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# Ni-Co-O Hole Transport Materials: Gap Sates Assisted Hole Extraction with Superior Electrical Conductivity

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Organic-inorganic hybrid perovskite solar cells (PSCs) have been rapidly evolving as a promising candidate for the nextgeneration photovoltaic technologies. P-type organics or polymers are generally used as hole transport materials (HTMs), which are expensive and non-sustainable for long-term applications. Herein, we demonstrate an inorganic Ni-Co-O hole conductor that displayed fast hole extraction and transport by the presence of gap states and relative high hole conductivity. Detailed structural inspection reveals that the  $Co^{3+}$  and  $Ni^{2+}$  ions would reform into  $Co^{2+}$  and  $Ni^{3+}$  sites with the incorporation of Co, which contributes to the greatly enhanced hole concentration. Inverted heterojunction devices based on NiCoO<sub>x</sub> hole transport layer yielded a maximum power conversion efficiency (PCE) of 20.03%, with 16.9% improvement compared with those based on NiO<sub>x</sub> layer (17.14%). This novel HTM with facile synthesis process provides a new strategy for designing efficient carrier transport materials such that efficient charge collection and transport are achieved.

# Introduction

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The superior photophysical properties of metal halide perovskites (e.g. intense light absorption, long diffusion length and low exciton energy),<sup>1-6</sup> are responsible for their highly efficient solar cells with power conversion efficiency (PCE) over 25%.<sup>7</sup> To assist in the charge extraction and conduction from the perovskite thin film, additional charge transport layers are required. To date, most of the best-performing PSC devices with efficiencies over 20% relied on doped organic or polymeric hole transport materials (HTMs), such as 2,2',7,7'tetrakis(N,N-di-pmethoxyphenyl-amine)9,9'-spirobifluorene (spiro-OMeTAD)<sup>8-10</sup> and poly-triarylamine (PTAA).11,12 Unfortunately, these organic HTMs are costly and unstable for large-scale and long-term applications. Moreover, dopants, lithium-bis(trifluoromethane)sulfonimide, such as are necessary for these HTMs to offer sufficient hole mobility.

To address these issues, several inorganic-based p-type semiconductors have been explored as HTMs in the past few years, including metal oxides,<sup>13-18</sup> metal sulfides,<sup>19-21</sup> iodides<sup>22</sup> thiocyanates.<sup>23</sup> Despite the electron blocking and characteristics of p-type HTMs, a significant fraction of carriers may still recombine at HTM/perovskite interface or in the bulk HTM layer before reaching the electrodes, thus limiting the device fill factor (FF) and the open-circuit voltage (Voc). Recently, time-resolved spectroscopic studies revealed that the hole extraction kinetics in the state-of-the-art spiro-OMeTAD layer can be further improved by incorporation conductive carbon materials,<sup>24</sup> which suggested that the photoexcited charge carriers must to reduce chances of recombination. Therefore, the development of inorganic HTMs with excellent hole extraction and transport ability is critical to achieve higher power conversion efficiency (PCE).

Herein, a Ni-Co-O hole conductor has been developed as an inexpensive and solution-processable inorganic HTM for PSCs (Fig. 1). Ni-Co-O hole conductors are referred to NiO<sub>X</sub>, NiCoO<sub>x</sub> and CoO<sub>x</sub> with different Co and Ni ratios. We found that the incorporation of Co species into NiO<sub>x</sub> provided unique gap states above the valance bands (VB) region, which can facilitate holes extraction from perovskite films. Furthermore, the formation of Ni and Co antisites with varied charge state could modify the electronic structure and improved the electrical conductivity of the HTM layer by over one order of magnitude. Owing to the large enhancement in the charge extraction and conductivity, the inverted planar PSC devices with NiCoO<sub>x</sub> HTM layers exhibited a champion PCE of 20.03%,

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**Fig. 1** a) Device structure of perovskite solar cells. B) Energy-level diagrams of perovskite solar cells (relative to the vacuum level). The dashed line shows the fermi level of the hole conducting materials deposited on FTO glass. The occurrence of gap states in NiCoO<sub>x</sub> and CoO<sub>x</sub> could provide electronic pathways for hole transfer from perovskites.

which is significantly better (> 16%) compared with to controls with NiO<sub>x</sub> layer (17.14%).

# **Results and discussion**

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The Ni-Co-O films in this work were prepared by a simple spincoating process of Ni and Co precursor, followed by thermal annealing (see more details in the experimental section). The concentration of all metal ions in the precursor solution was found to be 0.214 M, as determined by the performances of the resultant devices (Fig. S1). Scanning electron microscope (SEM) images of the NiO<sub>x</sub>, NiCoO<sub>x</sub> and CoO<sub>x</sub> films revealed similar compacted and conforming surface morphologies (Fig. S2). In order to investigate the structure of HTM, we performed X-ray diffraction (XRD) measurements. Only the diffraction peaks of SnO<sub>2</sub> from fluorinedoped tin oxide (FTO) can be observed in Fig. S3, which indicate that the as-prepared Ni-Co-O materials are amorphous. Furthermore, the identities of these films were confirmed by Raman spectroscopy which showed the presence of CoO<sub>x</sub> and NiO<sub>x</sub> as evident from their signature Raman bands (Fig. S4).

Ultraviolet photoelectron spectroscopy (UPS) and ultraviolet-visible (UV-vis) spectroscopy measurements were carried out to investigate the energy levels of the NiO<sub>x</sub>, NiCoO<sub>x</sub> and CoOx layers on FTO substrates. The optical band gaps of NiOx, NiCoOx and CoOx were measured to be 3.66, 2.70 and 2.30 eV, respectively (Fig. S5). As shown in Fig. S6a, the sample work functions were determined from their secondary electron cut-offs, and their valence band maximums were determined from their the main on-set of phot electrons. The energy levels of HTMs and the perovskite layer (Fig. S6b) shows that the Fermi levels of NiCoO<sub>x</sub> (-4.39 eV) and CoO<sub>x</sub> (-4.38 eV) layers are higher compared to that of pristine NiO<sub>x</sub> (-4.07 eV) and are accompanied by lowering of their VB edges (with respect to vacuum level). Most intriguingly, apparent broadening of VB edges for the Co-containing samples can be observed, which suggests the existence of gap states. The edges of these gap states

are located at ~0.44 and ~0.59 eV below the Fermi level for NiCoO<sub>x</sub> and CoO<sub>x</sub>, respectively. Assuming these gap states are normally distributed, the energy levels of these states are centered at about - 5.40 and -5.49 eV for NiCoO<sub>x</sub> and CoO<sub>x</sub>, both of which are well aligned to the VB of MAPbl<sub>3</sub> (Fig. 1b and Fig. S6b).

Steady-state and time-resolved photoluminescence (TRPL) decay measurements (Fig. S7) were then performed to reveal the charge transfer behaviors of different HTM layers. With the presence of Co species in HTM layer, PL quenching behavior in the perovskite films were dramatic in which the PL intensity of NiCoO<sub>x</sub> and CoO<sub>x</sub> samples were ~8.6% and ~3.4% relative to that of NiO<sub>x</sub>, at excitation wavelength of 515 nm (Fig. S7a). As shown in Fig. S7b, the TRPL decay of perovskite films with different HTM layers showed a biexponential decay with a fast and a slow component and was fitted to a biexponential equation:  $Y = A_1 exp(-t/\tau_1) + A_2 exp(-t/\tau_2)$ <sup>25</sup> We attributed the quenching of the fast decay process to the fast charge transfer from perovskite into the hole conductor layers, and the slow decay to bimolecular radiative recombination. Evidently, the HTM layers had a major influence on the fast decay process which we attributed to the matching energy level alignment between the gap states induced by Co species and the perovskite layer, thus facilitating the charge transfer at the interface. The fast decay lifetime of NiCoO<sub>x</sub> and CoO<sub>x</sub> samples were calculated to 4.5 and 2.7 ns, which is 4.8 and 8.0 times faster than the  $NiO_x$  sample (21.7 ns). Additionally, the  $NiO_x$ ,  $NiCoO_x$  and  $CoO_x$  samples displayed similar slow decay lifetimes of 22.6, 23.6 and 27.3 ns, respectively, suggesting that the HTM layers did not affect radiative recombination velocity in the perovskite films.

X-ray photoelectron spectroscopy (XPS) was employed to probe the surface electronic structure of Ni-Co-O HTM samples. As shown in Fig. 2a, the Ni  $2p_{3/2}$  peaks can be resolved into three distinct components which are consistent with previous reports for NiO<sub>x</sub> films obtained via solution methods. The peaks centered at binding energy of ~853.2 eV and ~855.1 eV are attributed to Ni<sup>2+</sup> and Ni<sup>3+</sup>, respectively.<sup>26,27</sup> It is noteworthy that the atomic ratio of Ni<sup>3+</sup> was

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**Fig. 2** a,b) The XPS spectra of (a) Ni 2p and (b) Co 2p for the samples of  $CoO_x$  and  $NiCoO_x$ . XANES spectra in the range of (c) Ni K-edge and (d) Co K-edge for the samples of  $NiCoO_x$  and controlled samples. Corresponding Fourier transforms of (e) Ni K-edge XAFS and (f) Co K-edge XAFS oscillations for the samples of  $NiCoO_x$  and controlled samples. Notes: the intensities of Ni foil and Co foil in (e) and (f) were reduced by half. The xy dimensions of the analyzed area of the films are  $100 \times 100 \ \mu m^2$ .

increased from ~63.7% of NiO<sub>x</sub> film to ~78.7% of NiCoO<sub>x</sub> film determined by the integral area of XPS peaks. The XPS spectra of Co 2p (Fig. 2b) show four fitted peaks at binding energies of ~778.9, ~780.7, ~794.2 and ~795.9 eV, which correspond to  $Co^{3+}$  2p<sub>3/2</sub>,  $Co^{2+}$  2p<sub>3/2</sub>,  $Co^{3+}$  2p<sub>1/2</sub> and  $Co^{2+}$  2p<sub>1/2</sub>, respectively.<sup>28</sup> The  $Co^{3+}$ :Co<sup>2+</sup> ratios for the NiCoO<sub>x</sub> and CoO<sub>x</sub> are estimated to be 0.50 and 0.61, respectively. These observations suggest that Ni atoms may occupy Co<sup>3+</sup> sites and lead to higher Ni<sup>3</sup> but lower Co<sup>3+</sup> ratios in NiCoO<sub>x</sub> film. The O 1s high-resolution spectra (Fig. S8) show four distinct components of O1, O2, O3 and O4 ascribed to metal-oxygen bonds, OH- groups, defect sites with low oxygen coordination, and multiplicity of physi- and chemi-sorbed water, respectively.<sup>26,29-32</sup>

To further investigate into the bulk electronic structures, X-ray absorption near edge structure (XANES) spectra were collected. The pre-edge of  $NiCoO_x$  films in the Ni K-edge spectra shifted to higher absorption energy compared to NiO and NiO<sub>x</sub> samples, revealing a higher bulk valence states than Ni<sup>2+</sup> (Fig. 2c). Meanwhile, the bulk valence of Co species in NiCoO<sub>x</sub> resembles that of  $Co_3O_4$  and  $CoO_x$ controlled samples (Fig. 2d). In addition, the Fourier-transformed (FT) spectra extended X-ray absorption fine structure (XAFS) spectra of all the samples were collected and analyzed. Interatomic distances are shorter owing to the fact that FT spectra were not phase-corrected. In Fig. 2e, the first (at ~ 1.5 Å) and second (at ~ 2.5 Å) peak can be attributed to the single scattering paths of the Ni-O and the closest neighboring transition metals around absorbing atoms Ni (Ni-Ni), respectively. It is noted that the third peak (at ~ 3.0 Å) can only be observed in NiCoO<sub>x</sub> films, suggesting that the closest neighboring transition metals of Ni atom consisted of two

different types of bond distances (Ni-Ni or Ni-Co bonds). While in Co K-edge range, three FT peaks located at ~ 1.5 Å, ~ 2.5 Å and ~ 3.0 Å can be attributed to Co-O, Co-Co and Co-Ni, respectively (Fig. 2f). This phenomenon suggests that the closest neighboring atoms of Co atoms in NiCoO<sub>x</sub> are similar with Co<sub>3</sub>O<sub>4</sub> and CoO<sub>x</sub> samples. Regarding the enhanced bulk valence states of Ni in NiCoO<sub>x</sub> films are in agreement with the XPS analysis. Hence, we can reasonably conclude that more Ni<sup>3+</sup> sites were formed at the expense of the Co<sup>3+</sup> sites.

Solar cells with the various sandwiched HTM layers were fabricated inverted planar heterojunction configuration with an [FTO/HTM/MAPbl<sub>3</sub>/phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM)/ bathocuproine (BCP)/Ag]. The UV-vis absorbance spectra of perovskite films deposited on the different HTM layers exhibited in slight light absorbance efficiency depression caused bv incorporation of Co (Fig. S9). The J-V curves of the PSCs with different Co contents were shown in Fig. 3a, and the photovoltaic parameters were summarized in Table S1. The NiOx device had a short-circuit current density (Jsc) of 22.71 mA cm<sup>-2</sup>, an open-circuit voltage (Voc) of 1.035 V and a fill factor (FF) of 0.730, yielding a power conversion efficiency (PCE) of 17.14%. With the addition of Co from 25% to 50%, the highest recorded Jsc, Voc, and FF of the resulted devices improved from 21.95 to 22.27 mA cm<sup>-2</sup>, 1.045 to 1.080 V and 0.780 to 0.833, respectively, improving the PCE from 17.89% to 20.03%. Further increase of Co content resulted in poorer performance: PCE of devices with 75% Co content reduced to 17.12%, whereas the pure  $CoO_x$  devices produced a low efficiency of only 9.95%.



**Fig. 3** Photovoltaic performance. a) *J*–*V* curves of PSCs based on NiCoO<sub>x</sub>, films with different Co contents. b) *J*-*V* metrics for 15 independent devices based on different HTM layers. c) *J*–*V* curve (reverse and forward scans) of the best NiCoO<sub>x</sub> device with Co content of 50%. All *J*–*V* measurements were operated under AM 1.5G irradiation with a reverse scan rate of 0.15 V s<sup>-1</sup> for small-area (0.0625 cm<sup>-2</sup>) devices.

Fig. 3b shows the *J-V* metrics for 15 independent devices. Similar trend was observed for species *Voc* values are 1.038, 1.039, 1.068, 0.943 and 0.974 V and the mean FF are 0.699, 0.768, 0.785, 0.769 and 0.452 with the Co content of 0%, 25%, 50%, 75% and 100%, respectively. The results clearly show the synergistic improvement of HTM performance with the optimized 50% CoO<sub>x</sub> and NiO<sub>x</sub> content in which the role of Co can help to optimize the charge transfer at the interface and enhance the FF and *Voc* as expected. On the other hand, the NiO<sub>x</sub> also plays an equal important role, which may be related to charge transport and reduction of the surface trap states.<sup>33,34</sup>

The champion PCE of 20.03% was achieved by using NiCoO<sub>x</sub> layer with a *Jsc* of 22.27 mA cm<sup>-2</sup>, *Voc* of 1.080 V, and FF of 83.3 % under forward and reverse scanning with negligible hysteresis, as shown in Fig. 3c. The *Jsc* of the device was also confirmed by external quantum efficiency (EQE) spectra, with an integrated photocurrent of 21.2 mA cm<sup>-2</sup> (Fig. S10). Furthermore, this NiCoO<sub>x</sub> device was held at a forward bias of 0.894 V to monitor the stability of power output as a function of time (Fig. S11). The photocurrent stabilized within seconds to a value of approximately 21.23 mA cm<sup>-2</sup> that is similar to that obtained by the *J-V* tests. A stabilized PCE of 18.99% was measured upon 100 s.

For photovoltaic devices, charge transport loss in bulk carrier transport layers could be another key factor to evaluate a hole transport layer and thus it is critical to examine the electrical conductivity of the HTM films. All electrical conductivity test are conducted based on the structure of FTO/HTM/Au under dark condition. The conductivity of the NiO<sub>x</sub> film was estimated to increase over one order of magnitude from ~1.8×10<sup>-7</sup> S m<sup>-1</sup> to ~2.5×10<sup>-6</sup> S m<sup>-1</sup> by substituting 50% of Ni with Co species in the

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precursors (Fig. 4a). Interestingly, CoO<sub>x</sub> filmowas found to exhibit low electrical lookdoct( $Mty^{3}$  of ~3.8×10<sup>-8</sup> S m<sup>-1</sup>. Mott–Schottky plots of the oxide films are generated based on the capacitances under AC condition (Fig. 4b). All three samples show obvious P-type electrical characteristic. The carrier density can be calculated according to the following equation:<sup>35</sup>

#### $N = (2/e_0 \epsilon \epsilon_0 A^2) [d(1/C^2)/dV]^{-1}$

where  $e_0$  is the electron charge,  $\varepsilon$  is the dielectric constant,  $\varepsilon_0$  is the permittivity of vacuum, N is the carrier density, and C is the capacitance derived from the electrochemical impedance. The carrier density of NiO<sub>x</sub> of 2.1×10<sup>18</sup> cm<sup>-3</sup> is lower comparable to that of CoO<sub>x</sub> films of 6.1×10<sup>18</sup> cm<sup>-3</sup>, whereas, the carrier density of NiCoO<sub>x</sub> significantly larger (10.2×10<sup>18</sup> cm<sup>-3</sup>) approaching the carrier density of metallic materials (>10<sup>19</sup> cm<sup>-3</sup>).

We continued to measure the devices under operational conditions using electrochemical impedance spectroscopy (EIS) to identify the recombination behavior in devices and the typical Nyquist plots of perovskite devices based on different HTMs are depicted in Fig. 4c. The

experiment data were fitted using the equivalent circuit shown in the inset in Fig. 4c. The Nyquist plots typically show two distinct arcs at low and high frequency for perovskite devices.  $R_s$  is an additional contribution from series resistance.<sup>36</sup> The high frequency arc in the Nyquist plots is ascribed to the diffusion of holes through



**Fig. 4** Charge carrier transport behavior. a) *J-V* curves of NiO<sub>x</sub>, NiCoO<sub>x</sub> and CoO<sub>x</sub> films deposited on FTO glass. The thickness was 120 nm for all metal oxide films. Insets is the corresponding electrical conductivity extracted from the *J-V* results. b) C-V profiling of NiO<sub>x</sub>, NiCoO<sub>x</sub> and CoO<sub>x</sub> films. c,d) Nyquist plots and recombination resistance ( $R_{rec}$ ) of devices based on NiO<sub>x</sub>, NiCoO<sub>x</sub> and CoO<sub>x</sub> and CoO<sub>x</sub> films.

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the HTM layer which is modeled by a charge transfer resistance (R<sub>tr</sub>) and chemical capacitance (C<sub>tr</sub>). The lower frequency arc is ascribed to the recombination resistance (R<sub>rec</sub>) and chemical capacitance (C<sub>µ</sub>) which are associated with the recombination of the carriers in the whole device. Normally, the R<sub>tr</sub> is almost indistinguishable due to the simplified transmission line model.

The  $R_{rec}$  under different applied bias voltages extracted from nyquist plots are listed in Fig. 4d. The  $R_{rec}$  of NiCoO<sub>x</sub> based device is much larger than that of CoO<sub>x</sub> device, indicating the carriers' lifetime is much shorter (about 1~2 order of magnitude) than that of the NiCoO<sub>x</sub> devices. Based on aforementioned results, we can concluded that that excess Co contents generate the trap states, which cause quick charge recombination and large electrical resistance. Co also improve the charge transfer rate at HTL/perovskite interface, benefiting from the existence of suitable gap states. On the other hand, the incorporation of moderate amount of Co into NiO<sub>x</sub> can substantially not only enhance the interfacial charge transfer by introducing gap states, but also improve the hole concentration and electrical conductivity without obvious reduction of carrier lifetime.

## Conclusions

In this paper, we demonstrated a new type of hole conductor Ni-Co-O, which enables gap states assisted charge extraction and electrical transport capacities. Devices based on NiCoO<sub>x</sub> layer showed a high PCE of 20.03% with 16.9% enhancement compared with that based on conventional NiO<sub>x</sub> layer because of accelerated charge collection and transport. Further improvement of the crystallinity and morphology of Ni-Co-O based materials is expected to improve the carrier scatting time and mobility. We believe such material system holds great promise in developing low-cost and high-performance perovskite devices and is highly compatible with other electronic devices, such as photoreactors, light-emitting diodes and organic photovoltaics.

## **Conflicts of interest**

The authors declare no competing financial interest.

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An inorganic NiCoO<sub>x</sub> hole conductor was developed as HTM in PSCs. The champion device yielded a PCE of 20.03%.

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