Combustion Processed Nickel Oxide and Zinc Doped Nickel Oxide Thin Films as a Hole Transport Layer for Perovskite Solar Cells

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Abstract: Combustion processed nickel oxide (NiOₓ) thin film is considered as an alternative to the sol-gel processed hole transport layer for perovskite solar cells (PSCs). In this paper, NiOₓ thin film was prepared by the solution–combustion process at 250 °C, a temperature lower than the actual reaction temperature. Furthermore, the properties of the NiOₓ hole transport layer (HTL) in PSCs were enhanced by the incorporation of zinc (Zn) in NiOₓ thin films. X-ray diffraction and X-ray photoelectron spectroscopy results revealed that the formation of NiOₓ was achieved at lower annealing temperature, which confirms the process of the combustion reaction. The electrical conductivity was greatly improved with Zn doping into the NiOₓ crystal lattice. Better photoluminescence (PL) quenching, and low PL lifetime decay were responsible for better charge separation in 5% Zn doped NiOₓ, which results in improved device performance of PSCs. The maximum power conversion efficiency of inverted PSCs made with pristine NiOₓ and 5% Zn-NiOₓ as the HTL was 13.62% and 14.87%, respectively. Both the devices exhibited better stability than the PEDOT:PSS (control) device in an ambient condition.

Keywords: perovskite solar cells; hole transport layer; nickel oxide; combustion reaction; zinc doping; low temperature

1. Introduction

Researchers have promised that the perovskite solar cells (PSCs) could soon be released as a commercial product in the near future [1,2]. PSCs have become a hot topic among researchers because of their superior optoelectronic properties [3–7]. The ease of device fabrication kept this device in the limelight among other next-generation solar cells [8]. In inverted PSCs, the most commonly used HTL is poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT:PSS); it can exhibit better device performance at lower processing temperature, but the stability of the device is worse because of its hygroscopic and acidic nature [9]. Replacing the organic PEDOT:PSS as hole transport layer (HTL) in perovskite solar cells with inorganic p-type metal oxide materials is an effective way to improve the device’s performance and stability [10]. The basic requirement of the HTL is to be highly transparent throughout the solar spectra, good electrical conductivity, and a high work function for effective charge transport [11]. Among the various metal oxides, nickel oxide (NiOₓ) is an ideal candidate for this special purpose [11–15]. In physical vapor deposition techniques, these metal oxides require special processing conditions, including a vacuum environment and heat treatment, etc. [16]. In contrast, solution-processed NiOₓ has a variety of options that does not require any special processing conditions [17]. The preparation of the NiOₓ HTL by the sol-gel method requires it to be annealed at a high temperature above 300 °C to achieve high performance from the PSCs [18,19]. This high-temperature process increases the cost of device fabrication at an industrial scale and
restricts the substrate options [20]. Low-temperature processing or crystallization of metal oxide thin films has become popular research in the last few years [21].

During the solution process, the temperature of NiO\textsubscript{x} must be raised to a minimum of 275 °C to commence converting the Ni precursor into NiO\textsubscript{x} [22,23]. Another means of implementing the sol-gel process is to employ combustion chemistry to create solution-processed transition metal oxide (TMO) films with high crystallinity without using high temperatures [24–27]. The unique properties of self-generated energy and exothermic reactions permit the use of lower processing temperatures, replacing sol-gel endothermic reactions that require high levels of thermal energy to enable the formation of TMO lattices and the removal of any organic impurity. Combustion chemistry has been employed for the successful preparation of a variety of TMO thin films and at lower temperatures than sol-gel technique. In PSCs, the combustion processed NiO\textsubscript{x} was first reported by Bai et al. It was annealed at 175 °C, with glycine as a fuel [28]. Later, Jen et al. replaced glycine with acetylacetone and developed NiO\textsubscript{x} HTL at 150 °C [24]. Chang et al. used a similar method but annealed at 250 °C and achieved a PCE of 20.2% for mixed cation PSCs [29]. Recently, Cai et al. studied the effect of various concentrations of fuel in the combustion processed NiO\textsubscript{x} HTL for PSCs [30]. Zhang et al. improved the efficiency with a two-step coating of mixed perovskites [31]; however, the intrinsic electrical conductivity of NiO\textsubscript{x} is very low, which restricts the device’s performance. Metal ion doping into NiO can improve its electrical conductivity even at lower annealing temperatures. This has been successfully used in sol-gel processed NiO\textsubscript{x} doped with various metal ions such as Ag [32], Cs [23], Y [33], K [34], Co [35], etc. Even in the combustion reaction, Cu doped NiO\textsubscript{x} thin film was successfully developed as the HTL in inverted PSCs [24]. Influenced by this idea, we adopted this technique to prepare zinc doped NiO\textsubscript{x} thin film as the HTL in PSCs.

Here, we report the successful development of NiO\textsubscript{x} and Zn doped NiO\textsubscript{x} at a relatively low annealing temperature as the HTL for inverted PSCs. It was achieved by utilizing combustion chemistry, which significantly reduces its actual reaction temperature compared with traditional sol-gel methods. The effect of Zn doping in NiO\textsubscript{x} was studied by investigating the structural, morphological, and optoelectronic properties and the carrier dynamics of the films. The photovoltaic performance was analyzed and the average PCE of NiO\textsubscript{x} and 5% Zn doped NiO\textsubscript{x} was 13.52% and 14.67%, respectively. Overall, the device performance was significantly improved with Zn doping in the NiO\textsubscript{x} HTL.

2. Materials and Methods

2.1. Synthesis of NiO\textsubscript{x} and Zn Doped NiO\textsubscript{x} Thin Films

Preparation of the NiO\textsubscript{x} precursor solution took place as previously described [25] with certain adaptations. Briefly, 0.145 g of nickel nitrate hexahydrate underwent dissolution in 5 mL of 2-methoxyethanol; this solution underwent stirring for 30 min until complete dissolution of the precursor was achieved. This solution was then supplemented with 50 µL of acetylacetone and stirring was maintained overnight. Following this, a polytetrafluoroethylene (PTFE) syringe filter was used to filter the solution. To deposit the thin film, the precursor solution underwent spin coating onto a clean fluorine-doped tin oxide (FTO) substrate for 45 s at 2500 rpm. A hotplate was then used to anneal the spin-coated films in the air for one hour at 250 °C. These prepared films were then given UV-ozone treatment for five minutes prior to being placed in the glovebox. To make the doping successful, zinc nitrate hexahydrate was used to replace the variety of mole percentages of nickel precursors.

2.2. PSC Device Fabrication

An ultrasonic bath was employed to clean the laser patterned FTO substrates in sequence with detergent, acetone, and IPA for 10 min. Subsequently, drying of the substrate occurred employing a nitrogen gun and then exposed to ultraviolet (UV)-ozone treatment (15 min). A spin coater was used to deposit the NiO\textsubscript{x} and Zn-NiO\textsubscript{x} thin films with annealing occurring at 250 °C as previously described. Following cooling, these substrates were then
placed in the glovebox. Following this, production of a perovskite active layer occurred by dissolving 1.4 M methylammonium iodide (MAI) and 1.4 M lead iodide (PbI$_2$) in γ-butyrolactone (GBL) and dimethyl sulfoxide (DMSO) (7:3). This solution was then subjected to overnight stirring inside the glove box at 60 °C. A 0.45-µm PTFE syringe filter was used to filter the solution before deposition. The solution underwent spin coating onto FTO/NiO$_x$ substrates (1000 rpm/15 s and 5000 rpm/25 s). Toluene was employed as an anti-solvent and was added precisely five seconds prior to completing the second stage. Following this, the substrates were annealed for 10 min at 100 °C. Preparation of the electron transport layer (ETL) was achieved in the following manner: 20 mg/mL of phenyl-C$_6$1-butyric acid methyl ester (PCBM) in 1,4-dichlorobenzene (DCB) underwent spin-coating onto the substrates at 2000 rpm for 30 s, and a saturated solution of bathocuproine (BCP) in methanol was dynamically spin-coated at 6000 rpm for 30 s. Lastly, thermal evaporation of an Ag electrode was achieved employing a metal mask.

2.3. Characterization

Characterization of the NiO$_x$ and Zn-NiO$_x$ thin films was undertaken implying X-ray diffraction (XRD) techniques using a Rigaku D/Max-2500V system (Rigaku Corp, Tokyo, Japan). The surface morphology and topography underwent inspection using a field emission scanning electron microscope (FESEM) (morphology) (JEOL JSM-7000F, JEOL Inc., Tokyo, Japan) and an atomic force microscope (AFM) (AutoProbe CP, Thermomicroscopes, Sunnyvale, CA, USA) (topography). Elemental composition analysis was undertaken using X-ray photoelectron spectroscopy (XPS) (Thermo K-Alpha, Thermo Fisher Scientific, Inc., Waltham, MA, USA). Measurement of UV-visible absorption and transmission spectra was undertaken employing a UV-Vis spectrophotometer (Hitachi U 3900, Tokyo, Japan). Measurements of steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) were undertaken employing a solid-state laser (λ = 405 nm, PDL 800-D, PICOQUANT, Berlin, Germany) equipped with a laser scanning confocal microscope and a spectrometer equipped with a thermoelectrically cooled charge-coupled detector (for PL) and a time-correlated single-photon counting detector (TCSPC) (for TRPL). Analysis of the PSC device performance was undertaken employing current density–voltage (J–V) curves, external quantum efficiency (EQE), and electrochemical impedance spectroscopy (EIS). Measurement of PSC J–V characteristics was undertaken using a 1 sun illumination (AM 1.5 G spectrum) employing a 550 W Xenon lamp solar simulator (Sun 3000 Class AAA, Abet Technologies, Milford, MA, USA).

3. Results and Discussion

As mentioned, the NiO$_x$ and Zn doped NiO$_x$ thin films were prepared using the combustion spin-coating technique, and the films were annealed at a lower temperature (250 °C) than the sol-gel technique. The inverted PSCs with an architecture of FTO/NiO$_x$/MAPbI$_3$/PCBM/BCP/Ag were fabricated, as shown in Figure 1a. Figure 1b,c show the energy level diagram of inverted PSCs and the photograph of the fabricated device. The current density–voltage (J–V) curves of the PSCs made with NiO$_x$ and Zn doped NiO$_x$ HTL are shown in Figure 2a. The device made with 5% Zn-NiO$_x$ exhibited the best PCE of 14.87% versus pristine NiO$_x$ (13.62%). The detailed device parameters of the PSCs made with both the NiO$_x$ and Zn doped NiO$_x$ thin films annealed at 250 °C are summarized in Table 1. The results were reproducible and the average values were calculated from eight best devices from different batches. The devices performed well with NiO$_x$ HTL annealed at a relatively lower temperature. The current density (Jsc) of the pristine NiO$_x$ device was improved with an increase in Zn doping and may be due to an improvement in the electrical conductivity of HTL. The lower doping concentration of 2% Zn-NiO$_x$ exhibited relatively similar efficiency with a minimal increase in Jsc. The device made with 5% Zn-NiO$_x$ showed improved Jsc and minimal reduction in FF and Voc. There was no significant change in Voc perhaps because there were no major changes in valence band edge position after Zn doping with lower concentration. The Voc and FF
were decreased with further increasing of Zn concentration (10%) into NiO$_x$ HTL. It may be due to the higher Zn$^{2+}$ dopant concentration induce the transformation of p-type to n-type NiO$_x$, which results in poor device performance [36]. The $J$–$V$ characteristics revealed that the current flow across the device was increased due to the Zn doping into NiO$_x$. The external quantum efficiency (EQE) spectra of the devices made using NiO$_x$ and Zn doped NiO$_x$ HTL are shown in Figure 2b. The devices made with NiO$_x$ and Zn doped NiO$_x$ films displayed satisfactory results throughout the entire visible region. In comparison, a similar kind of EQE curve was observed in all the devices. The increment in the EQE value for the 5% Zn-NiO$_x$ device versus the pristine NiO$_x$ device indicates the improvement in device performance. These results agreed with the $J$–$V$ characteristics results. Therefore, the pristine NiO$_x$ and 5% Zn-NiO$_x$ were chosen for further detailed studies.

Figure 1. (a) Device architecture, (b) energy level diagram of inverted PSCs, and (c) photograph of the fabricated device.

Figure 2. (a) $J$–$V$ characteristics and (b) EQE spectra of PSCs made with NiO$_x$, Zn-NiO$_x$, and PEDOT: PSS (control) HTLs.
Table 1. Summary of device performance of the PSCs made with NiO<sub>x</sub>, Zn-NiO<sub>x</sub>, and PEDOT:PSS (control) HTLs.

| HTL            | Voc (V) | Jsc (mA/cm<sup>2</sup>) | FF | PCE (%) | Rs (kΩ/cm<sup>2</sup>) | R<sub>sh</sub> (kΩ/cm<sup>2</sup>) |
|----------------|---------|--------------------------|----|----------|--------------------------|----------------------------------|
| NiO<sub>x</sub> |         |                          |    |          |                          |                                  |
| Average        | 1.047 ± 0.01 | 17.47 ± 0.16            | 0.74 ± 0.01 | 13.52 ± 0.10 | 6.9                     | 2.59                             |
| Best           | 1.051               | 17.39                  | 0.75         | 13.62                  |                                        |
| 2% Zn-NiO<sub>x</sub> |         |                          |    |          |                          |                                  |
| Average        | 1.045 ± 0.02 | 17.87 ± 0.42            | 0.73 ± 0.01 | 13.61 ± 0.15 | 6.8                     | 1.87                             |
| Best           | 1.046               | 18.02                  | 0.73         | 13.76                  |                                        |
| 5% Zn-NiO<sub>x</sub> |         |                          |    |          |                          |                                  |
| Average        | 1.046 ± 0.01 | 19.26 ± 0.62            | 0.73 ± 0.02 | 14.67 ± 0.20 | 6.9                     | 1.78                             |
| Best           | 1.046               | 19.67                  | 0.72         | 14.87                  |                                        |
| 10% Zn-NiO<sub>x</sub> |         |                          |    |          |                          |                                  |
| Average        | 0.942 ± 0.01 | 20.17 ± 0.19            | 0.57 ± 0.01 | 10.77 ± 0.13 | 9.2                     | 0.19                             |
| Best           | 0.949               | 20.28                  | 0.57         | 10.90                  |                                        |
| Control        |         |                          |    |          |                          |                                  |
| PEDOT:PSS      | 0.905 ± 0.02 | 17.91 ± 0.46            | 0.68 ± 0.01 | 11.21 ± 0.22 | 7.5                     | 0.45                             |
| Average        | 0.925               | 18.03                  | 0.69         | 11.43                  |                                        |

Apart from the performance provided by the HTL, it has a strong impact on the stability of PSCs. This study performed an investigation on the stability of unencapsulated devices stored in dark conditions at room temperature with about 40% of relative humidity. Figure 3a, b show the stability graph and the photograph of PSCs based on PEDOT:PSS, NiO<sub>x</sub>, and 5% Zn-NiO<sub>x</sub> HTLs, respectively. It can be seen that the device made with PEDOT:PSS degrades fast and lost its total efficiency in 4 days. The fast degradation of perovskite happened at the active area of PEDOT:PSS device was due to the reaction of Ag electrodes with volatile degradation products from the perovskite and ion migration. The acidic and hygroscopic nature of PEDOT:PSS degrades the MAPbI<sub>3</sub> into PbI<sub>2</sub> and releases its by-products in the form of I<sub>2</sub>, CH<sub>3</sub>I, and HI, which can readily react with Ag to form AgI [37]. By contrast, the rate of degradation is usually very slow in NiO<sub>x</sub> based PSCs. Both NiO<sub>x</sub> and 5% Zn-NiO<sub>x</sub> based PSCs have retained 80% of their initial efficiency after 108 h.

Figure 3. (a) Stability graph and (b) photograph of the PSCs made with NiO<sub>x</sub>, 5% Zn-NiO<sub>x</sub>, and PEDOT: PSS (control) HTLs without encapsulation (under ambient air at room temperature for 4 days).

The XRD pattern of NiO<sub>x</sub> and 5% Zn-NiO<sub>x</sub> thin films on glass substrate and annealed at 250 °C is shown in Figure 4. The cubic structure of NiO has peaked at 37.3°, 43.3°, and 62.9°, corresponding to the hkl value of (111), (002), and (022), respectively. This can be observed in both NiO<sub>x</sub> and 5% Zn-NiO<sub>x</sub> thin films. It clearly shows that thin films had...
poor polycrystalline nature but significantly higher crystallinity than the film annealed at 250 °C in the sol-gel process in previous work [38], and similar kinds of results were reported [29,33]. This result shows that the formation of NiO\textsubscript{x} occurred below the actual reaction temperatures. It confirms the process of the combustion reaction.

X-ray photoelectron spectroscopy (XPS) was used to analyze the elemental composition of the NiO\textsubscript{x} and 5% Zn-NiO\textsubscript{x} thin films annealed at 250 °C. Figure 5a,b illustrate the XPS spectra for the Ni 2p and O 1s core levels of NiO\textsubscript{x} and 5% Zn-NiO\textsubscript{x} thin films. The NiO\textsubscript{x} peaks primarily comprise Ni\textsuperscript{2+} and Ni\textsuperscript{3+} states. At 861 eV, there is a satellite peak attributable to the NiO\textsubscript{x} shake-up process. The deconvoluted peak at 854 eV corresponds with NiO (Ni\textsuperscript{2+}), 856 eV with Ni\textsubscript{2}O\textsubscript{3} (Ni\textsuperscript{3+}), and 857 eV with NiOOH [39]. Similarly, the O 1s spectra has three peaks, the deconvoluted peak at 529 eV corresponding with NiO (Ni\textsuperscript{2+}), 531 eV with Ni\textsubscript{2}O\textsubscript{3} (Ni\textsuperscript{3+}), and 533 eV with NiOOH. Generally, Ni\textsuperscript{3+} states cause p-type conductivity, indicating that quasi-localized holes have been formed around the lattice position’s Ni\textsuperscript{2+} vacancies [40]. There is a higher Ni\textsuperscript{3+} state with 5% Zn-NiO\textsubscript{x} versus pristine NiO\textsubscript{x} as seen in the spectra of Ni 2p and O 1s. This was due to the replacement of the Ni atom with Zn in the crystal lattice. Zn incorporation could alter the electronic structure of NiO\textsubscript{x}. The increase in the Ni\textsuperscript{3+} state denotes the presence of more Ni vacancies. The higher Ni\textsuperscript{3+}/Ni\textsuperscript{2+} ratio in 5% Zn-NiO\textsubscript{x} indicates the reduction in ionization energy of the Ni vacancies and increased hole density [41]. The successful incorporation of Zn in NiO\textsubscript{x} can be seen in Figure 5c,d. The divalent state of Zn peaks of 2p\textsubscript{3/2} and 2p\textsubscript{1/2} were observed at 1021 eV and 1045 eV, respectively.
incorporation of Zn in NiO\textsubscript{x} can be seen in Figure 5c, d. The divalent state of Zn peaks of 2\textit{p}\textsubscript{3/2} and 2\textit{p}\textsubscript{1/2} were observed at 1021 eV and 1045 eV, respectively.

Figure 5. XPS spectra of (a) Ni 2\textit{p}, (b) O 1\textit{s}, (c) Zn 2\textit{p}, and (d) survey scan for NiO\textsubscript{x} and 5% Zn-NiO\textsubscript{x} thin films.

The surface morphology of NiO\textsubscript{x} and 5% Zn-NiO\textsubscript{x} thin films annealed at 250 °C was analyzed by field emission scanning electron microscopy (FESEM). The top view of the FESEM image and energy-dispersive X-ray spectroscopy (EDS) results for NiO\textsubscript{x} and 5% Zn-NiO\textsubscript{x} thin films are shown in Figure 6a,b, respectively. Both films exhibit similar morphology and better coverage without any voids on FTO substrate. A fine layer of these thin films is clearly seen on the FTO, and the 5% Zn doped NiO\textsubscript{x} film looks somewhat smoother than the pristine film. This observation was confirmed by AFM results. EDS results confirmed the presence of Zn in NiO\textsubscript{x} thin films. The atomic composition ratio was closely related to stoichiometry. Figure 6c shows the cross-sectional FESEM image of the device. The device was fabricated with an architecture of FTO/NiO\textsubscript{x}/MAPbI\textsubscript{3}/PCBM/BCP/Ag. All layers can be well distinguished from the cross-sectional FESEM image.
Figure 6. FESEM image and EDS result of (a) NiO$_x$ and (b) 5% Zn-NiO$_x$ thin films, (c) cross-sectional FESEM image of the device.

Figure 7a,b show the AFM images of NiO$_x$ and 5% Zn-NiO$_x$ thin films annealed at 250 °C. The films exhibited similar smooth and compact surface topography on FTO substrates for both NiO$_x$ and 5% Zn-NiO$_x$. The root-mean-squared (RMS) roughness values of NiO$_x$ and 5% Zn-NiO$_x$ are 37.1 nm and 33.9 nm, respectively. The roughness of the film decreased with Zn doping because of the tendency of ZnO to form a crystalline nature at the lower annealing temperature [42]. This result is well-matched with other literature reports [41,43].
The impact of Zn doping on NiO\textsubscript{x} thin-film electrical conductivity was examined by measuring the current–voltage (I–V) characteristics of the hole-only device (FTO/NiO\textsubscript{x}/Ag). Figure 9 shows the I–V curves for the hole-only devices based on NiO\textsubscript{x} and 5% Zn-NiO\textsubscript{x} thin films that underwent annealing at 250 °C. This demonstrates that there are improvements in electrical conductivity when Zn doping is applied as the dopants have a high level of affinity with electrons.

Figure 8a illustrates the transmittance spectra for NiO\textsubscript{x} and 5% Zn-NiO\textsubscript{x} thin films that underwent annealing at 250 °C. Each film showed a high transmittance level within the visible spectrum range, with average values being above 80%. Figure 8b illustrates the graph of absorption coefficient as a function of excitation energy; calculation of the optical bandgap value was undertaken through an additional plot of the linear portion of (αhν)^2 to the x-axis employing a Tauc plot [44]. This bandgap value (E\textsubscript{g}) was around 3.95 eV both for NiO\textsubscript{x} and 5% Zn-NiO\textsubscript{x} thin films. Very high HTL transmittance is required for minimization of incident light loss for enhancement of the light that reaches the perovskite layer. Any variations in optical properties when Zn is incorporated into NiO\textsubscript{x} are minimal due to lower film thicknesses (~20 nm).
The impact of Zn doping on NiO\textsubscript{x} thin-film electrical conductivity was examined by measuring the current–voltage (I–V) characteristics of the hole-only device (FTO/NiO\textsubscript{x}/Ag). Figure 9 shows the I–V curves for the hole-only devices based on NiO\textsubscript{x} and 5\% Zn-NiO\textsubscript{x} thin films that underwent annealing at 250 °C. This demonstrates that there are improvements in electrical conductivity when Zn doping is applied as the dopants have a high level of affinity with electrons.

![Figure 9. I–V characteristics of hole-only devices made with NiO\textsubscript{x} and 5\% Zn-NiO\textsubscript{x} thin films.](image)

Charge extraction and non-radiative recombination at the perovskite and HTL interface was evaluated using steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL). Figure 10a,b show the PL spectrum and TRPL profile for perovskite films over NiO\textsubscript{x} and 5\% Zn-NiO\textsubscript{x} thin films. The offset in the valence band edge plays a major role in charge recombination. Mismatches in the valence band edge between HTL and perovskite layer leads to more recombination at the interface and results in lowering of the Voc [45]. PL exhibited by the perovskite layer was significantly reduced by the HTLs. Noteworthy levels of PL quenching were shown with both types of film, demonstrating high levels of efficiency of charge extraction for Zn doped NiO\textsubscript{x} thin films. These findings accord with previous research [43]. The TRPL profile was measured employing time-correlated single-photon counting. Calculation of the PL lifetime decay was undertaken using tail fit with a biexponential decay function, as shown in Equation (1),

\[ y = y_0 + A_1 e^{-(x-x_0)/\tau_1} + A_2 e^{-(x-x_0)/\tau_2} \]  

where \( \tau_1 \) represents the photogenerated excitons diffusing into defects, and \( \tau_2 \) representing intrinsic electron-hole recombination. The formula illustrated in Equation (2) was employed for the calculation of average PL lifetime values [46]; a detailed summary of these values can be found in Table 2.

\[ \tau_{avg} = \frac{\Sigma_i A_i \tau_i^2}{\Sigma_i A_i \tau_i} \]  

Table 2. PL lifetime parameters from the fitting curves of NiO\textsubscript{x} and 5\% Zn-NiO\textsubscript{x} thin films.

| Sample | \( A_1 \) (\%) | \( \tau_1 \) (ns) | \( A_2 \) (\%) | \( \tau_2 \) (ns) | \( \tau_{avg} \) (ns) |
|--------|----------------|-----------------|----------------|----------------|-------------------|
| FTO/PSK | 69.4 | 20.4 | 30.6 | 46.0 | 33.2 |
| FTO/NiO\textsubscript{x}/PSK | 84.9 | 4.3 | 15.1 | 17.9 | 10.1 |
| FTO/5\%Zn-NiO\textsubscript{x}/PSK | 82.0 | 4.4 | 18.0 | 15.6 | 9.3 |
This research employed EIS measurements to undertake further verification of NiOx and 5% Zn-NiOx thin film-based devices’ charge transport properties. Figure 11 illustrates the Nyquist plots for devices fabricated using NiOx and 5% Zn-NiOx thin films annealed at 250 °C. EIS measurement was taken at one solar illumination using a frequency range from 10 Hz to 1 MHz with an AC amplitude of 0.01 V and providing a bias voltage that matched the open-circuit voltage. The impedance curve was observed at three frequency regions where the high-frequency (HF) regime correlates with charge transport resistance ($R_{ct}$) at the HTL/perovskite interface, mid-frequency (MF) region is related to charge recombination, and low-frequency (LF) has been associated to iodide ion modulated recombination/injection process [47]. The curves were fitted with the equivalent circuit and the calculated $R_{ct}$ values are ~60.38 Ω and 45.62 Ω for NiOx and 5% Zn-NiOx devices, respectively. Typically, low impedance values are expected for better carrier transport functions [48,49]. The device fabricated using Zn doped NiOx had lower impedance values than those fabricated using pristine NiOx. It is clear that interface charge accumulation is suppressed, thus, improving exciton charge separation. Improved charge separation leads to increases in EQE and $J_{sc}$ values. These findings clearly indicate that charge transport at the HTL-perovskite interfaces can be improved by doping NiOx with Zn, leading to a general improvement in the performance of NiOx HTL.

Figure 10. (a) PL spectra and (b) PL lifetime decay of NiOx and 5% Zn-NiOx thin films.

Figure 11. EIS spectra of PSCs with NiOx and 5% Zn-NiOx HTL.
4. Conclusions

In this work, we investigated the effect of extrinsic Zn doping in NiO$_x$ HTL in inverted PSCs by the combustion technique. Comparatively, the devices made with both pristine and Zn doped NiO$_x$ films performed well with the annealing temperature of 250 °C, showing average PCE values of 13.62% and 14.87%, respectively. Both the devices have exhibited better stability than the PEDOT:PSS (control) device in an ambient condition. The crystallinity of both pristine and Zn doped NiO$_x$ films is better than the sol-gel derived thin film annealed at 250 °C. The XPS results revealed that the presence of compound formation below its reaction temperature and intensity of the Ni$^{3+}$ peak (Ni vacancy) was higher in Zn doped NiO$_x$ than the NiO$_x$ film. The presence of Zn in NiO$_x$ was confirmed in XPS but not observed in XRD. Both films exhibited similar optical transparency, and the effect of Zn incorporation on optical properties is negligible. The electrical conductivity was greatly improved with Zn doping into the NiO$_x$ crystal lattice. The better PL quenching and low PL lifetime decay responsible for better charge separation were observed in Zn doped NiO$_x$. A small impedance value from the Zn doped device showed less transport charge resistance than the pristine one. Overall, the NiO$_x$ thin films made by the combustion technique were the films annealed at 250 °C, which can work as HTL in inverted PSCs. The performance of combustion processed NiO$_x$ HTL was improved by Zn doping, showing better efficiency and overall superior performance than pristine NiO$_x$ films.

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