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Zinc as a New Dopant for NiO$_x$ based Planar Perovskite Solar Cells with Stable Efficiency near 20%

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Abstract

Organic-inorganic lead halide perovskite solar cells are potential alternatives to commercial silicon solar cells due to the attractive photon conversion efficiency and general material costs except the widely adopted organic hole transporting polymers which are currently expensive and have low conductivity. Inorganic hole transporting layer (HTL) have recently garnered attention due to their excellent stability and relatively effective cost. Nickel oxide (NiO\textsubscript{x}) is a typical p-type oxide semiconductor with deep valance band (VB) and expected to be used as HTL. Unfortunately, the charge extraction efficiency has been hindered by its poor conductivity, resulting in lower efficiency when compared with organic HTLs based devices. Here, we report a new solution-processed doping strategy for NiO\textsubscript{x} with zinc dopant to improve its conductivity for perovskite solar cells. The NiO\textsubscript{x}:Zn HTL showed high transparency and significantly enhanced electrical conductivity in comparation with the pristine NiO\textsubscript{x}. Our best NiO\textsubscript{x}:Zn-based P-i-N planar device showed an efficiency of 19.6\% with negligible hysteresis, which is comparable with the reported planar solar cell with organic HTL. Moreover, the NiO\textsubscript{x}:Zn based perovskite device displayed distinguished stability in ambient conditions. This paper demonstrated important progress towards high-efficiency planar perovskite devices with low-cost inorganic HTLs.

Keywords: inverted planar structure, zinc dopant, hole extraction layer, high efficiency, perovskite solar cell
1. Introduction

Organic-inorganic halide perovskites solar cells with very high power conversion efficiency (PCE) up to 22% was realized only in few past years since its discovery in 2009.\textsuperscript{1} Their intriguing optoelectronic properties, e.g. direct and tunable band gap, low exciton binding energy, long carrier diffusion length, broad absorption range,\textsuperscript{2-7} and cost-effective processing have triggered the rapid advances in thin film solar cells.\textsuperscript{8} Planar structures for hybrid perovskite solar cells have recently attracted much attention, due to their simple and low-cost device fabrication processing. The hole extraction/transport layers are crucial to planar perovskite solar cells (PSCs), and tremendous efforts were devoted to optimize selective charge extraction layers for enhancing photocarriers extraction efficiency and reducing charge recombination at the surfaces.\textsuperscript{9-13} The organic hole-transporting layers (HTL), including PEDOT:PSS,\textsuperscript{14,15} PTAA,\textsuperscript{16} Spiro-OMeTAD\textsuperscript{17,18} have commonly used in the planar PSCs. However, the high price and poor stability of the organic HTLs impede the development of perovskite photovoltaic toward industrial technology.\textsuperscript{19,20} In contrast to organic HTLs, the inorganic HTLs like CuSCN,\textsuperscript{21,22} CuI,\textsuperscript{23} CuO,\textsuperscript{24} and NiO\textsubscript{x}\textsuperscript{25-29} demonstrate superior stability, lower cost and much higher carrier mobility. As most promising candidate, NiO\textsubscript{x} interlayer endorses numerous merits such as intrinsic p-type conductivity, high transmittance, and deep valence band (VB of 5.4 eV) that matches well with the VB of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}.\textsuperscript{30,31} However, the undesired conductivity and poor crystallinity of NiO\textsubscript{x} impedes the further development on improving the performance for PSCs, which results in increased recombination rate and reduced hole
extraction efficiency.\textsuperscript{32}

It is particularly to note that increasing the conductivity of wide bandgap metal oxide semiconductors like n-type ZnO and p-type NiO by doping is challenging as there exists a fundamental asymmetry with respect to the dopability by donors or acceptors. NiO\textsubscript{x} is a prototype p-type wide bandgap semiconductor with rather low intrinsic conductivity (~ 10\textsuperscript{13} S cm\textsuperscript{-1}).\textsuperscript{33} The p-type conductivity of NiO\textsubscript{x} is intimately connected to concentration of Ni vacancies, which arise from the composition nonstoichiometry because of the existence of a higher oxidation state of Ni\textsuperscript{3+} in Ni\textsubscript{2}O\textsubscript{3} in NiO matrix. Doping NiO\textsubscript{x} with metal ions like Cu, Li, Cs lowers the ionization energy of the Ni vacancies and thereafter improves the hole conductivity in NiO\textsubscript{x} films.\textsuperscript{34-36}

Recently, considerable attention has been devoted to the metal ion doped NiO\textsubscript{x} film, aiming to replace the organic HTL for high efficiency PSCs. Yao \textit{et al.}\textsuperscript{37} applied a composite NiO\textsubscript{x}:Cu HTL that can collect charges efficiently at the NiO\textsubscript{x}/perovskite interface and minimize interfacial recombination. Moreover, Li doping with pulsed laser deposition (PLD) to reduce the resistivity of NiO\textsubscript{x} films has been reported by our group,\textsuperscript{38} which affords a powerful growth technique for thin films to tune the crystalline and physical properties. Furthermore, Chen \textit{et al.}\textsuperscript{39} selected the NiO\textsubscript{x}:Cs films as a hole extraction layer to achieve a memorable device efficiency. However, these works does not discuss the physical origin of the device performance and the doping effect on the implication of Ni vacancies for the creation of free carriers also remains unknown.
In this study, we introduce zinc (Zn) doping strategy to improve the p-type conductivity of NiO\textsubscript{x} for high-efficiency inverted planar PSCs and address the mechanism of conductivity enhancement by Zn doping which is supported by density functional theory (DFT) simulations. The NiO\textsubscript{x}:Zn films exhibit morphology uniformity, high transparency, enhanced conductivity, and reliable reproducibility, which facilitate the high performance inverted planar PSCs with efficiency of 19.6%. Moreover, the PSCs based on NiO\textsubscript{x}:Zn showed decent stability, with 90% of original efficiency after 720 hrs of storage in ambient conditions. This result provides a highly promising route to realize high efficiency and stable inverted planar PSCs using abundant low cost inorganic HTLs.

2. Results and Discussions

![Figure 1](image-url)  
**Figure 1.** Spin-decomposed density of states of a 2 × 2 × 2 NiO\textsubscript{x} supercell with a Ni vacancy (the top panel), with one Ni atom replaced by a Zn atom (the middle panel), and the supercell containing a Ni vacancy plus a substituted Zn atom (the bottom panel). Zero energy is set at the Fermi level. Positive and negative scale corresponds to the spin-up and spin-down components, respectively.
Doping is an effective method to tune the electrical attributes of semiconductors. In this work, Zn is selected as a dopant as it has a similar atomic radius 134 pm with Ni atom 125 pm, which will facilitate the incorporation of the dopant into the NiO\textsubscript{x} matrix lattice. To deeply understand the effects of Zn doping on the electronic structures of NiO\textsubscript{x}, we checked the electronic density of states of three supercell systems: (a) with a Ni vacancy by removing a Ni atom (Ni\textsubscript{31}O\textsubscript{32}), (b) with a Zn atom replaced by a Ni atom (ZnNi\textsubscript{31}O\textsubscript{32}), and (c) having both a Ni vacancy and a substituted Zn atom (ZnNi\textsubscript{30}O\textsubscript{32}). It is clearly seen from the spin-decomposed density of states (DOS) (Figure 1) that the calculated band gap of NiO\textsubscript{x} using DFT methods is 2.73 eV, which is closer to our experimental data. Moreover, total spin-up and spin-down DOS of all systems we studied are asymmetric, and significantly different near the Fermi level. Our spin-polarized calculations revealed the ferromagnetic behavior in NiO\textsubscript{x} and Zn-doped NiO\textsubscript{x}, which is consistent with the previous work.\textsuperscript{40} Figure 1 also shows that Zn-doped NiO\textsubscript{x} with a Ni vacancy has the dramatically different electronic states near the Fermi level compared with other systems. It is clear that the introduction of Zn atom in NiO\textsubscript{x} induces more electronic states in the Fermi level, and makes it to be a half-metallic ferromagnet. Thus, we speculate that Zn doping in NiO\textsubscript{x} can remarkably improve the electronic conductivity.

To investigate the thermodynamic stability of Zn-doped NiO\textsubscript{x}, we calculated the formation energies of Ni\textsubscript{31}O\textsubscript{32} and ZnNi\textsubscript{30}O\textsubscript{32}. The formula to calculate formation energies of neutral defects can be expressed as:\textsuperscript{41}

\[
E_f = E_{\text{defect}}^{\text{tot}} - E_0^{\text{tot}} - n_+\mu_+ + n_-\mu_-
\]
$E_{\text{defect}}^{\text{tot}}$ is the total energy of the supercell with a relaxed defect, and $E_0^{\text{tot}}$ is the total energy of the same supercell without defects. $n_+$ and $n_-$ are the number of atoms added to and removed from the supercell in forming the defect cell, respectively. $\mu_+$ and $\mu_-$ are the corresponding energies of the species. For Ni$_{31}$O$_{32}$, $n_+ = 0, n_- = n_{\text{Ni}} = 1$, the calculated formation energy of a Ni vacancy is 0.58 eV, which is in good accordance with the reported values in references. While, for ZnNi$_{30}$O$_{32}$, $n_+ = n_{\text{Zn}} = 1$ and $n_- = n_{\text{Ni}} = 2$, the formation energy derived from DFT calculation is -2.64 eV, much smaller than that of Ni$_{31}$O$_{32}$. These results show that Zn-doped NiO$_x$ is more energetically stable than undoped NiO$_x$. Thus, the introduction of Zn atoms in NiO$_x$ is favorable for the formation of Ni vacancies and leads to the improvement of the conductivity in NiO$_x$. Our calculations predict that Zn-doped NiO$_x$ (NiO$_x$:Zn) with enhanced conductivity could be a good candidate for high efficiency PSCs.

To directly prove our theoretical predictions, we fabricate NiO$_x$:Zn and NiO$_x$ films by spin-coating method and characterized their morphology and electronic properties. The surface morphologies of NiO$_x$:Zn and NiO$_x$ films were first studied using scanning electron microscope (SEM). As shown in Figure 2a-b, the NiO$_x$:Zn film exhibits very compact and continuous morphology without pinholes or crevices in comparison with the NiO$_x$ films. Clearly, the Zn doping enhanced grain growth within the NiO$_x$ film. The atomic force microscope (AFM) was used to further characterize the roughness of the compact NiO$_x$ films as shown in Figure 2c-d. The results demonstrate that Zn-doping results in a gratifying smooth surface with a
Figure 2. SEM images of a) the NiO$_x$ and b) NiO$_x$:Zn on FTO glass. 3D AFM images of c) the corresponding NiO$_x$ and d) NiO$_x$:Zn films. The scan area is 25µm$^2$ (5 µm × 5 µm). SEM images of perovskite films on e) NiO$_x$ and f) NiO$_x$:Zn. All scale bars are 2 µm.

smaller root mean square (Rms) surface roughness (2.61 nm) compared to undoped NiO$_x$ film with a Rms of 6.15 nm. Similarly, when such NiO$_x$:Zn film was employed as hole extraction layers for invert PSC, a continuous, full coverage, and smooth MAPbI$_3$ perovskite film are grown onto such NiO$_x$:Zn film, which is one desired property for obtaining high efficient perovskite solar cell devices.

Figure 3 shows the X-ray photoelectron spectroscopy (XPS) spectra of Zn 2p and Ni 2p3/2 core level for NiO$_x$ and NiO$_x$:Zn films. Figure 3a demonstrates that Zn is incorporated into NiO$_x$:Zn film in its divalent state with an atomic ratio of 4.73% as shown in Table 1 and Figure S1. The Ni 2p3/2 spectra (Figure 3b) can be well fitted with three different states including NiO$_x$ (Ni 2p3/2 at 853.8 eV), Ni$_2$O$_3$ (Ni 2p3/2 at 855.3 eV), and satellite peak of Ni$^{3+}$ (Ni 2p3/2 at 856.1 eV). As calculated
Figure 3. High-resolution XPS spectra of the Zn (a) and Ni (b) elements in NiO$_x$ and NiO$_x$:Zn films, respectively. After doping, Zn$^{2+}$ signal and increasing Ni$^{3+}$ composition were clearly detected simultaneously.

Table 1 Summary of the Ni, O and Zn Atomic ratio in NiO$_x$ and NiO$_x$:Zn films respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni (%)</th>
<th>Ni$^{3+}$/Ni$^{2+}$</th>
<th>O (%)</th>
<th>Zn (%)</th>
<th>Ni/O ratio</th>
<th>(Ni+Zn)/O ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO$_x$</td>
<td>39.36</td>
<td>1.06</td>
<td>44.06</td>
<td>0</td>
<td>0.89</td>
<td>0.89</td>
</tr>
<tr>
<td>NiO$_x$:Zn</td>
<td>34.92</td>
<td>1.27</td>
<td>44.86</td>
<td>4.73%</td>
<td>0.78</td>
<td>0.86</td>
</tr>
</tbody>
</table>

from the integrated peak area, the Ni$^{3+}$/Ni$^{2+}$ ratios are obtained to be 1.06 and 1.27 for NiO$_x$ and NiO$_x$:Zn samples respectively, and we observe a clear increasing Ni$^{3+}$ composition in the Ni 2p spectra of the doped samples. Thus, this indicates more nickel vacancies are produced as a result of Zn doping. NiO$_x$ is also known for its
tendency to contain Ni vacancies (Ni/O:0.89), which is also the defect nature for its intrinsic p-type conductivity.\textsuperscript{44} As a typical ionic material, its metallic character often drives substitutional site preference and makes Zn atoms substitute in Ni sites. The improvement of the Ni\textsuperscript{3+}/Ni\textsuperscript{2+} ratio further reveals Zn doping reduces the ionization energy of the Ni vacancies, and thus improving the hole densities, which is in good agreement with our DFT predictions.

The electrical conductivities of NiO\textsubscript{x} and NiO\textsubscript{x}:Zn films were investigated by conductive AFM (c-AFM) scanning measurement, as shown in Figure 4a-b. Replacing the undoped NiO\textsubscript{x} with doped NiO\textsubscript{x}:Zn film can significantly increase the

Figure 4. Conductive atomic force microscopy (c-AFM) images of a) the undoped NiO\textsubscript{x} film and b) doped NiO\textsubscript{x}:Zn film (the scan area is 4 µm x 4 µm); c) I-V conducting curves of the NiO\textsubscript{x} and NiO\textsubscript{x}:Zn films measured from the c-AFM mode; d) Transmittance spectra of the NiO\textsubscript{x} and NiO\textsubscript{x}:Zn films coated on glass substrates..

The electrical conductivities of NiO\textsubscript{x} and NiO\textsubscript{x}:Zn films were investigated by conductive AFM (c-AFM) scanning measurement, as shown in Figure 4a-b. Replacing the undoped NiO\textsubscript{x} with doped NiO\textsubscript{x}:Zn film can significantly increase the
vertical current, which indicates the better electrical conductivity of NiO$_x$ film after Zn doping. Due to the existence of Schottky barrier potential, the current changes in the range of -2~2 V is minor, as shown in Figure 4c. However, the I-V curves exhibit dramatically enhanced electrical current from 0.25 to 3.9 nA at a bias potential of 4.0 V. The optical property of NiO$_x$ and NiO$_x$:Zn films is compared in the UV-vis absorption spectra, as shown in Figure 4d. The transmittance of the NiO$_x$ and NiO$_x$:Zn film express extremely similar transmission spectra and both the films exhibit above 95% transmittance over a broad spectral range from 300 to 800 nm using the bare glass as the reference. Such high transparent substrate and HTM is another reason for achieving high perovskite solar cell PCE.

**Figure 5.** a) Device architecture of the inverted planar perovskite solar cell (PSCs). b) Energy band level diagram of the various layers in the PSCs. c) Cross-section SEM image of a complete perovskite device with NiO$_x$ or NiO$_x$:Zn film as HTM.

To further prove the influence of NiO$_x$ doping on the PSC performance, PSCs with an P-i-N inverted planar structure of glass/FTO/NiO$_x$(NiO$_x$:Zn)/MAPbI$_3$/PCBM/BCP/Ag multi-layers and the
corresponding energy band diagrams are depicted in Figure 5a-b. Figure 5c is a
typical cross-sectional SEM image of the PSC device. The NiO$_x$ or Zn doped NiO$_x$
layer was prepared on the top of the glass/FTO substrate by spin-coating NiO$_x$ or
NiO$_x$:Zn precursor solution in glycol (Experimental Section). The MAPbI$_3$ film of
250–300 nm was then prepared by one-step solvent engineering method, as reported
by Zhang et al.$^{45}$ PCBM as ETM was spin-coated on MAPbI$_3$ film with thickness of
30 nm. Thereafter, 15 nm BCP film was adopted as an electrode interface layer to
reduce energy barrier for electron transporting. Finally, the Ag cathode was deposited
by vacuum vapor deposition to complete the device structure.

**Figure 6.** a) The ultraviolet photoelectron spectroscopy (UPS) of the NiO$_x$ and
NiO$_x$:Zn films coated on glass, measured under 21.2 eV bias. b) PL spectra and c)
Time-resolved PL spectra for perovskite films on different substrates: glass (black),
NiO$_x$ (blue), and NiO$_x$:Zn (red). d) Transient photovoltage (TPV) as function of time
for solar cells with NiO$_x$ and Zn-doped NiO$_x$ film as hole transport interlayers,
respectively.
Figure 6a compares the ultraviolet photoelectron spectroscopy (UPS) spectra of the NiO$_x$ with NiO$_x$:Zn films and the work function of the NiO$_x$ and NiO$_x$:Zn are calculated by the formula $\Phi = h\nu - (E_0 - E_F)$. The VB spectra were determined with a monochromatic He I light source (21.2 eV), and the work function ($\phi$) can be calculated by the difference between the photon energy and the binding energy of the secondary cutoff edge. NiO$_x$:Zn doped film has a higher work function, and generates the descending VB from -5.2 eV to -5.3 eV, which is similar to that of MAPbI$_3$ (-5.4 eV). According to the energy level diagram as presented in Figure 5b, the shifted VB makes energy level distribute between NiO$_x$ hole transport layer and perovskite VB, and, therefore, improves hole extraction efficiency tremendously. To verify this inference, photoluminescence properties of different samples were measured in Figure 6b-c. Steady-state photoluminescence (PL, Figure 6b) and time-resolved PL spectra (TRPL, Figure 6c) for perovskite films on glass substrate (black), NiO$_x$ (blue), and NiO$_x$:Zn (red) films illustrate that the NiO$_x$:Zn hole transport layer forms a more favorable ohmic contact with perovskite photosensory layers and obviously improves the hole extraction efficiency. Furthermore, the charge-recombination lifetime of the NiO$_x$:Zn based solar cell device measured by transient photovoltage spectrum (Figure 6d) is 1.21 $\mu$s, which is much bigger than that of NiO$_x$ based device (0.47 $\mu$s). Longer interfacial recombination lifetime can guarantee effective charge collection efficiency, and, as a result, higher device output photovoltage. Moreover, the improvement of such interfacial engineering can also be attributed to the improved film morphology discussed earlier in Figure 2, and can further decipher the reason for enhancing the
performance of devices.

**Figure 7.** a) I-V curves of the PSCs with NiO$_x$:Zn HTM of different Zn content in NiO$_x$:Zn and b) the corresponding external quantum efficiency spectra with various Zn content in NiO$_x$:Zn. c,d) Photovoltaic property parameters of the unencapsulated PSCs with different Zn content in NiO$_x$:Zn.

In order to optimize the Zn dopant concentrations in NiO$_x$, NiO$_x$:Zn films were prepared by adding Zn precursors with different molar ratios (3–7 mol%). The current density–voltage (J-V) characteristics of the best devices based on NiO$_x$:Zn HTL with various amount of Zn dopant are shown in Figure 7a. The corresponding external quantum efficiency (EQE) spectra are also shown in Figure 7b. We can conclude that
adding Zn precursors at 5 mol% molar ratios can gain the best device performance. Therefore, all of the following devices are prepared with this optimized dopant concentration. We compared the photovoltaic (PV) parameters of the PSCs with different HTLs (NiO$_x$ and NiO$_x$:Zn). In striking contrast, the devices with NiO$_x$:Zn HTL layer exhibited significantly improved performance with a $J_{SC}$ of 22.8 mA cm$^{-2}$, $V_{OC}$ of 1.1 V, FF of 78%, and according PCE of 19.6%. Moreover, the obtained photovoltaic performances properties for devices with various Zn contents are summarized in Figure 7c-d, and it shows that the promotion of the efficiency for the device with doped HTL is mainly due to the increasing photocurrent, which is also further confirmed by higher EQE value compared with that of the pristine device with HTL without Zn doping.

Figure 8. a) Steady-state photocurrent output at the maximum power point of the corresponding cells under continuous simulated AM1.5G light illumination for 500 s. b) Stability of the NiO$_x$:Zn based devices in a dry environment without encapsulation by measuring the normalized $V_{OC}$, $J_{SC}$, FF, and PCE.

The steady-state photocurrent output at the maximum power point over 500 s has been measured by setting a bias at the maximum power output point ($P_{max}$, 0.95 V). There is no performance degradation under long illumination and the light current
stabilizes quickly when the light was on, as shown in Figure 8a. The performance enhancement and hysteresis-free behavior were tentatively attributed to the improved hole extraction efficiency. Finally, in order to examine the device stability, we monitored the PV parameters of the unencapsulated devices which were stored in dry air and tested in ambient environment with a relative humidity of 50%-60%. The corresponding photovoltaic performance parameters were measured for over one month, as shown in Figure 8b. Meanwhile, we compared with the pristine NiO$_x$-based system, and found that the stability of Zn-based system did not change significantly as shown in Figure S2. Finally, we observed a distinguished devices stability that maintained about 85% initial efficient after one month, which is very promising for future development of inverted planar PSCs.

3. Conclusion

In summary, we have successfully demonstrated effective and stable Zn doped NiO$_x$ films as the HTL for inverted planar PSCs and addressed the effects of Zn doping on electronic properties of NiO$_x$ HTL and therefore the solar cell device performance. The new Zn dopant could improve the surface morphology and conductivity of NiO$_x$:Zn film and thereafter significantly enhance the photon conversion efficiency of P-i-N planar PSC using NiO$_x$:Zn as HTL. The best-performing device exhibited a remarkable efficiency of 19.6% with negligible hysteresis and a praiseworthy stability over long time, which is a promising candidate for future development of inverted planar PSCs.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 

Experimental Section; XPS from NiO\textsubscript{x} film and NiO\textsubscript{x}:Zn film respectively; Stability of the NiO\textsubscript{x} based devices in a dry environment without encapsulation. 

The authors declare no competing financial interest. 

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