Zinc-Tin-Oxide Composite Films as an Alternate Electron Transport Layer in Perovskite Solar Cell

Ramarajan Ramanathan1, Ranjith Kumar Poobalan1, Ganesh Kumar K2, Chellakumar R3, Michel Zinigrad1, and K. Ravichandran3

1Ariel University
2Saveetha School of Engineering
3University of Madras - Guindy Campus

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Abstract

Enhancing the performance of perovskite solar cells (PSCs) is one of the prime concerns of researchers worldwide. For PSC devices, it is essential to develop the individual layer efficiently and cost-effectively. This work emphasizes the possibility of employing Zn-Sn oxide-based composite materials as an alternative electron transport layer (ETL) in PSC devices. Pristine Zn2SnO4 (ZTO), composite ZTO-ZnO, and ZTO-SnO2 heterostructure-based ETL were prepared by simple solid-state calcination technique and proposed as an alternative for the TiO2 photoanode used in the PSC devices. The power conversion efficiency of the designed PSC was studied based on crystallinity, morphology, cross-section, roughness, contact angle, work function, and Raman analysis of the ETL material. TEM analysis confirms the phase pure ZTO and heterostructure formation as a function of material stoichiometry. Compared to the pristine ZTO, the ZTO-ZnO and ZTO-SnO2 composites have an enhanced PSC performance. The ZTO-SnO2 composites exhibit better band matching and charge transfer behavior with the perovskite layer than the pristine ZTO and ZTO-ZnO composites. ZTO-SnO2 ETL-based PSC device displays a maximum efficiency of 15.6 %, while ZTO-ZnO shows a maximum efficiency of 13.1 %, which is more than 10.5 % for the pristine ZTO. The results indicate that Zn2SnO4-based composites can be suitable for ETL in PSC device fabrication.

1. Introduction

The need to transition from dependency on nonrenewable energy sources to renewable energy sources and to reduce global warming is a great concern.1 The sun provides an enormous amount of energy (23000 TW) in a year compared to other renewable energy resources.1 By 2050, the world is estimated to need about 28 TW of electrical energy per year, which cannot be obtained from nonrenewable energy sources alone. In addition, the over-dependency on nonrenewable energy sources would lead to adverse effects like global warming.1 We must use technologies to trap and convert solar energy to valuable energy to solve this energy crisis. Although unlimited energy can be obtained from the sun, it requires efficient techniques to convert solar energy to electric power due to its low energy density. Photovoltaic technology has attained incredible consideration and are being utilized in various devices for the past few decades.2 Recent research reports that by 2030 the photovoltaic market is estimated to be about US$5 billion.3

Perovskite solar cell (PSC) is a cost-effective solar energy harvesting technology because of its facile way of fabrication and efficient solar power conversion compared to other technology.4 PSC technology is an effective way to develop a flexible energy source for wearable devices.5 Additionally, from the material point of view, perovskite material possesses unique properties like high absorption coefficients across the visible spectrum.4 The bandgap of the perovskite layer can be tuned by changing the material composition.4 PSC fabrication advanced initially from 2013 to 2022 through materials engineering processes.6 As a result,
researchers had to work on materials engineering, and these efforts led to the development of a single junction PSC-certified efficiency of 25.5 % under standard light illumination.\(^7\) Additionally, the PSCs have the advantage of fabricating multijunction and tandem structures with Si-based solar cells and achieving higher conversion efficiency.\(^8\) However, when it comes to commercialization, the stability of the PSC is a significant concern.\(^4\) Researchers have been working on different ways to enhance the stability of PSCs.\(^9\)

Recently, the focus on interface modification of charge transport layers, the electron transport layer (ETL) and hole transport layer (HTL), which play a pivotal role in the PSC device, has gained attention.\(^10\) The interface surface between the charge transport and perovskite layers has been chiefly studied to enhance the device’s performance, especially by modifying the charge carrier injection, extraction, recombination, and ion migration at the interfaces.\(^9\) This is evident from several reports on improving the performance of PSC devices by modifying the ETL and HTLs.\(^11\)\(^,\)\(^12\) TiO\(_2\) is the more widely used ETL material in PSC devices.\(^4\) However, TiO\(_2\) material is subjected to a post-deposition high temperature (\(\sim\)550 °C) heat treatment process to obtain the desired anatase phase formation and surface modification like mesoporous structure.\(^13\) This high-temperature preparation process restricts use in flexible devices.\(^13\) Also, the over-dependency on TiO\(_2\) for various applications has become a concern.\(^14\) Therefore, exploring non-toxic alternate ETL materials with low-temperature processing is necessary to replace the traditional TiO\(_2\) for PSC device fabrication.\(^9\) Metal oxides such as: ZnO, SnO\(_2\), WO\(_3\), SrTiO\(_3\), and Zn\(_2\)SnO\(_4\) were studied as an alternative to TiO\(_2\) ETLs in PSCs.\(^15\)\^-\(^19\) Ashok et al. investigated Zn\(_2\)SnO\(_4\) as an alternate ETL for improved power conversion efficiency (PCE) by modifying the surface features and obtained an efficiency of about 13.4%.\(^20\) Abuhelaiqa et al. studied the effect of SnO\(_2\)/TiO\(_2\) bilayer ETL to enhance charge carrier injection from the perovskite layer. They reported a considerable enhancement in Fill-Factor (FF) and open circuit voltage (Voc) values along with decreased J-V hysteresis.\(^21\) In recent years researchers also explored heterostructure-based composite materials for ETL application due to their improved charge transport properties.\(^22\) Surface modification and band gap tuning processes have promoted charge transfer by minimizing the interfacial defect using heterostructures.\(^21\) Also, heterostructure-based ETL improves the recombination process and charge transport resistance and enhances the stability of the devices.\(^23\) Sawanta et al. studied the charge carrier dynamics and transport behaviors of the perovskite layer and the top electrode by interface engineering process to improve device performance.\(^24\) Snaith et al. reported that the first few hundred hours of device performance are mainly affected by an electrical shunting mechanism of PSCs.\(^25\) The Zn-Sn-based composite heterostructure-based materials are also proposed for ETL application.\(^26\) The composite heterostructure materials exhibit better band matching with the perovskite layer. In addition to moisture resistance and chemical stability, the ZTO-based metal oxides effectively block the hole transport toward the photoanode site and improve the device’s performance.\(^20\) Moreover, their excellent optoelectronic properties lead to enhanced charge transport properties.\(^20\) This improvement comes from the heterostructure formation offering an effective charge transfer process at the perovskite-ETL interface.\(^26\)

In this work, pristine ZTO, composite ZTO-ZnO, and ZTO-SnO\(_2\) heterostructures were studied as electron transport material in PSC devices. The PCE of the fabricated PSC was evaluated using the developed ZTO-based ETLs. The performance of the fabricated PSC devices was investigated based on the crystallinity, surface, optical, and electrical transport properties of the ETL material. An accelerating aging test was carried out to identify the stability of the fabricated devices. A possible transport mechanism between the perovskite and ETL is proposed based on the obtained results. The heterostructure provides a low-cost path to manufacture highly efficient and stable PSC devices.

2. Experimental Method and Characterization

2.1. Materials and Method

Pristine ZTO, composite ZTO-ZnO, and ZTO-SnO\(_2\) heterostructures were synthesized by a simple solid-state calcination technique for ETL in PSC devices. The detailed synthesis process has been reported in our earlier work.\(^27\) In brief, the required amount of zinc and tin metallic powders were ball milled for 12 h in ethanol media to obtain homogenous composite powders. Subsequently, the obtained powders were annealed at 950 °C for 8 h in oxygen presence to obtain the final products.
2.2. Characterization

The structural and morphological properties of the prepared powder composites were characterized using a high-resolution transmission electron microscope (HR-TEM) operated at 300 kV (ThermoFisher® Titan Themis) and analyzed using Image J software. The powder samples were dispersed in absolute ethanol by ultrasonication and drop-casted on amorphous carbon-coated copper grids for TEM analysis. Raman spectroscopy analysis (LabRam HR Evolution, Horiba) was performed to study the obtained product’s vibrational properties and chemical composition. The spectra were obtained using a 532 nm laser from 100 to 800 cm\(^{-1}\). Before acquiring the spectra, calibration was performed using Si (520.7 cm\(^{-1}\)) as a reference. The cross-section and surface morphology of the developed composite films were examined using field-emission scanning electron microscopy (FESEM; Carl Zeiss Supra 40 VP) and Focussed-Ion-Beam (FIB; ThermoFisher® Helios G4-UX). The surface features and roughness of the films were characterized by atomic force microscopy (AFM; ANTON PARR) with probe radius > 10 nm and scan area of 15 x 15 \(\mu\)m\(^2\). The microscopic contact angle analyzer (OCA 50EC, Data Physics) assessed the wettability of the developed coatings in static mode. The surface work function of the films was determined using a Kelvin Probe technique (Park NX20). All measurements were performed at room temperature. All measurements were performed at room temperature.

2.3. Fabrication of heterostructure ETL-based PSC devices

The PSCs were developed in normal (n-i-p) device structure on fluorine-doped tin oxide (FTO) coated glass substrates. Pristine ZTO, and composite ZTO-ZnO, ZTO-SnO\(_2\) heterostructure materials were used as ETLs to fabricate three different PSC devices. The ETLs were prepared as follows: 2 g of each prepared material (ZTO, ZTO-ZnO, and ZTO-SnO\(_2\)) were individually mixed with 5 mL ethanol (mixer), 0.2 mL Triton X-100 (binder), and 0.5 mL acetylacetone (solvent). The mixture was ground in an agate mortar pestle for one hour to obtain a homogeneous colloidal solution. Subsequently, the colloidal mixer was coated on the FTO substrates (1.2 x 1.2 cm\(^2\)) by the doctor blade technique. Then the coated samples were annealed at 500 °C for 30 min in a muffle furnace and naturally cooled to room temperature. The thickness of these different ETL layers is optimized around 300 nm. The post-annealed photoanodes were treated with Ozone for 10 min. Then the photoanodes were transferred to a glove box (VTI- vacuum technology) to deposit the perovskite (methylammonium lead iodide, MAPI) and hole transport layer (HTL) (Spiro-MeOTAD) by a spin coating method. The MAPI and Spiro-MeOTAD precursor solutions were prepared following previous reports.\(^{20}\) The thickness of the perovskite and HTL coatings were optimized via several trials. Finally, an Au electrode of thickness 120 nm was deposited by the thermal resistive evaporation method with a suitable mask. Three series of devices were fabricated and tested following similar fabrication procedures.

2.4. PSCs Testing

The power conversion efficiency (PCE, \(\eta\)) of the different fabricated PSC devices was analyzed based on the photocurrent-voltage (J–V) characterization under AM1.5 illumination conditions using a Sol3A Class AAA Solar Simulator Measurements were conducted using a 150W Xe lamp with a light intensity of 100 mWcm\(^{-2}\). An Oriel SRC1000TC cell was used for calibration. The electrochemical impedance spectroscopy (EIS) analysis was performed using an electrochemical workstation (PARSTAT4000A AMETEK Scientific Instruments) at 10 mV in the frequency range of 0.1 Hz to 1 MHz. The photo-stability of the fabricated PSCs was investigated in indoor environments. To understand the degradation mechanism of the fabricated PSCs, the cells were stored under continuous illumination using a white LED lamp. The performance of photovoltaic devices was evaluated periodically by the protocol adopted at the international summit on organic photovoltaic stability (ISOS).\(^{28}\)

3. Results and Discussion

Transmission Electron Microscopy analysis
Figures 1(a-c) show the HR-TEM micrographs of the synthesized ZTO, ZTO-ZnO, and ZTO-SnO\textsubscript{2} powders. It can be observed that the synthesized powder samples have polyhedron structures with average crystallite dimensions above 500 nm. The composites ZTO-SnO\textsubscript{2} and ZTO-ZnO have a relatively smaller crystallite size compared to ZTO. Due to the grain boundary effect, this smaller crystallite size might contribute to the effective charge transfer process.\textsuperscript{29} Selected area electron diffraction (SAED) pattern study was conducted to investigate the crystallinity and crystal structure of the systems. Figures 1(d-f) display the obtained SAED pattern of ZTO, ZTO-ZnO, and ZTO-SnO\textsubscript{2} powder samples. The pattern confirms the polycrystalline and heterostructure formation of the samples, as reported in our earlier publication.\textsuperscript{27} The obtained diffraction pattern of the pristine ZTO sample can be indexed as (111), (012), (113), and (222) planes of the cubic spinel structure of Zn\textsubscript{2}SnO\textsubscript{4} phase (JCPDS file No: 98-001-0595).\textsuperscript{30} In the case of ZTO-ZnO composite heterostructures, in addition to the Zn\textsubscript{2}SnO\textsubscript{4} phase, diffraction patterns conforming to the (011), (110), and (013) planes of the hexagonal ZnO phase (ICSD code: 98-005-2827) can be observed.\textsuperscript{31} Moreover, the ZTO sample exhibits a highly intense bright spot indicating the higher crystalline nature. In comparison, ZTO-ZnO and ZTO-SnO\textsubscript{2} samples exhibited bright rings, with multiple spots indicating the heterostructure formation. Figure 1(g) shows the HRTEM Bragg’s pattern of the ZTO sample with the interlayer planer spacing of approximately 0.305, 0.261, and 0.241 nm conforming to the (111), (012), and (113) planes, respectively.\textsuperscript{30} Similarly, the HRTEM Bragg’s pattern (Figures 1(h, i)) of the ZTO-ZnO and ZTO-SnO\textsubscript{2} heterostructure samples shows the presence of pristine ZTO planes along with the interplanar
spacing of 0.247, 0.167 nm, and 0.243, 0.172 nm that can be attributed to the (110), and (013) planes of ZnO phase and (121), and (112) planes of SnO₂ phase, respectively. Thus, the obtained results confirm the heterostructure formation, and it also shows that the final product’s phase depends on the precursors’ stoichiometric ratio. The heterostructure formation is known to play an effective role in the charge transfer process of optoelectronic devices. Samples with larger crystallite sizes lead to larger grains with a grain boundary. A polycrystalline crystal structure has effective grain boundaries that control the mobility of charge carriers. The presence of more significant grain boundaries can affect the charge carrier transport properties due to the scattering process. As a result, the stoichiometric ratios of the precursors can be adjusted to alter the charge transport properties of the samples.

**Surface morphology analysis**

Figures 2(a-f) depict the FESEM surface morphology images and Focussed-Ion-Beam (FIB) cross-sectional images of fabricated PSC devices in planer device structure with the different ETL layers. ETL layer of all the devices exhibited the polyhedron surface morphology, which significantly impacts the performance device. The FESEM images show a significant variation in surface morphologies based on their composition ratio (Figures 2a-c). A sample with an excess of Zn content (ZTO-ZnO) has relatively bigger particles, whereas Sn excess sample (ZTO-SnO₂) shows a homogeneous particle formation with dense film formation. In the case of the pristine sample has agglomerated particle formation lead to more surface roughness which can significantly affect the charge transfer process of the devices. It has been reported that surface roughness of the thin film effectively controls the charge transfer process of the PSC device. The cross-sectional FIB images exhibited significant variations in cross-sectional film thickness due to different-sized particle formations. It is also notified that ZTO-SnO₂ film exhibited a relatively lower cross-sectional film thickness of 272 nm compared to other films. This high compactness of the film can facilitate the charge transfer process more effectively.

**Fig. 2.** (a-c) FESEM surface morphology images of fabricated ZTO, ZTO-ZnO, and ZTO-SnO₂ ETL-based perovskite solar cell devices, respectively. (d-f) FIB cross-sectional images of the ZTO, ZTO-ZnO, and ZTO-SnO₂ ETL layers used PSC devices. (d-f) AFM images of the ZTO, ZTO-ZnO, and ZTO-SnO₂ coated on FTO substrates, respectively.

The surface structure feature of ETL layers strongly depends on Zn, Sn, and O elements in their stoichiometric
ratio. However, the variation in the samples’ stoichiometric ratio can create structural and surface defects. Generally, an oxygen vacancy and/or ionic defects are the primary point defect in a metal oxide-based system. These defects also play an important role in charge transport properties.

**AFM analysis**

Figures 2(d-f) illustrate the AFM images of the 3D surface topography of the pristine ZTO, ZTO-ZnO, and ZTO-SnO$_2$ composite heterostructures coated on FTO substrates. The significant impact of the heterostructures on surface topology compared to pristine samples was observed. The surface topography changes from needle-like to granular structures for pristine ZTO to heterostructure samples. Hence, the sample with the needle-like has a relatively higher surface roughness than that with the granular structure. Figures 2(d-f) show the sample’s root mean square (RMS) roughness evaluated from the AFM data. The ZTO-SnO$_2$ sample exhibited the lowest roughness value of about 13.47 nm. ZTO and ZTO-ZnO coatings showed higher roughness values of 28.46 and 19.82 nm, respectively, due to their needle-like surface structures. The RMS roughness and average roughness ($R_{avg}$) show similar variation for different ETL samples (Figures 2(d-f)). These changes in the surface roughness might be due to the difference in the kinetics of grain growth during synthesis. Grain growth increases due to decreasing in the grain boundary effect. During the film formation, two or more larger grains might combine to form a needle-like structure, contributing to surface roughness. The higher surface roughness of the films has a great impact on the charge transport process. It is reported that carrier mobility decreases due to the increased surface roughness of the film.

**Contact angle measurement**

The variation in the climate and moisture in the atmosphere degrade the PSC devices. The contact angle measurement was carried out to examine the wettability of the coating and understand the stability of the fabricated devices upon exposure to water. Figures 3(a-c) display the contact angles of water on ZTO, ZTO-ZnO, and ZTO-SnO$_2$ samples coated over the FTO substrate. The average contact angles of ZTO, ZTO-ZnO, and ZTO-SnO$_2$ coatings were 80.4, 89.1, and 96.0°, respectively. The ZTO ETL layer has a smaller contact angle than the heterostructure-based coatings. Coatings based on ZTO-ZnO and ZTO-SnO$_2$ heterostructures demonstrated better hydrophobicity, which can prevent moisture penetration and control device degradation. Also, the hydrophobic properties of the heterostructure-based ETL layers would influence the surface charge transport of the PSC device. Generally, the TiO$_2$-based ETL layer shows relatively low charge transport behavior compared to surface modified TiO$_2$ layer due to its lower contact angle value.

![Fig. 3. Contact angles measurement of synthesized (a) pristine ZTO, (b) ZTO-ZnO, and (c) ZTO-SnO$_2$ samples coated over the FTO substrates.](image)

It is reported that the low hydrophobic behavior of the ETL layer could affect the nucleation and growth of the perovskite layer and therefore affect the charge transport/extraction behaviors. This result indicates that the heterostructure has better hydrophobicity which is valuable to the nucleation of the perovskite layer to form a uniform and dense film. Hence, the hydrophobic features of the ZTO-ZnO and ZTO-SnO$_2$ heterostructure ETLs may prevent moisture from the perovskite devices and improve the cell’s stability.

**Surface work function analysis**
The surface work function (SWF) of the ETL layer plays an essential role in the charge transfer process in PSC devices. Defining the work function of a semiconductor is the Fermi level position relative to the vacuum level (\( F = \text{Evac} - \text{EF} \)). In ETL materials, the valence band maximum and the conduction band minimum can be modified by altering the band gap of the material, which in turn changes the work function. Also, the SWF can be altered due to variations in surface electronic properties. The SWF of the different ETL layers was estimated from contact potential difference (CPD) values, which were recorded using the Kelvin probe method at room temperature. Stainless steel was used as the reference electrode (work function = 4.83 eV). The working principle of a Kelvin probe is similar to a conducting AFM tip, and the sample’s CPD (work function) is recorded for the reference electrode. The CPD of the samples scanned over the 0.1 to 1 mm² area range was recorded, and the acquired values were plotted as a contour map, as shown in Figures 4(a-c). The different ETLs show significant variation in the CPD values. The surface CPD of a coating is modified by surface properties such as roughness and homogeneity. It is seen that the ZTO sample exhibit more variation in CPD values compared to heterostructure-based devices. The estimated average SWF of the ZTO sample is 5.14 eV, ZTO-ZnO is 5.10, and ZTO-SnO₂ is 5.05 eV (refer to Figure 4d), and these values are in matched well with the previously reported values in the literature. The variation in the SWF of the different ETLs effectively controls the band matching with other layers. The suitable SWF of charge transport layers can facilitate an effective charge carrier injection/collection and the recombination process. Hence, the SWF study indicates the possible applicability of synthesized ZTO, composite ZTO-ZnO, and ZTO-SnO₂ heterostructures samples as an ETL layer in a PSC device.

Fig. 4. Contact potential difference of (a) ZTO, (b) ZTO-ZnO, and (c) ZTO-SnO₂ samples coated over the FTO substrates scanned over an area of 1 x 1 mm². (d) The average surface work function of the ZTO, composite ZTO-ZnO, and ZTO-SnO₂ heterostructure samples.

Raman analysis

The molecular vibrational modes and the surface functional group activity of the prepared pristine ZTO, composite ZTO-ZnO, and ZTO-SnO₂ heterostructure systems were investigated through the Raman spectroscopy technique. Figure 5 shows the obtained Raman active vibrational signals from the synthesized
samples, which confirms the presence of Zn$_2$SnO$_4$, ZnO, and SnO$_2$ phases. The intense peak at 669 cm$^{-1}$ is related to the typical A$_{1g}$ symmetry of Zn$_2$SnO$_4$, which is the occurrence of the symmetric stretching of the Zn–O bonds in the ZnO$_4$ tetrahedra of the cubic spinel Zn$_2$SnO$_4$. In addition, the other phonon modes at 530 cm$^{-1}$ can be assigned to the F$_{2g}$ due to the symmetric bending of O atoms in the M–O bonds of the MO$_6$ octahedra (M = Zn or Sn). The intense peak appearance at 438 cm$^{-1}$ is analogous to the E$_g$ mode related to the silent mode of Zn$_2$SO$_4$, and this peak position is also associated with the ZnO phase Raman-active mode (E$_2$). In ZnO and SnO$_2$ samples characteristic Raman active modes were absent in the pristine ZTO sample, thereby confirming the formation of a pure Zn$_2$SnO$_4$ phase. In contrast, ZTO-ZnO and ZTO-SnO$_2$ heterostructures exhibited the dominant Zn$_2$SnO$_4$ phase-related peaks and the ZnO and SnO$_2$ secondary phase peaks, respectively.

Fig. 5. Raman spectra of synthesized ZTO, ZTO-ZnO, and ZTO-SnO$_2$ heterostructure samples.

In the case of ZTO-ZnO, the vibrational mode detected near 99 cm$^{-1}$ can be attributed to the vibrations of the zinc sublattice in ZnO. The peaks at 330 cm$^{-1}$ and 379 cm$^{-1}$ are due to the second-order vibration mode (E$_{2L}$) and the A$_1$ transverse-optical (TO) mode, respectively. The peak at 332 cm$^{-1}$ is analogous to the multi-phonon scattering processes. In contrast, the E$_1$ longitudinal optical (LO) mode at 583 cm$^{-1}$ can be attributed to the oxygen defects such as vacancies or interstitials in ZnO. ZTO-SnO$_2$ exhibits the characteristic Raman peaks at 632 cm$^{-1}$ and 776 cm$^{-1}$ that can be attributed to the A$_{1g}$ and B$_{2g}$ vibration modes, respectively. The vibration occurs in the A$_{1g}$, B$_{1g}$, and B$_{2g}$ modes in the plane perpendicular to the c-axis, while in the E$_g$ mode in the direction of the c-axis. The observed Raman peaks from the ZTO-ZnO and ZTO-SnO$_2$ samples indicate the heterostructure formation in the systems. Moreover, the spectrum of the heterostructure-based samples shows a significant difference in relative intensity and width of the vibrational peaks when compared with the pristine Zn$_2$SnO$_4$ sample. This confirms the heterostructure formation of the sample compared to a pristine ZTO sample.

4. Perovskite solar cell testing

The performance of the pristine ZTO, composite ZTO-ZnO, and ZTO-SnO$_2$ heterostructures as an ETL in PSC was tested as an alternative to standard compact/mesoporous TiO$_2$ material. Figure 6 shows the schematic of the fabricated PSC devices with different ETLS and appropriate layer thickness. The standard planner device structure (FTO/(ZTO/ZTO-ZnO/ZTO-SnO$_2$)/MAPbI$_3$/spiro-MeOTAD)/Au) has been fol-
allowed for all the devices. Band matching of each layer with the perovskite active layer is pictorially represented in Figure 6b. The J-V performance of the fabricated pristine ZTO, composite ZTO-ZnO, and ZTO-SnO$_2$ heterostructures ETL-based PSC devices was compared. J-V characterization of all the devices in forward and reverse-biased conditions is shown in Figure 6c. The active light exposure area of the fabricated PSC devices is around 2×2 mm$^2$. The power of the incident light (100 mWcm$^{-2}$) is kept constant for all the devices.

Fig. 6. (a) Schematic representation of the fabricated ZTO/ZTO-ZnO/ZTO-SnO$_2$ electron transport layer used PSCs devices with appropriate film thickness, (b) Energy band diagram of the different ETL layer-based PSC device, and (c) J-V curves of the fabricated PSC devices results compared with forward and reverse bias conditions.

**Photocurrent–Voltage (J–V) curve analysis**

The power conversion efficiency ($\eta$) of pristine ZTO and ZTO-ZnO, ZTO-SnO$_2$ composite heterostructure-based PSC devices was examined using the photovoltaic parameters, open-circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$), and fill factor ($FF$). The respective photocurrent–voltage (J-V) plot is shown in Figure 6c with two different biasing conditions (forward and reverse). The estimated $V_{oc}$, $J_{sc}$, and $FF$ values are given in Table 1. Based on the obtained results of the studies on forward bias conditions, the pristine ZTO-based PSC device exhibits $V_{oc} = 0.96$ V, $J_{sc} = 11.8$ mAcm$^{-2}$, $FF = 54.2$, and $\eta = 10.5 \%$. In forward bias, it has been observed that the ZTO-ZnO composite-based device has $V_{oc} = 0.98$ V, $J_{sc} = 14.5$ mAcm$^{-2}$, $FF = 55.3$, and $\eta = 13.1 \%$. At the same time, the PSC device based on ZTO-SnO$_2$ composite structure displays $V_{oc} = 1.01$ V, $J_{sc} = 16.2$ mAcm$^{-2}$, $FF = 59.6$, and $\eta = 15.6 \%$. In the case of the reverse bias condition, all the devices show significant variation and follow a similar profile to the forward bias condition. Hence, the ZTO-SnO$_2$-based device shows a relatively improved photovoltaic behavior compared to ZTO-ZnO and pristine ZTO-based devices. Enhanced fill factor and current density were achieved due to a more surface-to-volume ratio of dense and homogeneous surface morphology of the ZTO-SnO$_2$ sample compared to the surface morphology of the ZTO-ZnO sample. Sheet-like surface morphology can promote effective charge transport at the interfaces between perovskite and ETL heterostructures. The multiband structure of the heterostructure with other layers can be another cause for improved efficiency. However, the devices’ reverse biased J-V characteristic behavior showed relatively lower performance than the forward bias condition. These variations in the J-V curve indicate the hysteresis behavior of the device. Hysteresis can be due to the presence of several interfacial defects present in the device. The stability of a PSC device is easily affected by this hysteresis behavior. The heterostructure interface decreases J-V hysteresis due to the reduction of interfacial charge accumulation and improves charge carrier extraction. Also, it is reported that the SnO$_2$/TiO$_2$-based heterostructure materials are introduced into the ETL layer for the stable change transport process to decrease the hysteresis behavior. Agresti et al, have studied the influence of light
intensity on the current density in the n-i-p devices structure.\textsuperscript{59} They reported that the J\textsubscript{sc} becomes higher in the presence of graphene-SnO\textsubscript{2} heterostructure, which can reduce the hysteresis and enhance the charge extraction at the interface. PSC device based on standard TiO\textsubscript{2} ETL has Voc of 0.99 V, J\textsubscript{sc} of 20.0 mA cm\textsuperscript{-2}, FF of 73.0, and \textgamma of 15.0 \%.\textsuperscript{13} These values are relatively higher than our pristine ETL-based device since pristine ETL-based device exhibits lower photovoltaic performance due to their low FF value. The low FF can facilitate the charge carrier recombination more effectively and decrease the current density.\textsuperscript{59}

The higher sheet resistance of the photoanode material is also one of the causes of yielding a very lower photocurrent density. The fabricated ZTO-based device result is compared with other heterostructure-based devices reported in the literature and summarised in Table 1.\textsuperscript{23,34,37,38,54–58}

Table 1 Photovoltaic performance of pristine ZTO and composite ZTO-ZnO and ZTO-SnO\textsubscript{2} heterostructure-based PSC devices with other reported heterostructure-based PSC devices.

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<th>Ref.</th>
<th>(\eta) (%)</th>
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<th>J\textsubscript{sc} (mA cm\textsuperscript{-2})</th>
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<td>25.4</td>
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<td>SnO\textsubscript{2}-ZnO</td>
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<td>ZnO-SnO\textsubscript{2}</td>
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<td>80.15</td>
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<td>1.11</td>
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<td>SnO\textsubscript{2}/BaSnO\textsubscript{3}</td>
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Charge transport mechanism of PSC device
The charge transport mechanism of the fabricated PSC devices can be explained based on their surface structure and multiband structure properties. The pristine ZTO ETL-based PSC device exhibits a charge transport mechanism similar to a TiO$_2$ layer. In a PSC device, sunlight illumination leads to the excitation of the free carriers in the perovskite (MAPbI$_3$) absorber from the HOMO to the LUMO level. During this process, these photo-excited charge carriers (exciton) separate in a fraction of a second [46]. Subsequently, the separated charges are collected by the respective electrodes. The power conversion efficiency of the PSC device strongly depends on the properties of the charge transport layers (CTL), like structure, surface morphology, and charge carrier transport process of the ETL and HTL. CTLs must control the charge carrier injection/extraction, recombination, and diffusion process more effectively. The ETL/HTL layers are in contact with the perovskite layer. Therefore, a suitable band matching of the ETL/HTL can lead to better performance. In the case of a composite heterostructure-based device, the charge transport mechanism is different from the pristine ZTO-based PSC device. In a pristine ZTO ETL-based device, the charge carrier transfer from perovskite to ZTO ETL is based on the single charge transfer process. Figures 7(a, b) shows the cross-section schematics of the ZTO ETL-based PSC device structure and the energy band structure with the charge transfer process of the device. Effective electron carrier transport occurs from the HOMO level of the perovskite into the ETL conduction band ($E_C$) during light illumination. Hence, the ETL charge transport properties effectively control the charge carrier collection of the photoanode. The surface behavior of the ETL plays a vital role in the charge transfer process. The compact structure of the pristine ZTO sample has relatively high charge transport resistance due to interfacial defects that affect carrier mobility. Also, a large amount of generated charge carriers from the perovskite absorber is accumulated at the interface due to the low carrier transfer ability of the ETL layer. Such accumulation of charge carriers at the interface can facilitate recombination processes. Therefore, the surface modification of the ETL influences the transport mechanism of the device. The heterostructure formation of the ZTO-ZnO and ZTO-SnO$_2$ composites offers a multi-charge transfer process due to their multiband structure. Figures 7(c, d) and (e, f) show the cross-section schematics of the ZTO-ZnO and ZTO-SnO$_2$ ETL-based PSC device and the corresponding energy band structure with the charge transfer process. In heterostructure-based devices, charge transport occurs in two ways; transfer via the ZTO phase and second is through the ZnO/SnO$_2$ phase. For example, in the ZTO-SnO$_2$ heterostructure-based device, the band matching happened two ways from the perovskite layer. Band matching between the perovskite-ZTO and perovskite-SnO$_2$ phase
offers two-way charge transport. Multi transfer process of this heterostructure effectively controls the charge carrier accumulation at the interface and hence regulates the recombination process. Also, it can be noted that the ZTO-SnO$_2$ ETL-based PSC device exhibits better performance compared to the ZTO-ZnO-based device due to its sheet-like surface morphology.

Fig. 7. Schematic representation of pristine ZTO (a, b), ZTO-ZnO (c, d), and ZTO-SnO$_2$ (e, f) heterostructure-based ETLs used PSCs device structures and with appropriate energy band diagram with different ETL layer.

Transferring the charges in dense surface structures is relatively more accessible than in agglomerated surface structures. Because, the mobility of the charge carrier is affected by agglomerated surface structure, whereas in dense surface structures, charge transfer occurs more effectively. Hence, the heterostructure-based device has an advantage over the pristine device due to its effective charge transfer process.

Study of electrochemical impedance spectroscopy (EIS)

The charge transfer mechanism in the pristine ZTO and ZTO-ZnO, ZTO-SnO$_2$ composite heterostructure-based PSC devices was investigated as a function of frequency using electrochemical impedance spectroscopy (EIS). Figures 8 (a and b) show the obtained Nyquist plots of the different ETLs, and the corresponding equivalent circuits are shown in Figures 8 (c and d). The high-frequency region of the real axis denotes the sheet resistance (Rs) between the photoanode and perovskite interface. This low-frequency region denotes the diffusion resistance (R1) at the interface between the counter electrode and perovskite. The constant phase elements (Q) further analyzed the charge transport and diffusion resistance behavior. The equivalent circuit of the EIS analysis was calculated using the EC-lab software. The Nyquist plot shows that all the devices exhibit a single semicircle. The higher frequency region from 1 MHz to 1 kHz shows a relatively smaller semicircle indicating the sheet resistance (Rs) of the pristine and heterostructure-based photoelectrodes. The second larger semicircle in the lower frequency, from 1 kHz to 1 Hz, presents more charge transport resistance at the perovskite-photoelectrode interface. Injection and collection of charge carriers are affected by higher charge transport resistance. However, no diffusion resistance is formed between the counter electrode and perovskite layer, indicating the effective charge carrier collection. It is identified that the charge transport properties of the PSCs significantly changed with heterostructure. The modified surface structure of the composite phase leads to decreases in the charge transport resistance and diffusion resistance at the interface. The device fabricated with heterostructure shows low sheet and charge transfer resistance, which might cause improved PCE compared to the pristine ZTO sample.
The pristine ZTO ETL-based PSC device exhibits a much higher $R_1$ value of 8734 Ω, leading to a decline in carrier mobility. The ZTO-based device shows a high Q value which indicates a relatively low charge collection at the counter electrode side. Whereas the Q values of the heterostructure-based devices are lower, they exhibit improved charge carrier collection at the counter electrode. However, we do not deny that the lower charge transport resistance identified from the second semicircle region facilitates more charge carrier recombination, which is confirmed by lower Q values. The Bode plot provides an insight into the charge transport process more precisely. Notably, the Bode plot provides the lifetime of charge carriers using the following relation ($\tau = 1/2pf_{\text{max}}$, where $f_{\text{max}}$ is the highest cut-off frequency. Figure 8(e) illustrates the Bode plots of the pristine ZTO and ZTO-ZnO, ZTO-SnO$_2$ composite heterostructure-based PSC devices. From the plot, it can be estimated that the highest cut-off frequency of ZTO is 794 Hz, ZTO-ZnO is 251 Hz, and ZTO-SnO$_2$ is 100 Hz. The determined lifetime of the charge carriers for the pristine ZTO, ZTO-ZnO, and ZTO-SnO$_2$ heterostructure ETL-based devices is 1.2 ms, 3.9 ms, and 10 ms, respectively. The longer lifetime of the charge carriers in heterostructure-based devices effectively suppresses the charge carrier recombination process. ZTO-based devices also have a shorter lifetime compared with other devices. As a result, carrier density has decreased, and recombination resistance has been reduced at the interface between the photoanode and electrolyte. However, decreasing interface resistance is one of the effective techniques to enhance the charge transfer process and avoid the recombinational process. It was primarily based on minimizing the charge carrier trap, and this trap is responsible for reducing perovskite efficiency. Thus, the obtained J-V curves and EIS measurements provide many hints for further improving the efficiency of the PSC device.

**Stability analysis**
Figure 9 shows the stability analysis of the pristine ZTO and hybrid ZTO-ZnO, ZTO-SnO$_2$ composite-based PSC devices. The ISOS-L-1 standard protocol was followed to explore the stability of the devices. The devices were illuminated by a lamp rated at 100 mWcm$^{-2}$, at an ambient temperature and humidity of 24 ± 4 °C and 45 ± 5%, respectively. We measured the photovoltaic performance of the fabricated devices periodically and kept them under continuous illumination at all times. All the fabricated PSC devices decreased stability in the presence of light, similar to the observations of Huang et al.\textsuperscript{64}

![Figure 9](image)

**Fig. 9.** (a) Stability egging test for the pristine ZTO, and composite ZTO-ZnO, ZTO-SnO$_2$ heterostructure-based PSC devices; open-circuit voltage, (b) short circuit current, (c) fill factor, and (d) power conversion efficiency.

Under continuous lamp illumination, we find significant decreases in the PSCs devices’ photovoltaic performance (Figures 9(a-d)). Pristine ZTO-based PCE devices diminished with time due to decreased Jsc and FF levels. In the case of ZTO-ZnO and ZTO-SnO$_2$ heterostructure-based PSCs devices, a relatively low degradation was observed compared to the pristine ZTO-based device. Also, the electrode materials have not deteriorated strongly with time, as the Voc appeared to show low degradation. Degradation of the active
layer and the device constituents was the primary cause of the performance degradation. A reduction in Jsc and FF can be attributed to the photodegradation of perovskites. Photodegradation of organo-metal halide perovskite semiconductors is observed, although the degradation rate varies with the intensity of the incident light. Decomposition of perovskites into constituents results in their loss of optical and electrical properties. These results suggest that the photoanode side is relatively stable under the white LED lamp illumination. In the long run, the decline in Voc and FF overtook the increase in Jsc, reducing PCE. Figure 10 shows the visible degradation of the fabricated PSC devices. The photographs were taken as fabricated after 10-, 20-, and 30-day time intervals. It is identified that the fabricated PSC devices have a maximum lifetime of less than a month. However, making an encapsulation layer on top of devices can aid in improving the lifetime of the devices to some extent. Thus, the obtained stability results indicate the potential application of ZTO-ZnO and ZTO-SnO₂ heterostructure as ETL materials for PSC device fabrication and a further improvement in the device performance.

**Fig. 10.** Visible degradation of the pristine ZTO, and composite ZTO-ZnO, ZTO-SnO₂ heterostructure-based PSC devices; (a) as-fabricated, (b) after 10 days, (c) after 20 days, and (d) after 30 days.

**Conclusion**

Pristine ZTO, composite ZTO-ZnO, and ZTO-SnO₂ heterostructure systems were prepared by simple solid-state calcination technique and employed as an ETL for PSC devices. The HR-TEM analysis confirms the crystallinity and its dependence on the stoichiometric ratio of the precursors. Synthesized samples exhibited polyhedron surface morphology, which significantly impacts the change transport process of the PSC devices. The suitable surface work function of an ETL can facilitate an effective charge carrier injection/collection, as well as control the recombination process. Perovskite solar cells fabricated using composite ZTO-ZnO and ZTO-SnO₂ electron transport layers exhibited enhanced power conversion efficiency due to the multiband charge transport mechanism compared to the ZTO-based devices. Moreover, the PSC device based on ZTO-SnO₂ exhibited a maximum efficiency of 15.6%, whereas the ZTO-ZnO exhibited a maximum efficiency of 13.1%, which is relatively higher than the 10.5 % for pristine ZTO. Hence, the results suggest that ZTO-SnO₂ heterostructure can be a potential ETL material for constructing stable PSC devices.

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