Research Article

Electrospun Networks of ZnO-SnO$_2$ Composite Nanowires as Electron Transport Materials for Perovskite Solar Cells

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Here, we report on the fabrication of one-dimensional (1D) zinc oxide-tin oxide (ZnO-SnO$_2$, ZTO) hollow nanostructures by coaxial electrospinning followed by investigations of their electron transport properties in regular perovskite solar cells (PSCs). The as-electrospun nanowires (NWs) were obtained as core-shell nanostructures comprised of polymeric core and metal oxide precursors-polymer shell. Thermal analysis studies of the as-electrospun NWs revealed the optimum calcination temperature for complete removal of the polymer and formation of phase pure ZTO. The obtained nanostructured ZTO materials revealed a porous morphology with tubular nanostructures, i.e., NTs. The porous structure of nanoparticles, i.e., NTs in this case, is of particular interest due to the following reasons: (a) structure, particularly 1D, has a profound influence on the electron transport properties, and (b) suitable porosity helps in effective infiltration of perovskite material and hence supports better charge transport at the ZTO-perovskite interface. The nanomaterials were characterized by Fourier transform infrared (FTIR), diffuse reflectance spectroscopy (DRS), and energy dispersive X-ray spectroscopy (EDX) to confirm the presence/absence of functional groups, establish band gap energies ($E_g$), and determine the elemental compositions, respectively. The ZTO NTs were used as electron transport media in the fabrication of perovskite solar cells (PSCs) and established the structure-property (electron transport) relationships. The highest solar to power conversion efficiency (PCE) of 13.0% (average: 11.90%) was measured for the PSCs based on ZTO NTs obtained by calcination of as-electrospun NWs at 800°C. It indicates the fact that the calcination temperature influenced the structure which as a result influenced the electron transport property of the material used as ETL in PSCs.

1. Introduction

Nanostructured metal oxides (MOs) have gained tremendous attention during the course of research for the last many years owing to their exceptional properties which make them suitable for applications in diverse fields including but not limited to photocatalysis, energy harvest and storage, sensing, and drug delivery [1]. Among the large number of MOs, zinc oxide (ZnO) [2] and tin dioxide (SnO$_2$) [3] are of particular interest owing to their highly favorable properties which make them suitable for practical applications. For example, ZnO and SnO$_2$ are both $n$-type semiconductors with a wide direct band gap energy ($E_g$) of 3.37 eV and 3.60 eV, respectively [4]. The excellent optical and electrical properties have made them promising electron transport materials for solar cells [5, 6] besides photocatalysis [7], thin-film transistors [8], and gas sensors [9]. Owing to their exceptional charge collection and transport properties, ZnO and SnO$_2$ have particularly benefited the emerging third-generation photovoltaic devices such as dye-sensitized (DSSCs) and perovskite solar cells (PSCs) [10–12].
PSC is an organic-inorganic hybrid solar cell whose current certified efficiency has surpassed 25%, challenging the commercial silicon solar cells and thus making its way towards commercialization on a large scale [13, 14]. The tremendous performance of the PSCs is attributed to their tunable direct band gap in the visible region, a high absorption coefficient, excellent charge carrier transport properties, low exciton binding energies, and comparatively low cost of fabrication [15, 16]. High-performance PSCs are typically made by sandwiching the light harvesting perovskite layer between an n-type electron transport layer (ETL), typically a semiconductor MO, and a p-type hole transport layer (HTM), usually an organic semiconductor [17]. Among the functional components in PSC, the ETL plays a critical role by collecting electrons from the perovskite and transporting them towards the respective electrode. Furthermore, it ensures a low recombination rate of electron-hole pairs in the perovskite layer [18, 19].

The most frequently used ETLs in the fabrication of PSCs are TiO₂, ZnO, and SnO₂ [20–23]. TiO₂ is the most commonly used ETL in PSCs due to its ease of fabrication, favorable energy level alignment, and its long electron lifetime [24]. However, despite being a good absorber of ultraviolet light, the low electron mobility (6.21 × 10⁻⁵ cm²/Vs) [25], which is responsible for the accumulation of charge at the interface between ETL and perovskite, limits its use in practical PSCs [26, 27].

As an alternative, ZnO equipped with suitable properties like high transparency, wide E_0, high electronic mobility (bulk mobility reaches 200–300 cm²/Vs) [28], and low processing temperatures is one of the highly suitable ETL candidates to be employed in the fabrication of practical PSCs [29]. However, despite its comparable efficiency to that of TiO₂, ZnO contains OH residues at its surface at a lower processing temperature [30] and is unstable in an acidic medium, thus causing degradation of the perovskite layer [31, 32]. Like ZnO, SnO₂ has also found attention as potential ETL material owing to its wide E_0, excellent optical transparency, and high electron mobility (bulk mobility of 240 cm²/Vs) [33, 34]. Furthermore, SnO₂ absorbs lesser ultraviolet (UV) light making it more robust than TiO₂ for PSCs [35]. However, SnO₂ due to its lower value of conduction band (CB) edge, gives rise to higher electronic recombination and thus produces low open circuit voltage and gives lower PCE [36].

To overcome their intrinsic limitations and alleviate their shortcomings, individual ZnO and SnO₂ as ETLs in PSCs are needed to be combined into a nanocomposite. The improvement in functional properties of individual MOs with nano-composite formation has numerous reported examples. For instance, mixed MOs like TiO₂-ZnO [37], TiO₂-SnO₂ [38], SnO₂-MgO [39], and TiO₂-In₂O₃ [40] have shown improved properties and thus rendered good results as ETLs in PSCs compared to their individual components, i.e., monometal oxides.

Previously, ZTO nanocomposites have also been prepared and employed as efficient ETL materials in both DSSCs and PSCs [11, 41, 42]. For example, Shalan et al. [43] synthesized ZTO composite nanoparticles by the simple coprecipitation method and used them as ETL in PSCs, achieving PCE of ~17.81%. Song et al. [12] on the other hand synthesized ZTO composite nanoparticles at low temperature via the solution spin coating method and found maximum PCE of ~15.2%. Recently, Li et al. [44] developed core-shell ZTO nanoparticles by the solvothermal method and reported PCE of 14.35%. It is pertinent to mention here that besides ZTO nanocomposites, ternary zinc tin oxide, Zn₅SnO₈, has also been exploited as ETL materials with limited success [14, 45].

As presented in the preceding paragraph, ZTO composite nanoparticles have shown improved properties as ETL materials compared to the individual ZnO and/or SnO₂. However, no substantial attention is paid in these reports to the nanoengineering of ZTO particles especially to the fabrication of 1D ZTO hollow nanoarchitectures. It is pertinent to mention here that the influence of structure on the properties of materials is by now an established fact [46], and the influence of 1D nanostructure is more prominent on the properties of ETL materials. It has been found that the use of 1D nanostructures as ETL in PSCs such as NWs [47], nanorods [48], and particularly the nanotubes [49] are of significant interest due to their unique size- and dimensionality-dependent properties. In fact, compared to ETLs made up of various morphologies, 1D nanostructures such as NWs provide improved interfacial contact with the photoabsorber material, superior transport of charge carriers, and better light trapping and absorption efficiency [50–53].

Although TiO₂-based 1D nanostructures including nanotubes have been greatly employed as ETLs in PSCs, structure-property relationships were established. But, to the best of our knowledge, no such 1D hollow structures of ZTO have been extensively explored as ETL materials in PSCs.

Therefore, here in this article, we report on the development of 1D hollow structures of ZTO nanocomposite as efficient ETL material in PSCs. Following a reported protocol [54], first were realized core-shell NWs comprising of PVP core and MOs-precursors-PVP shell. Afterwards, the PVP in the core as well as in shell was removed by heating the NWs very carefully at a rate of 2 °C/min. To explore the effect of calcination temperature on the structure of ZTO nanocomposite materials and thus the influence of structure upon the property, the calcination was performed at three different temperatures, i.e., 600°C, 700°C, and 800°C. It was found that the efficiency improves with increasing calcination temperature as the highest PCE of 13.0% was obtained for the PSC fabricated with the ETL layer composed of 1D hollow nanostructure of ZTO achieved by calcination of the as-electrospun NWs at 800°C.

2. Materials and Methods

2.1. Materials. The precursors for the synthesis of electrospun ZTO core-shell NWs, i.e., zinc chloride (ZnCl₂, ~99%) and polyvinylpyrrolidone (PVP, Mw = 1,300,000 g/mol), were purchased from Sigma-Aldrich, and tin dichloride dihydrate (SnCl₂·2H₂O, ~99%) was purchased from Duksan Chemicals. The solvent, dry N-N-dimethylformamide (DMF, 99.9%), was obtained from Alfa
Aesar. A commercial electrospinning unit model TL-01 purchased from Tong Li Company, China, was used for the fabrication of NWs.

The materials for PSC assembly were obtained from different commercial suppliers. Fluorine doped tin oxide (FTO, 7 Ω/sq) conducting glass substrates (2.2 mm), ethyl cellulose ([(C$_6$H$_{10}$O$_2$)(OR)$_2$]), OR$_1$ and OR$_2$ = CH$_3$CH$_2$), terpineol (α-C$_{10}$H$_{18}$O, 95%), and Triton X-100 (t-Oct-C$_3$H$_7$- (OCH$_2$CH$_2$)$_x$OH, x = 9-10) were used from Sigma-Aldrich. Hellmanex III from Hellma Analytics, 1-octanol (C$_8$H$_{18}$O, 98%) from AppliChem GmbH and cesium iodide (CsI) of abcr GmbH were supplied by commercial suppliers. Both formamidinium iodide (CH$_3$N$_2$I, FAI) and methylammonium iodide (CH$_3$NH$_3$I, MAI) were purchased from the Greatcell Solar while lead bromide (PbBr$_2$, 99.999%) and lead iodide (PbI$_2$, 99.999%) were obtained from TCI Europe. 2,2′,7,7′-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9′-spirobi-fluorene (C$_{8}$H$_{8}$N$_2$O$_9$, 99%, HPLC grade) commonly known as spiro-MeOTAD, bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 95%), and tri[bis-(trifluoromethane)sulfonylimide] (FK209) were obtained from Sigma-Aldrich. 4-tert-Butylpyridine (4-TBP) was obtained from Fluorochem, and extra dry chlorobenzene (C$_6$H$_5$Cl, 99.8%) and dimethyl sulfoxide (DMSO, 99.7%) and HPLC grade absolute ethanol (C$_2$H$_5$O, 99.5%) were obtained from Acros Organics.

2.2. Synthesis of ZTO NWs and Nanotubes. Following Reference [54], an equimolar solution was prepared by dissolving 1 g of ZnCl$_2$ (7.33 mmol) and 1.65 g of SnCl$_2$.2H$_2$O (7.33 mmol) in 10 mL DMF. After complete dissolution of both the salts, 1.4 g of PVP was added to this solution. Afterwards, the whole mixture was kept at continuous stirring until a uniform viscous solution was obtained with no granules of PVP left behind. Parallelly, 1.4 g of PVP was weighed and added into 10 mL DMF in a separate beaker and kept stirred for 5 to 6 hours to get a clear solution.

Afterwards, the two solutions prepared above were transferred to two separate plastic syringes each of 5 mL capacity and named syringe 1 (S1) and syringe 2 (S2). Special care was taken during the filling of the solutions into syringes to avoid any bubbles trapped. S1 was filled with the solution comprised of a mixture of metal salts and PVP and was mounted in the electrospinning syringe pump in such a way to form the outer layer (sheath) of the NWs. S2 was filled with PVP solution and mounted in such a way in the electrospinning syringe pump to make the core of the NWs. After filling and cleaning the syringes, the coaxial needles were connected to them through capillary tubes. The syringes were then clamped in a syringe pump. The distance between the tip of the coaxial needle and the collector (rotating drum) was kept at 15 cm. A positive voltage of 15 kV was applied between the tip of the needle and the grounded collector. The solutions from syringes were fed at a feeding rate of 0.3-0.4 mL/h, and core-sheath NWs (PVP@ZTO/PVP) formation started as a collection on the rotating drum which was covered with aluminum foil. The NWs were then scratched with a spatula after drying. The schematic diagram of the coaxial electrospinning is given in Scheme 1.

To obtain NTs of ZTO, the core-shell NWs were calcined in a furnace at three different temperatures, i.e., 600°C (ZTO-1), 700°C (ZTO-2), and 800°C (ZTO-3), for 2 hours at a heating rate of 2°C/minute. The calcined ZTO NTs were then used as ETLs in PSCs.

2.3. Fabrication and Assembling of Solar Cells. FTO glass substrates (2 cm × 2 cm) were mechanically etched from the sides with a manual drill (Timber Tech). The substrates were then sonicated in a 2% water solution of Hellmanex III for 10 minutes followed by rinsing with deionized water (DI) several times. The thoroughly rinsed substrates were then consecutively and subsequently sonicated in DI water and ethanol for 15 minutes each. Finally, the substrates were dried with compressed air. Before the deposition of blocking layers, all the substrates were kept in a UV/ozone chamber for 15 minutes to remove any traces of organic residues on their surfaces.

The thoroughly prepared substrates were coated with a blocking layer (ZTO-BI) according to the recipe reported elsewhere [55]. Typically, a solution of ZnCl$_2$ and SnCl$_2$.2H$_2$O in a 1:1 ratio was spin-coated upon the FTO substrate at a speed of 3000 rpm for 30 s. Then, it was heated under ambient temperature, first at 100°C for 5 minutes to avoid any cracks and sudden evaporation of the solvent and then at 350°C for 15 minutes. The blocking layer-coated FTO substrate was then coated with a porous layer of ZTO nanotubes as the following. A paste of ZTO nanotubes was prepared by dispersing the active material in a mixture of ethanol/ethyl cellulose/terpineol/octanol/Triton X-100. This solution was spin-coated over the substrate and then heated at 450°C. The multicationic perovskite solution was prepared according to the work reported elsewhere [56] by dissolving FAI (1.0 M), PbI$_2$ (1.1 M), MABr (0.2 M), PbBr$_2$ (0.2 M), and CsI (1.5 M) in a 4:1 mixture of anhydrous DMF and DMSO.

The perovskite precursor solution was ready after stirring for about five hours inside the glovebox. One-step deposition and antisolvent method were employed for the deposition of the perovskite layer. The perovskite solution was spin-coated over the ZTO porous layer in a three-step program accelerating at 1000 rpm for 10 s, 2000 rpm for 20 s, and 4000 rpm for the rest of the time. During the third step at 45 s, 100 μL of chlorobenzene was drop casted in the center of the perovskite layer which turned the yellow color of the perovskite layer to dark brown. The substrates were then annealed for one hour at 100°C inside the glovebox. The spiro-OMeTAD solution was prepared by dissolving 85.780 mg of spiro-OMeTAD in 1 mL of chlorobenzene (70 mM). This solution was further doped with the additives LiTFSI (0.5 mM), FK-209 (0.03 mM), and TBP (3.3 mM). The spiro-OMeTAD solution was spin-coated over the perovskite layer at 4000 rpm for 20 s. Finally, a gold electrode of 70 to 80 nm thickness was thermally evaporated on the surface of the spiro-OMeTAD layer under high vacuum after which the solar cell was ready for measurements.
2.4. Characterization Techniques. The TG analyses were performed on TG/DSC1 (METTLER-TOLEDO GmbH Germany) apparatus in ambient temperature at a heating rate of 10°C/minute ranging from room temperature up to 800°C. The XRD analyses were performed on a STOE-STADI MP diffractometer equipped with Mo-Kα1 (λ = 0.70931 Å) radiations. The XRD patterns were obtained in the range of 10° to 50° with a step size of 0.01°. The search and match operation for the obtained XRD patterns was done with X’Pert HighScore software. The crystallite size was also calculated from the same software using Scherrer’s calculator based on Scherrer’s formula given in

\[ D = \frac{k\lambda}{\beta\cos\theta}, \]

where \( D \) is the crystallite size (nm), \( k \) is the proportionality constant (\( k = 0.9 \)), \( \lambda \) is the wavelength of the X-ray source (Mo, \( \lambda = 0.70931 \) Å) used in the X-ray diffraction, \( \beta \) is the peak full width at half maximum (FWHM), and theta (\( \theta \)) is Bragg’s angle of diffraction. Both \( \beta \) and \( \theta \) were measured in radians. The infrared spectra of the ZTO nanotubes were recorded in the range of 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) in the transmittance mode using a Perkin Elmer 1650 spectrometer. The morphology of the as-spun and calcined NWs was produced and captured with a field emission scanning electron microscope (FE-SEM) (model: Nova Nano SEM 430). The elemental composition of the polymeric NWs as well as the calcined ZTO NTs was determined by energy dispersive X-ray spectroscopy (EDXS). The Lambda 950 UV-Vis spectrometer from PerkinElmer was used for the DRS study. TEM images were obtained on a JEOL-2200 FS using a highly diluted dispersion of NTs in ethanol. The photocurrent-voltage (IV) measurements were carried out on a Keithley 2400 source meter and a solar simulator operating at 100 mW (1 sun, calibrated by a silicon standard cell). A mask with an area of 0.15 cm\(^2\) was applied to the front face of the cells during the measurements. Data handling has been performed using Oriel IV Test Station software.

3. Results and Discussion

3.1. Thermal Analysis. The thermogravimetric (TG) analysis of the as-electrospun PVP@ZTO/PVP NWs exhibited transformation steps related to the removal of the water/moisture contents and the decomposition of the green composite into the respective oxide phases (Figure 1). From the TG curve of the as-electrospun NWs, it can be seen that the decomposition and weight loss as a function of temperature are occurring in four distinct steps with a total weight loss of 83%. The first weight loss (~10%) from room temperature to ~100°C can be attributed to the removal of the absorbed water molecules and the residual solvent contents of DMF [57–59]. The second weight loss (~24%) in the thermogram between 241°C and 326°C accompanied by the endothermic dTG peak (maximum weight loss rate at 323°C) corresponds to the thermal decomposition of PVP [60]. The third minor weight loss and fourth major weight loss (~50%) from 336°C up to 481°C accompanied by endothermic dTG peaks (maximum weight loss rate at 421°C and 468°C, respectively) are corresponded to the complete decomposition of the PVP chain [60]. No significant weight loss beyond 481°C is observed as evident from the plateau till 800°C. However, this stage may involve the decomposition of Zn and Sn precursors and formation, growth, and reorganization of ZTO grains. The TG data is completely in line with the reported thermogram of identical nanostructures fabricated through the same method [60].

From the thermal data, it could be concluded that 481°C is the optimum temperature for the complete decomposition of PVP. After this temperature, the resulting ZTO nanomaterial is free from any PVP. Furthermore, it shows the high thermal stability of the residual ZTO material as after this temperature no weight loss occurs up to 800°C.

3.2. Structural Characterization. The evolution of the crystal structure of ZTO NWs as a function of calcination temperature was followed by XRD measurements. Figure 2(a) shows diffractograms of the as-electrospun NWs as well as the ZTO NTs obtained by calcination of the as-electrospun NWs at 600°C (ZTO-1), 700°C (ZTO-2), and 800°C (ZTO-
As expected, the XRD pattern of the uncalcined ZTO NWs showed no distinct peaks except a broad hump in the range of $2\theta = 12^\circ$ to $18^\circ$ possibly due to the presence of amorphous PVP, which is the main constituent of the NWs at this stage (Figure 2(a), i).

Contrary to the uncalcined ZTO NWs, the sample calcined at $600^\circ C$ showed distinct peaks corresponding to individual metal oxides (Figure 2(a), ii). Upon increasing the calcination temperatures from $600^\circ C$ to $700^\circ C$ and then to $800^\circ C$, improvement in crystallinity was observed indicated by the sharpening of XRD peaks. The peaks observed in the XRD patterns of ZTO-1, ZTO-2, and ZTO-3 are predominantly matched with the standard XRD patterns of ZnO (red sticks) and SnO$_2$ (blue sticks), verified by comparing with powder diffraction files (PDF) (01-077-0449) and (01-079-0205), respectively (Figure 2(a)). The peaks identified for ZnO appeared at $2\theta$ positions of 14.51°, 15.71°, 16.49°, 21.40°, 25.20°, 27.80°, 29.80°, and 37.90° corresponding to the lattice planes (100), (002), (101), (102), (110), (103), (112), and (312), respectively. For SnO$_2$, the peaks observed at $2\theta$ positions of 12.10°, 15.40°, 17.20°, 23.20°, 24.40°, 27.40°, 28.45°, 28.50°, 29.80°, and 33.90° correspond to (110), (101), (200), (211), (220), (310), (112), (301), (202), and (321) lattice planes, respectively. In all three samples, the crystal structure of ZnO was identified as the typical hexagonal Wurtzite and that of SnO$_2$ as tetragonal rutile.

The average crystallite sizes determined by employing Scherrer’s formula (Equation (2)) were found to be 17.45 ± 0.1 nm, 19.15 ± 0.1 nm, and 20.12 ± 0.1 nm for ZnO and 10.80 ± 0.1 nm, 15.45 ± 0.1 nm, and 16.35 ± 0.1 nm for SnO$_2$. The crystal structures of ZnO and SnO$_2$ are shown in Figure 2(b).
SnO₂ in samples ZTO-1, ZTO-2, and ZTO-3, respectively. It is pertinent to mention here that besides ZnO and SnO₂, no other phases, particularly Zn₂SnO₄, were observed in diffractograms of all the samples (Figure 2(a)). The formation of Zn₂SnO₄ was avoided by keeping lower the calcination temperature and time, as this phase is usually achieved by prolonged calcination at elevated temperatures (~1000 °C) [61]. The absence of Zn₂SnO₄ peaks in the XRD patterns of all the samples could not further be corresponded to its solubility in the ZnO and/or SnO₂ phases as solubility of the former is negligible in the latter [62]. However, ZnO possesses limited solubility in SnO₂. Therefore, the relatively less intense peaks of ZnO compared to SnO₂, although the two were equimolar, may be due to the comparatively higher solubility (1.5 mol%) of the former in the latter [63]. This increased solubility then may lead to a decrease in X-ray scattering power of ZnO and thus its peak intensities [64]. Nevertheless, there could be other factors influencing the ZnO peak intensities like electron density of elements present in the crystal [65].

3.3. FTIR Spectroscopic Characterization. The ATR-FTIR spectra of the as-electrospun ZTO NWs as well as the calcined ZTO NWs, i.e., ZTO-1, ZTO-2, and ZTO-3, are given in Figure 2(b). Primarily, the FTIR spectroscopy was performed over the samples to confirm the complete removal of the PVP from the resulting ZTO NWs as purity of the resulting nanomaterials to be used in PSCs is highly desirable. As the precalcined samples contain a high content of PVP, its FTIR spectrum shows intense peaks for different functional groups in the range of 4000 cm⁻¹ to 400 cm⁻¹. The broad peak centered at 3414 cm⁻¹ is corresponded to the O-H stretching vibration of the adsorbed water molecules [66]. The next absorption peaks appearing at 2954 cm⁻¹ along a small shoulder-like peak at 2891 cm⁻¹ are due to the asymmetric and symmetric, respectively, stretching of CH₂ group of the pyrrolidine ring and the vinyl chain [67]. The strong signature peak at 1656 cm⁻¹ is attributed to the stretching mode of the amide carbonyl group (C=O) of the PVP [67, 68]. The absorption peaks appearing at 1460 cm⁻¹, 1420 cm⁻¹, 1374 cm⁻¹, and 1320 cm⁻¹ are attributed to the bending vibrations of the C-H bond of CH₂ group [69]. The strong peak appearing at 1288 cm⁻¹ and the small peak at 1015 cm⁻¹ are attributed to the C-N bending vibrations [70, 71]. The weak vibrational bands appearing in the region from 1200 cm⁻¹ onwards can be ascribed to the different bending vibrations like scissoring, wagging, rocking, and out-of-plane vibrations due to bonds like C-H, C-C, and N-CO [67, 72]. The infrared absorption bands for MOs appear due to the interatomic bonding vibrations which...
generally exhibit in the fingerprint region (below 1000 cm\(^{-1}\)) [56]. However, in this case, as the ZTO NWs are uncalcined, the metal-oxygen vibrational peaks are not clear. On the other hand, in the FTIR spectra of the calcined ZTO NWs, i.e., ZTO-1, ZTO-2, and ZTO-3, only two distinct peaks are visible which are obviously due to the ZnO and SnO\(_2\). No other absorption bands in the FTIR spectra of ZTO-1, ZTO-2, and ZTO-3 are visible on the higher wavelength side confirming the complete removal of PVP and any adsorbed hydroxyl residues from the atmosphere.

The absence of hydroxyl group is very beneficial for the stability of PSCs because it can lead to degradation of the perovskite absorbing layer [30]. The first absorption band appearing at 470 cm\(^{-1}\) is due to the stretching mode of Zn – O bond while the second absorption band appearing at 606 cm\(^{-1}\) is due to the stretching mode of Sn – O [73, 74]. From the FTIR spectra of ZTO NTs, it can be seen that as the calcination temperature of NTs increases; the absorption bands for both ZnO and SnO\(_2\) are getting sharper which can be attributed to the enhanced crystallinity of the ZTO NTs as was also observed in the XRD analyses (Figure 2(a)).

3.4. Electron Microscopic Investigations. The FE-SEM micrographs of the coaxially as-electrospun and calcined ZTO NWs are presented in Figure 3. The as-electrospun ZTO NWs displayed a smooth and compact morphology (Figures 3(a) and 3(b)), owing to the fact that the PVP and ZTO nanoparticles are homogenously mixed. The diameter of the ZTO NWs varied between 240 nm and 190 nm, while their respective lengths reach several tens of micrometers. The SEM micrograph in Figure 3(c) of ZTO nanostructures obtained by calcination of as-electrospun NWs shows tubular structures. Upon increasing the magnification, the SEM image in Figure 3(d) shows that the tubular structures have dense walls composed of tiny nanoparticles. The presence of a large number of NTs of uniform diameter in SEM images in Figures 3(c) and 3(d) indicates the successful formation of the desired ZTO NTs for application as ETL in PSCs. Furthermore, the SEM micrographs of the ZTO NTs (Figures 3(c) and 3(d)) show a porous structure resulting from the elimination of polymeric aid (PVP). However, with the removal of the polymeric contents, the diameter of the ZTO NWs was found to shrink to approximately 100 nm.

The surface porosity of the fibrous tubes can play a critical role in better interfacing with the perovskite layer thereby boosting the efficiency of the PSCs [75]. The very small pores on the surface of the ZTO NTs could facilitate the perovskite layer to infiltrate and would lead to better

Figure 4: NWs with diameters of around 100 nm consist of joined 10-15 nm sized primary particles (a). Crystalline primary particles (b) can be identified using FFT of detailed image (c). The halo on the higher resolution image originates from defocusing the 3D NW structure to reveal crystalline lattice. The lattice distances of FFT reflection correspond to d-spacings of 4.94 Å, 3.25 Å, 2.62 Å, and 1.72 Å (from center to border).
interfacial contact between the ETL and perovskite [76].

Furthermore, the obtained ZTO NTs show tremendous uniformity and monodispersity. This could be attributed to the polymeric aid (PVP) which would have acted as a structure directing and protecting agent during the calcination process [77].

A detailed structural analysis of the calcined ZTO nanotubes by TEM revealed a porous structure consisting of small primary particles with diameters of around 10-15 nm forming an anisotropic tubular structure with intergranular porosity (Figure 4(a)). Despite their three-dimensional (3D) tubular arrangement, lattice planes could be identified at higher magnifications (Figure 4(b)) which can be directly visualized by Fourier transformation of the image into the frequency domain (Figure 4(c)). In this image, four distinct lattice plane distances can be identified (from center): \( d = 4.94 \, \text{Å}, 3.25 \, \text{Å}, 2.62 \, \text{Å}, \) and 1.72 Å. While the lattice distance 2.62 Å can be attributed to the parent phases ZnO (002) or SnO\(_2\) (101) with 2.60 Å or 2.64 Å, respectively, lattice distances of 4.94 Å indicate the formation of ternary oxides like Zn\(_2\)SnO\(_4\) ((101); \( d = 5.00 \, \text{Å} \)).

3.5. Diffuse Reflectance Spectroscopic (DRS) Characterization.

UV-Vis DRS was used to measure the optical \( E_g \) of the ZTO NTs. Figure 5(a) shows the reflectance against the wavelength of the three samples, i.e., ZTO-1, ZTO-2, and ZTO-3. Beyond 367 nm, the reflectivity of the samples is increasing accordingly with temperature, i.e., maximum reflection is occurring for ZTO NTs obtained by calcination of the as-electrospun NWs at 800°C. The obtained UV-Vis DRS data were further evaluated for the estimation of \( E_g \) (Figure 5(b)) employing the modified Kubelka-Munk function:

\[
F(R) = \frac{\alpha}{S} = \frac{(1-R)^2}{2R},
\]

where \( F(R) \) is known as the Kubelka-Munk function or remission parameter, \( \alpha \) is the absorption coefficient, \( S \) is the scattering coefficient, and \( R \) is the diffused reflectance of the film. The function, \( F(R) \), is directly proportional to \( \alpha \) and inversely proportional to \( S \) [78, 79]. The values of \( [F(R) \cdot \text{hv}]^2 \) vs. photon energy (\( \text{hv} \)) were plotted as shown in Figure 5(b). A tangent is drawn on the obtained slope and is extended where it intercepts the \( x \)-axis (\( \text{hv} \)) at zero, giving direct \( E_g \) values of 3.45 eV, 3.43 eV, and 3.41 eV for ZTO-1, ZTO-2, and ZTO-3, respectively. The minute decrement in \( E_g \) with an increase in calcination temperature can be attributed to the increase in crystallite size as witnessed from the XRD data.

3.6. Photovoltaic Performance of the Solar Cells.

The schematic representation of the PSC based on the porous ZTO NTs with a device layout of FTO/c-ZTO/p-ZTO/perovskite/spiro-OMeTAD/Au is given in Figure 6(a). The energy level diagram based on the reported values for the ZnO-SnO\(_2\) composites is given in Figure 6(b). For an ideal ETL material, its conduction band (CB) edge should be minimally lower than the CB edge of the perovskite layer for easy electron transfer, and its valence band (VB) edge must be
sufficiently lower than the VB edge of the perovskite to hinder the electron-hole recombination. For ZTO composites, Shalan et al. [43] and Song et al. [12] have reported the CB edge value of -4.25 eV while the VB edge value of -7.55 eV. In both cases, these reported values of CB edge for ZnO and SnO₂ are lower than that of the lowest unoccupied molecular orbital (LUMO) of perovskite (-3.93 eV). Thus, the electrons at the interface can easily transfer from the perovskite layer to the ZTO NTs used as ETL, facilitating efficient electron-hole separation and transportation of electrons at the ZTO/perovskite interface. Nevertheless, the values of the parameters like electron affinity (E.A.), ionization energy (I.E.), and work function (W.F.) are dependent on the factors like the purity of the materials (doped or undoped), structure (surface crystallographic orientation), morphology (surface roughness), and surface composition (cleaned vs. contaminated) of the materials. Therefore, keeping in mind these surface-dependent parameters, energy differences of few electron volts (eV) will always be found during measurements [80].

The top view SEM micrograph of the triple-cation perovskite spin-coated on top of the porous ZTO NTs is given in Figure 7(a). The morphology of the film is uniform, and the grain size is ranging from 200 nm to 400 nm. The larger grain size of the perovskite layer with fewer grain boundaries indicates good crystallinity which is crucial for
The corresponding J-V parameters obtained for the champion PSCs of each sample of ZTO used as ETL.

| Cell  | V_OC (V) | J_SC (mA/cm²) | FF (%) | Efficiency (%) |
|-------|----------|---------------|--------|----------------|
| ZTO-1 | 1.071    | 18.2          | 62.1   | 12.1           |
| ZTO-2 | 1.078    | 18.3          | 65.1   | 12.9           |
| ZTO-3 | 1.084    | 18.5          | 65.3   | 13.0           |

efficient charge transport with fewer recombination losses. The ZTO porous NTs were used as an ETL in the PSCs, and their photovoltaic performances were measured and plotted as photocurrent against the applied voltage. The PSCs were fabricated from the three samples, i.e., ZTO-1, ZTO-2, and ZTO-3. The obtained current density-voltage (J-V) curves measured with the reverse scan voltage of the PSCs are given in Figure 7(b). The photovoltaic parameters of the champion PSCs of each sample are given in Table 1. A 12.1% PCE was measured for the ZTO-1, giving a V_OC of 1.071 V, J_SC of 18.2 mA/cm², and fill factor (FF) of 62.1%. However, insignificantly higher PCEs were shown by the cells made up of ZTO NTs, ZTO-2, and ZTO-3, as ETL. V_OC of 1.078 V and 1.084 V, J_SC of 18.3 mA/cm² and 18.5 mA/cm², FF of 65.1% and 65.3%, and PCEs of 12.9% and 13.0%, respectively, were obtained for the PSCs in which ETL layers were made up of ZTO-2 and ZTO-3. It can be seen that in the case of ZTO-3, V_OC and particularly J_SC have been improved. This increase in J_SC can be attributed to the enhanced crystallinity of the material upon increasing the calcination temperature, leading to a better charge collection property and hence suppressing the recombination of electron-hole pair in the perovskite layer. In addition to the crystallinity factor, the rise in the photocurrent of the ZTO-3 is confirming the presence of fewer density traps while in the case of ZTO-1 the slow rise of J_SC to the maximum photocurrent, and reduction in the photovoltage value indicates the presence of a relatively large number of deep trap densities in the device [81]. It is pertinent to mention here that the performance of the PSCs of each ZTO sample is consistent as shown by the statistics presented in Figure S3 (supplementary information (SI)). The average PCEs of four solar cells of each ZTO sample are 9.80% (ZTO-1), 10.72% (ZTO-2), and 11.90% (ZTO-3). The average J-V data are given in Table S1 (SI).

4. Conclusion

In this study, a combined effect of the ZTO NTs as ETLS was demonstrated in the organic-inorganic hybrid PSCs. The 1D ZTO NTs were successfully fabricated by the coaxial electrospinning method and calcination, characterized by different techniques such as TG-DTA, SEM, TEM, XRD, FTIR, EDX, and DRS, and finally applied as ETLS in PSCs. The as-electrospun ZTO NWs were calcined at three different temperatures, i.e., 600°C (ZTO-1), 700°C (ZTO-2), and 800°C (ZTO-3) which after the removal of the polymeric contents became porous as shown by the electron microscopic images. Furthermore, the ZTO were obtained after calcination of the as-electrospun NWs in the desired structure, i.e., NTs. The PSCs made up of sample ZTO-3 as ETL showed the highest PCE of 13.0% while those made up of sample ZTO-2 and ZTO-1 gave PCEs of 12.9% and 12.1%, respectively. The highest PCE of ZTO-3 is attributed to its high crystallinity, efficient charge transfer, and low-density trap states in the cell. It means that the calcination temperature has a profound impact on the crystal structure and thus the properties of the resulting ETL materials. With these preliminary results, further development and careful synthesis of the 1D ZTO NTs as ETL could be a new choice of material as an electron selective layer for the amazing PSCs.

Data Availability

All the data are included within the article and supplementary materials to support findings of this study.

Conflicts of Interest

The authors declare no conflict of interests.

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Supplementary Materials

Supplementary material file is available from the MDPI or from the author. Figure S1: simulated XRD patterns of ZnO (a) and SnO2 (b) embedded into XRD patterns of ZTO-NWs calcined at 600°C (c), 700°C (d), and 800°C (e). Figure S2: EDX spectra of as-electrospun ZTO-NWs (a) and of ZTO-NTs obtained by calcination of as-electrospun NWs at 600°C (ZTO-1) (b), 700°C (ZTO-2) (c), and 800°C (ZTO-3) (d). Figure S3: statistics of all the 12 PSCs made up of ETL layer of 1D ZTO NTs. Table S1: the corresponding average J-V parameters obtained for the PSCs of each sample of ZTO used as ETL. (Supplementary Materials)

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