from Dynic (HG sheet of 180 µm thickness) to adsorb any moisture permeating through the edge-sealing (Lens Bond UV epoxy) during long-term operation under elevated temperature conditions. The encapsulation of the devices was performed in a nitrogen-filled glove box (<1 ppm oxygen and moisture).

2.2.2. Flexible Device Fabrication

A roll of 25 mm wide PET film coated with a transparent conductive electrode (ITO-PET) (OC50, Solutia; 50 Ω sq\(^{-1}\)) comprising 4 mm wide ITO lines perpendicular to the coating direction was used as received without any further treatment. R2R coating of the synthesized SnO\(_2\) dispersion onto the patterned TCO-PET was carried out using a reverse-gravure (RG) coating method [33] on a Mino-Labo\textsuperscript{TM} coater (MAHY-1310; Yasui Seiki Co. Ltd., Kanagawa, Japan), followed by heating in-line at 135 °C for 10–15 s to remove the solvent. The coating was conducted at a web speed of 25 cm min\(^{-1}\) and reverse-gravure roll speed of 3 rpm to deposit the 13 mm wide continuous SnO\(_2\) layer in the middle of the substrate. Completing the fabrication of flexible PSC devices was carried out by cutting the SnO\(_2\)-coated ITO-PET film into individual pieces (25 mm × 25 mm) and mounting onto a glass carrier substrate using Kapton tape. The perovskite layer and the hole transporting layers (HTLs) were then deposited by spin-coating under ambient laboratory conditions, followed by evaporation of the Au electrode, as described above for the ITO-glass-based PSCs.

3. Characterization

3.1. Physical Characterization

Malvern, Zetasizer Nano-ZS particle size analyzer was used to analyze the particle size distributions of the aqueous SnO\(_2\) dispersions. OCA contact angle system was used to measure the contact angle of the SnO\(_2\) films, and Mettler Toledo TGA2 was used to conduct the thermogravimetric analysis (TGA). Transmission electron microscopic (TEM) images of SnO\(_2\) nanoparticles were measured using an FEI Tecnai G2 T20 TWIN TEM. An FEI
Magellan 400 FEG-SEM scanning electron microscope was used to obtain scanning electron microscopy (SEM) images at a 5 V accelerating voltage with a beam aperture of 30 µm. The structure of the films was investigated by X-ray diffraction (XRD) using a Bruker D8 Discovery x-ray diffractometer with a Cu Ka radiation source (λ = 1.5418 Å). Atomic force microscope (AFM) images of SnO$_2$-coated films on ITO-glass substrates were obtained using Bruker Dimension Icon AFM. The images were taken in PeakForce Tapping mode using TESP-A V2 probes (tip radius of curvature ~7 nm, resonant frequency (f0) = 320 kHz, spring constant (k) = 37 N m$^{-1}$). Carbon tape was used to reduce surface charges during the measurements. The elemental composition of the SnO$_2$ on ITO glass was derived from X-ray photoelectron spectroscopy (XPS, Nexsa, ThermoFisher Scientific) using an Al Ka and He (I) source (21.21 eV) with a pass energy of 200 eV (50 eV for a narrow scan) and 3 eV were used to emitting X-ray and UV photons, respectively. The measurement was conducted with a chamber pressure < 5.0 × 10$^{-8}$ Torr.

3.2. Optical Spectroscopy

Fourier-transform infrared (FTIR) spectra were performed using an FTIR spectrophotometer (Nicolet 6700, Thermo Fisher Scientific, Waltham, MA, USA). UV-Vis-IR absorption measurements were recorded using a Perkin Elmer Lambda 950 spectrometer. UV-Vis absorption spectra of SnO$_2$ thin films on quartz substrates were obtained from transmission and reflection measurements using an integrating sphere.

3.3. Electronic Properties

Photovoltaic performances were studied by obtaining current density-voltage (J-V) plots under inert atmosphere using a Keithley 2400 source meter (under AM 1.5, 100 mW cm$^{-2}$) coupled with an Oriel Sol 3ALSH-7320, class ABA solar simulator equipped with a 1000 W LED lamp. The light intensity was calibrated with the National Renewable Energy Laboratory (NREL)-calibrated Si solar cell and the intensity was adjusted with a Hamamatsu S1133 reference cell with KG5 filter (active area of 2.8 mm × 2.4 mm). The incident photon-to-electron conversion efficiency (IPCE) measurements were obtained in an ambient atmosphere, using an IPCE Measurement System PEC-S20 (Peccel). Photoluminescence (PL) measurements were performed using an Edinburgh Instruments Ltd. luminescence spectrometer (FLSP920). The excitation source was a pulsed diode laser (EPL-475, Edinburgh Instruments Ltd., Livingston, UK) having an output wavelength of 466 nm (100 ps pulse width, repetition rate 500 kHz, peak fluence ca. 0.2 nJ cm$^{-2}$).

4. Results and Discussion

The microwave-assisted solvothermal synthetic steps used here to synthesize SnO$_2$ nanoparticles are shown schematically in Figure 1. The reaction utilizes SnCl$_4$ as the tin precursor with a small amount of EDA. The strong chelating strength of EDA with metal ions leads to the formation of Sn$_n$(EDA)$_m^{4+}$ complexes in the precursor solution (reaction 1) [34]. These tin complexes react with excess OH$^-$ ions during the solvothermal process to form Sn$_n$(EDA)$_{m-x}$(OH)$_x^{(4-x)+}$ intermediates (Reaction 2), which gradually dissociate and condense to form SnO$_2$ nanoparticles (Reaction 3) [35].

\[
nSn^{4+} + mEDA \rightarrow Sn_n(EDA)_m^{4+} \quad (1)
\]

\[
Sn_n(EDA)_m^{4+} + xOH^- \rightarrow Sn_m(EDA)_{m-x}$(OH)$_x^{(4-x)+}$ + xEDA \quad (2)
\]

\[
Sn(OH)_4 \rightarrow SnO_2 + 2H_2O \quad (3)
\]
The concentration of EDA in the reaction medium is found to influence the average size and size distribution of the particles (Figure S1, Supplementary Information). As verified by dynamic light scattering, in the absence of EDA, the particle size distribution is broad, with an average particle size of ~8 ± 2 nm. Meanwhile, the addition of EDA at Sn^{4+}:EDA molar ratios of 1.0:0.75–3.3 results in a dramatic narrowing in the particle size distribution and a concomitant reduction in average particle size to ~2 ± 1 nm. The higher EDA concentrations result in slightly narrower size distributions and reduce average particle sizes. The large reduction in SnO$_2$ particle size induced by the EDA can be considered to partly arise from the decreased reactivity between Sn$^{4+}$ and OH$^-$ ions that occurs upon the formation of the Sn$_n$(EDA)$_m^{4+}$ complex [34,35]. The EDA present in the reaction medium assists in stabilizing nanoparticles by attaching them to the surface through hydrogen bonding [36]. Importantly, the SnO$_2$ nanoparticle dispersion displays excellent stability over several months’ storage at room temperature without the presence of any additional organic stabilizers (Figure S3).

The physical and electronic characteristics of the synthesized SnO$_2$ nanoparticles in this work are quantitatively compared with a commercially available aqueous SnO$_2$ dispersion (Alfa Aesar). The TEM micrographs in Figure 2a confirm a particle size of around 2 nm for the synthesized SnO$_2$, compared with around 4 nm for the commercial SnO$_2$ sample in Figure 2b. X-ray diffraction (XRD) measurements of the synthesized and commercial SnO$_2$ nanoparticles are shown in Figure 2c. The prominent peaks at (110), (101), (200), (211), and (002) confirmed the tetragonal crystal structure of SnO$_2$ (indexed in JCPDS card No. 41-1445). The absence of any impurity diffraction peaks indicates that there are no crystalline by-products formed during the synthesis of the SnO$_2$ particles. The broad diffraction peaks demonstrate the nanocrystalline nature of the SnO$_2$ nanoparticles, [37] with Scherrer analysis estimating the crystallite sizes to be ~2.2 and ~2.8 nm, respectively. The phase and its purity determined from XRD is consistent with selected area electron diffraction (SAED) measurements from TEM (insets in Figure 2a,b).

The results of TGA of the synthesized and commercial SnO$_2$ aqueous dispersions (Figure 2d) show that both materials have a major weight loss event at around 100 °C, which is attributed to the evaporation of water ($T_d = 100$ °C). The FTIR spectra provide evidence for the presence of EDA on the SnO$_2$ surface. Figure 2e and Figure S4 shows the FTIR spectra of synthesized and commercial SnO$_2$ films spin-coated on Si substrate after different annealing temperatures. The broad bands at around 3200 cm$^{-1}$ and 1650 cm$^{-1}$, respectively, correspond to stretching and bending vibrations of N-H bonds of EDA molecules attached to SnO$_2$ nanoparticles [34,38]. As the annealing temperature is increased from 80 °C to 200 °C, the intensity of these bands decreases because of the pyrolysis of the EDA.
Synthesized and commercial SnO$_2$ samples both demonstrate very strong absorption bands in the range of 420–700 cm$^{-1}$ which are attributed to the Sn–O antisymmetric and Sn–O–Sn vibrations [39].

Figure 2. TEM images of (a) synthesized and (b) commercial SnO$_2$ nanoparticles, insets are SAED patterns, (c) XRD patterns of synthesized and commercial SnO$_2$ nanoparticles, (d) Thermogravimetric plots of synthesized and commercial SnO$_2$ nanoparticles (inset of 1st derivative plots), (e) FTIR spectra of synthesized and commercial SnO$_2$ nanoparticles; (i) OH Str., (ii) C–H Str., (iii) O=O=C=O Str., (iv) C = O Str., (v) C–H Ben., (vi) O–H Ben., (vii) C=O Str., (viii) C–H Ben., (ix) Sn–O & O–Sn–O Vib. and (f) water contact angle images of synthesized and commercial SnO$_2$ coated on a Si substrate.

Figure 2f compares the water contact angles of spin-coated synthesized and commercial SnO$_2$ films on Si substrates, where the substrates are exposed to air–oxygen plasma (Harrick Plasma) at an RF power of 18 W for 5 min prior to coating. The contact angle is
an important parameter to consider for R2R coating processes. As shown in the figure, the SnO$_2$ coating made using synthesized ink shows a lower contact angle ($<10^\circ$) than the commercial SnO$_2$ film ($\sim22^\circ$), demonstrating its likely suitability for the R2R coating process [40]. The surface roughness of the synthesized and commercial SnO$_2$ films measured by atomic force microscopy (AFM) (Figure S5) shows that films from synthesized SnO$_2$ have a slightly lower RMS roughness ($\sim2.59$ nm) compared to films of similarly processed commercial SnO$_2$ ($\sim3.10$ nm), suggesting very smooth film properties in both cases.

The results of XPS measurements of synthesized and commercial SnO$_2$ nanoparticle coatings deposited on ITO-glass substrates are shown in Figure 3a–d. All spectra have been corrected with respect to the C1s peak. Figure 3a shows the survey spectrum comparison, and is consistent with literature reports of SnO$_2$ [41]. Figure S6 shows high-resolution Sn3d XPS spectra for commercial and synthesized samples with Sn 3d5/2 and 3d3/2 contributions appearing at binding energies of $\sim486$ and $\sim495$ eV, respectively. For both samples, the splitting between the Sn 3d doublet is $8.4 \pm 0.1$ eV which shows a dominant Sn$^{4+}$ character and matches well with the reported SnO$_2$ [41]. Since SnO and SnO$_2$ have similar binding energies, XPS valence spectra are also used to distinguish between these oxides. Figure 3b shows that the XPS valence band spectra of the synthesized and commercial samples clearly match with standard SnO$_2$ phase [42,43]. The first dominant peak at around 5.0 eV corresponds to the O 2p orbital. The higher energy features correspond to the hybridization between Sn 5p and O 2p orbitals [43]. Furthermore, the high-resolution XPS spectra of O1s orbital shown in Figure 3c–d are deconvoluted into two well-defined Gaussian-like peaks revealing the presence of two types of oxygen-related species. In agreement with the literature, the first major component ($\sim530$ eV) corresponds to lattice oxygen with an O–Sn$^{4+}$ bonding, Ref. [44] and the other higher energy component ($\sim532$ eV) has been assigned to either the chemisorbed oxygen-related species or the presence of oxygen vacancies [45–48]. Clearly, the synthesized SnO$_2$ nanoparticles show a lower contribution of this higher energy component than commercial SnO$_2$ nanoparticles. Previously, it has been shown for SnO$_2$ and TiO$_2$ nanoparticles that a decrease in oxygen vacancies improves charge extraction from the perovskite layer in PSC devices [49,50]. Therefore, having fewer oxygen vacancies as evidenced by XPS results, the synthesized SnO$_2$ can be expected to provide improved charge extraction when used as the ETL.

The UV-visible absorption spectra of SnO$_2$ thin films on quartz substrates (Figure 3e) display negligible absorption across the entire visible spectrum. This is consistent with the optical bandgaps of $\sim4.3$ eV for the synthesized SnO$_2$ film and $\sim4.1$ eV for the commercial product, estimated from the Tauc plots. These values exceed the 3.6 eV bandgap of bulk SnO$_2$ and can be considered to arise due to quantum confinement effects associated with the nano-sized SnO$_2$ particles in the dispersion [51,52]. Notably, this blue shift in absorption is potentially useful for photovoltaic applications as it decreases the parasitic absorption of sunlight by the SnO$_2$ layer [53]. The PL decay curves measured for FA$_{0.91}$Cs$_{0.09}$PbI$_3$ perovskite layers spin-coated on SnO$_2$-coated bare glass substrate, where the SnO$_2$ layer was prepared by spin-coating either the synthesized or commercial dispersion, are shown in Figure 3f. The inset of Figure 3f shows the corresponding PL emission spectra. Quenching of the perovskite PL is seen in both cases, indicating efficient electron transfer across the perovskite/SnO$_2$ interface [54]. However, the significantly greater PL quenching observed for the SnO$_2$ layer fabricated using the synthesized SnO$_2$ nanoparticles suggests a larger electron transfer rate from the perovskite absorber [55]. This could be due to the low oxygen vacancies in synthesized SnO$_2$ compared to the commercial ink as evident from XPS data. The low oxygen vacancies in SnO$_2$ allow efficient charge transport at SnO$_2$/perovskite interface by decreasing the trap-assisted charge carrier recombination, thus resulting in the extended charge carrier lifetime [56,57]. Notably, the higher residual PL peak energy from the perovskite interfacing with the synthesized SnO$_2$ is consistent with this interpretation and should result in a comparative increase in open circuit voltage from a completed photovoltaic device [58].
Figure 3. (a) XPS survey spectrum of synthesized and commercial SnO$_2$ films, (b) XPS valence spectrum and, high-resolution O1s spectra of (c) synthesized and (d) commercial SnO$_2$ nanoparticles, (e) UV-visible absorption spectra of SnO$_2$ films on quartz substrates (inset: corresponding Tauc plots), (f) TRPL with fitted exponential decay curves of SnO$_2$/perovskite films coated on plain glass (excitation 466 nm, emission 795 nm, excitation and emission from glass side) (inset: corresponding PL emission spectra).

The utility of the synthesized SnO$_2$ nanoparticle dispersion deposited on rigid ITO-glass substrates for use in PSCs was investigated using an n-i-p planar structured PSC device architecture consisting of ITO-glass/SnO$_2$/FA$_{0.91}$Cs$_{0.09}$PbI$_3$/Spiro-OMeTAD/Au (Figure 4a). The representative cross-sectional SEM image in Figure 4b shows the various functional layers. The SnO$_2$ ETL was formed on the ITO side of glass substrates by spin-coating using the synthesized or commercial SnO$_2$ nanoparticle dispersions followed by
annealing at 140 °C for 2 min in air. Here, the post-annealing temperature and duration of the SnO$_2$ ETLs were the same as the processing conditions used for R2R processing. The thickness of the SnO$_2$ ETL was ~20 nm and a highly conformal interface is formed between the SnO$_2$ ETL and the perovskite layers.

Figure 4. (a) Schematic of device structure and (b) cross-section SEM image for ITO-glass/SnO$_2$/perovskite/Spiro-OMeTAD, (c) short-circuit current, (d) open-circuit voltage, (e) fill factor, and (f) PCE of PSCs with spin-coated ETLs based on commercial or synthesized SnO$_2$ for the devices (active area 0.2 cm$^2$).

To investigate and compare the effectiveness of the ETL layer prepared using the synthesized aqueous SnO$_2$ nanoparticle dispersion, we fabricated PSCs on ITO-glass substrates using FA$_{0.91}$Cs$_{0.09}$PbI$_3$ perovskite as the light-absorbing layer and compared their photovoltaic performance with PSCs made using commercial SnO$_2$ as the ETL. All device fabrication steps, including the deposition of the perovskite and HTL layers, were carried out under ambient conditions using the spin-coating technique, as described in the experimental section.
The J-V performance parameters of the devices made using synthesized and commercial SnO$_2$ as the ETL are shown in Figure 4c–f and Table S1. The average J-V data (Table S2) based on the results from 45 cells fabricated with the above device configuration indicate a significant improvement in the PCE of the devices fabricated using the synthesized SnO$_2$ ETL compared to analogous devices featuring commercial SnO$_2$. This improved PCE for PSCs using ETLs based on the synthesized SnO$_2$ arises from an enhanced open circuit voltage ($V_{OC}$) and fill-factor (FF), which is consistent with the improved electron extraction properties across the perovskite/SnO$_2$ interface for the synthesized SnO$_2$ dispersion.

Figure 5a shows the J-V curve recorded for the best-performing PSC comprising an ETL using synthesized SnO$_2$. The forward and reverse J-V scans show PCE of 19.1% and 20.2%, respectively, and a low hysteretic behavior with a hysteresis index of 0.05. The integrated current density of 22 mA cm$^{-2}$ derived from the IPCE is in good agreement with the short-circuit current density ($J_{sc}$) obtained from the measured J–V curve (Figure 5b). Short-term maximum power point (MPP) stability of an average unencapsulated device tested under steady-state illumination conditions showed little change over the testing period of 500 s (Figure 5c).

Encapsulated PSC devices comprising synthesized SnO$_2$ as the ETL showed no noticeable degradation under continuous standard illumination at AM1.5 at 80 °C and 40–60% relative humidity. After the initial burn-in (first 200 min) the devices retained 95% of the initial performance after 1000 min of continuous illumination (Figure S9). Furthermore, the compatibility of the synthesized SnO$_2$ dispersions with performance-enhancing additives [59–61] was also investigated. The performance of un-optimized PSC devices
made using various amounts of additives in the synthesized SnO$_2$ ink [61–63] is shown in Figure 5d and Table 1. Preliminary results show that short-chained PEG-based additives help to enhance device performance, with an ~8% increase in mean PCE being observed due to enhancements in $V_{oc}$ and $J_{sc}$.

Table 1. Summary of J-V characteristics of perovskite solar cells with ETL spin coated using synthesized pristine SnO$_2$ ink or with NH$_4$Cl (1ppm), EDTA (0.1ppm), and PEG10K (1ppm) additives.

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<th>Vo/V</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
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<tr>
<td>SnO$_2$</td>
<td>FWD 1.12 (1.12 ± 0.01)</td>
<td>20.83 (20.78 ± 0.11)</td>
<td>0.74 (0.74 ± 0.01)</td>
<td>17.26 (17.22 ± 0.15)</td>
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<td>REV 1.13 (1.13 ± 0.01)</td>
<td>20.88 (20.73 ± 0.17)</td>
<td>0.76 (0.76 ± 0.01)</td>
<td>17.93 (17.71 ± 0.14)</td>
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<td>NH$_4$Cl- 1 ppm</td>
<td>FWD 1.14 (1.14 ± 0)</td>
<td>20.90 (20.82 ± 0.09)</td>
<td>0.76 (0.75 ± 0.01)</td>
<td>18.11 (17.92 ± 0.15)</td>
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<td>REV 1.15 (1.15 ± 0.01)</td>
<td>20.85 (20.79 ± 0.06)</td>
<td>0.78 (0.78 ± 0.01)</td>
<td>18.70 (18.52 ± 0.17)</td>
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<td>EDTA- 0.1 ppm</td>
<td>FWD 1.16 (1.16 ± 0)</td>
<td>21.01 (20.86 ± 0.22)</td>
<td>0.73 (0.73 ± 0.01)</td>
<td>17.79 (17.69 ± 0.07)</td>
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<tr>
<td></td>
<td>REV 1.16 (1.16 ± 0.01)</td>
<td>21.02 (20.85 ± 0.15)</td>
<td>0.77 (0.76 ± 0.01)</td>
<td>18.78 (18.51 ± 0.19)</td>
</tr>
<tr>
<td>PEG10K- 1 ppm</td>
<td>FWD 1.15 (1.15 ± 0.01)</td>
<td>21.21 (20.96 ± 0.24)</td>
<td>0.77 (0.76 ± 0.01)</td>
<td>18.79 (18.65 ± 0.14)</td>
</tr>
<tr>
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<td>REV 1.16 (1.16 ± 0)</td>
<td>21.68 (21.50 ± 0.22)</td>
<td>0.77 (0.77 ± 0.01)</td>
<td>19.45 (19.18 ± 0.20)</td>
</tr>
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Flexible Devices Comprising a R2R-Deposited SnO$_2$ ETL

Slot-die and reverse-gravure (RG) printing are standard industrial R2R coating techniques that are widely used for the deposition of low-viscosity solutions (aqueous or solvent-based), making them promising methods to deposit large-area functional layers of printable solar cells including PSCs [64,65]. The key benefits of these coating techniques for PSCs are in their ability to process suitable patterns at high coating speeds and with minimal material wastage during coating. To test the scalability of the developed SnO$_2$ dispersion for R2R coating, we assessed its deposition using the RG method. The synthesized SnO$_2$ dispersion was found to wet the flexible ITO-PET substrate surface when coated using the RG method and was found to dry immediately after deposition. The improved wetting using the RG method is possibly due to its shearing action between the gravure roller and the surface of the substrate during the deposition process. The RG-coated layers of synthesized SnO$_2$ were found to be very uniform, and flexible PSC devices comprising this layer as the ETL were fabricated using the R2R fabrication steps illustrated in Figure 6a. Flexible PSCs fabricated using a R2R RG-deposited SnO$_2$ layer, and spin-coated layers of FA$_{0.91}$Cs$_{0.09}$PbI$_3$ perovskite and Spiro-OMeTAD achieved a champion PCE of 17.0% (Figure 6b). These flexible PSCs showed a hysteresis index of 0.13, and a stabilized PCE obtained from MPP tracking of more than 15.5% (Figure 6c). To our knowledge, the highest PCE reported for flexible PSCs fabricated using a R2R deposited ETL is 17.4% [32]. Therefore, the highest PCE obtained in the present work is closer to the best-reported device efficiency for flexible PSCs, further highlighting the suitability of the synthesized SnO$_2$ dispersion for producing high-efficiency printed PSCs.
Figure 6. (a) Schematic representation of flexible PSC fabrication using R2R reverse-gravure coating of the ETL comprising synthesized SnO$_2$, (b) J-V characteristics of the best-performing flexible PSC, (c) MPP tracking over time of the champion device.

5. Conclusions

In summary, a facile SnO$_2$ nanoparticle aqueous dispersion has been successfully synthesized via a microwave-assisted solvothermal approach. The processability of the synthesized SnO$_2$ dispersion using roll-to-roll coating techniques and its applicability as the ETL in printable and flexible PSCs has been investigated. The dispersion features ~2 nm tetragonally phased SnO$_2$ nanoparticles that can be processed into thin coatings under ambient conditions at a temperature below 150 $^\circ$C. These films were integrated as ETLs within PSCs fabricated under ambient conditions to deliver champion devices having a PCE of more than 20% under a reverse scan. We also demonstrated the continuous R2R processability of the developed SnO$_2$ dispersion on flexible ITO-PET substrates, achieving a high efficiency of 17.0% under a reverse scan for the flexible PSC devices. Improvements in charge carrier management, which is closely related to the enhanced fill factor and the open-circuit voltage, have provided a path toward increasing the device performance of both glass-based and flexible PSCs. Optimization in the use of performance-enhancing additives and an understanding of the enhancement mechanisms remain as future work.
The results from the present work are expected to lead to the development of new strategies for the fabrication and design of R2R and ambient processable large-area PSCs having high efficiency and stability.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings12121948/s1, Figure S1: The chemical structures of (a) Ethylenediaminetetraacetic acid (ETDA) and (b) poly(ethylene glycol) (PEG). Figure S2: Particle size distribution of SnO\(_2\) nanoparticles synthesised with different Sn\(^{4+}\) to EDA ratios as obtained by dynamic light scattering. Figure S3: Particle size distribution of synthesised SnO\(_2\) nanoparticle dispersion over time. Figure S4: FTIR spectra of synthesised and commercial SnO\(_2\) thin films coated on plain glass and annealed at different temperatures. Figure S5: AFM surface topology and 3D images of (a) an ITO-glass substrate, (b) synthesised SnO\(_2\), and (b) commercial SnO\(_2\) coated on ITO-glass substrates. Figure S6: High-resolution Sn3d XPS spectra of (a) synthesised and (b) commercial SnO\(_2\) films deposited by spin coating on ITO and (c) high-resolution C1s XPS spectra of synthesised and commercial SnO\(_2\) nanoparticles. The presence of K2p orbital peaks along with C1s orbital is due to the use of KOH in water-based dispersion. Figure S7: Transmittance plots of SnO\(_2\) films on quartz substrates. Figure S8: The dark J-V of PSC device with spin-coated ETLs based on synthesised SnO\(_2\) the devices (active area 0.2 cm\(^2\)). Table S1: Summary of photovoltaic parameters of the spin-coated PSCs using commercial (Com.) and synthesised (Syn.) SnO\(_2\) as ETL. Device structure glass/ITO/SnO\(_2\)/perovskite/Spiro-OMeTAD/Au(20 nm)/Ag(80 nm). Table S2: Average of photovoltaic parameters of the above 45 devices made using the spin-coated PSCs using commercial (Com.) and synthesised (Syn.) SnO\(_2\) as ETL. Figure S9: PSC stability of the best-performing encapsulated device (ITO-glass/SnO\(_2\)/perovskite/Spiro-OMeTAD/Au).


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Conflicts of Interest: The authors declare no conflict of interest.

List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>PSCs</td>
<td>perovskite solar cells</td>
</tr>
<tr>
<td>R2R</td>
<td>roll-to-roll</td>
</tr>
<tr>
<td>PCE</td>
<td>power conversion efficiency</td>
</tr>
<tr>
<td>PV</td>
<td>photovoltaic</td>
</tr>
<tr>
<td>ETL</td>
<td>electron transporting layers</td>
</tr>
<tr>
<td>PET</td>
<td>polyethylene terephthalate</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>titanium dioxide</td>
</tr>
<tr>
<td>SnO(_2)</td>
<td>tin oxide</td>
</tr>
<tr>
<td>EDA</td>
<td>ethylene diamine</td>
</tr>
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</table>

PSCs perovskite solar cells
R2R roll-to-roll
PCE power conversion efficiency
PV photovoltaic
ETL electron transporting layers
PET polyethylene terephthalate
TiO\(_2\) titanium dioxide
SnO\(_2\) tin oxide
EDA ethylene diamine
rpm rotations per minute
PET polyethylene terephthalate
ITO tin doped indium oxide
TCO transparent conducting oxide
HTL hole transporting layer
TGA thermogravimetric analysis
TEM transmission electron microscopic
SEM scanning electron microscopy
XRD X-ray diffraction
AFM atomic force microscope
XPS X-ray photoelectron spectroscopy
UV-Vis ultraviolet-Visible
FTIR fourier-transform infrared
J-V current density-voltage
IPCE incident photon-to-electron conversion efficiency
PL photoluminescence
SAED selected area electron diffraction
V_{OC} open circuit voltage
FF fill-factor
J_{sc} short-circuit current density
MPP maximum power point
RG reverse-gravure

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