Inorganic Hole Conducting Layers for Perovskite-Based Solar Cells

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Supporting Information

ABSTRACT: Hybrid organic–inorganic semiconducting perovskite photovoltaic cells are usually coupled with organic hole conductors. Here, we report planar, inverse CH3NH3PbI3Cl-based cells with inorganic hole conductors. Using electrodeposited NiO as hole conductor, we have achieved a power conversion efficiency of 7.3%. The maximum Voc obtained was 935 mV with an average Voc value being 785 mV. Preliminary results for similar cells using electrodeposited CuSCN as hole conductor resulted in devices up to 3.8% in efficiency. The ability to obtain promising cells using NiO and CuSCN expands the presently rather limited range of available hole conductors for perovskite cells.

Inorganic hole conductors have been much less used for perovskite cells. Christians et al.,20 described the use of a CuI hole conductor with conversion efficiency of 6.0%. They also showed that unencapsulated CuI/perovskite cells showed better stability than corresponding spiro-OMeTAD ones. Inorganic NiO thin films have been employed successfully as a hole conducting material in p-type DSSC and OPV devices.21–25 They have also been previously explored in inverse architecture perovskite-based solar cells with very low efficiency (ca. 0.05%)26 and, very recently, using spin-coated NiO to give 7.8% cells.27 Doctor-bladed CuSCN has also been recently used in a conventional-architecture perovskite cell (i.e., CuSCN deposited on the perovskite) with 4.85% efficiency reported.28

In this communication, we investigate electrodeposited NiO (and preliminary results using electrodeposited CuSCN) as hole-conductors in planar CH3NH3PbI3Cl-based solar cells with inverse architecture (i.e., the perovskite is deposited on the hole conductor rather than the other way around). The p-i-n type device architecture consists of fluorine-doped tin oxide (FTO)-coated glass, electrodeposited hole conducting film of NiO (or CuSCN), vacuum evaporated perovskite absorber, and spin-coated [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) with an evaporated silver contact (FTO/NiO/CH3NH3PbI3Cl/PCBM/Ag). A maximum power conver-
sion efficiency (PCE) of 7.3% was obtained with NiO and 3.8% in preliminary experiments employing CuSCN.

The band energy diagram of the inverted architecture device employing NiO and CuSCN hole conductors is shown in Scheme 1. Though a wide range of HOMO positions have been reported for NiO in the literature, it is typically somewhat lower than that of CuSCN.

**Scheme 1. Band Energy Diagram of NiO- and CuSCN-Based Perovskite Cells Used in This Study.**

The NiO valence band position is a roughly average value from the large variation found in the literature.

Photoluminescence (PL) quenching of the perovskite emission was carried out to study the compatibility of the hole conducting materials. For PL measurements, CH₃NH₃PbI₃−ₓClₓ films with thickness of ca. 250 nm were deposited on microscope glass slides, FTO-coated glass, FTO/ NiO, and FTO/CuSCN substrates. The bandgap of the vapor deposited CH₃NH₃PbI₃−ₓClₓ film was determined from the direct bandgap Tauc plot and found to be 1.59 eV. For all PL measurements, an excitation wavelength of 530 nm was used. A broad PL emission peak at around 770 nm was found for the films on glass slides as shown in Figure 1. A considerable decrease in the PL intensities was observed when the perovskite was deposited either on FTO or on FTO/NiO. Apart from a small peak at 825 nm, no band-edge signal was observed for a film deposited on an FTO/CuSCN substrate. The PL quenching efficiency was found to be ca. 87% and 90% for FTO and NiO substrates, respectively, and >96% for CuSCN. Thus, the calculated PL quenching efficiency for inorganic hole conducting materials was comparable to that found for the traditionally used organic hole conductors reported earlier.²⁶

For cell formation, the annealed NiO films were subjected to UV light treatment (UV light source UVC 254 nm, which forms O₃ in the presence of oxygen) before depositing the absorber layer. Cells fabricated without UV light treatment showed a low fill factor. O₂ plasma treatment of NiO has been shown to increase the NiO work function and give better organic photovoltaic devices, presumed due to surface oxidation.³⁰ UV/ozone treatments of various oxides were shown to have a similar effect to O₂ plasma treatment.³⁰

Figure 2 shows a cross section SEM image of the inverse device architecture consisting of glass/FTO (bottom of image), NiO hole conducting layer with CH₃NH₃PbI₃−ₓClₓ and spin-coated PCBM as electron transport layer. The cross section SEM image also depicts a uniform deposition along the length of the device.

The J−V curves of champion and average cells using NiO as hole conductor are shown in Figure 3a. The champion NiO-based perovskite cells exhibited a power conversion efficiency of 7.3%, a short circuit current (J_sc) of 14.2 mA/cm² and an open circuit voltage (V_oc) of 786 mV. Although this V_oc was similar to the average value, a maximum value of 935 mV was attained, comparable to V_oc values obtained using Spiro-OMeTAD. The short circuit current, open circuit voltage, and other parameters were obtained from a batch size of 24 NiO-based perovskite solar cells, and the values are tabulated in Table 1. The champion NiO-based perovskite device performance is comparable to those reported earlier by Christians et al., using CuI as hole conductor²⁰ and the planar NiO devices published by Jeng et al. recently.²⁷

We also made some cells without the NiO (i.e., the perovskite deposited directly on the FTO). Though reasonable, if somewhat lower values of J_sc and V_oc (8−10 mA cm⁻² and 600−800 mV) were obtained, the fill factor was invariably <0.3. Some form of charge-selective contact seems to be necessary in this case.

From preliminary experiments using CuSCN instead of NiO, a conversion efficiency of 3.8% was obtained (Figure 4). The V_oc of 677 mV is on the low limit of those obtained from these cells, and a maximum value of 900 mV has been obtained in these preliminary experiments. Therefore, it seems likely that CuSCN will also turn out to be at least a reasonably good hole conductor for the iodide perovskites.

A simple one-diode model fit of the dark current voltage characteristics revealed that NiO-based cells exhibit a low series resistance value (Rₛ) compared to those using CuSCN. The best NiO cell showed an Rₛ of ca. 4.4 Ω cm², whereas the best CuSCN cell exhibited greater than an order of magnitude higher value of ca. 63 Ω cm². In addition, the typical shunt resistance (RₛH) is about an order of magnitude higher for the average NiO-based cells (RₛH ~ 800 Ω cm²) than for CuSCN-based ones (~70 Ω cm²). Thus, despite CuSCN showing a higher quenching ability than NiO, they exhibit a poorer photovoltaic performance. However, it is too early to know if this is an intrinsic difference or due to less experience with the perovskite–CuSCN combination.

To investigate the electrical properties of the electrodeposited inorganic hole transport materials, current–voltage
characteristics were obtained by sandwiching NiO or CuSCN films between FTO and Au contacts. Dark \( I-V \) characteristics showed a good diode behavior for NiO films of thickness 100 nm as shown in Figure 5 with low series and relatively high shunt resistances (Table 2). CuSCN showed a much poorer diode behavior that depended strongly on the CuSCN thickness. In fact, the CuSCN shows no clear blocking behavior except for the thickest (600 nm) film, suggesting that the shunting of the thinner films might be due to direct shorting paths through the thinner CuSCN. However, the high series resistance of the CuSCN films will degrade the device performance.

However, the impact of high series resistance of the CuSCN layer in the complete planar device architecture under dark conditions is considerably reduced upon illumination (see Figure 4). The CuSCN-based cell series resistance dropped to 7.4 \( \Omega \) cm\(^2\) under illumination from 63 \( \Omega \) cm\(^2\) in the dark, showing that upon hole injection from the absorber layer, the resistance of the material is decreased. It should be noted that CuSCN-based cells also exhibit a crossover of dark and light \( J-V \) characteristics, unlike NiO-based devices (compare Figures 3 and 4). Although there are a number of possible reasons for this, the hole injection mechanism (indirect photoconduction) is the simplest explanation.

In conclusion, we have shown that NiO and, to a lesser extent (at present), CuSCN inorganic hole conductors can serve as potentially feasible replacements for the organic hole conductors in perovskite solar cells. The use of inverse cell structures allows relatively high temperature processing, and the use of deposition techniques that would be incompatible

Table 1. Champion Cell, Mean, and Maximum Photovoltaic Parameters of a Batch of FTO/NiO/\( \text{CH}_3\text{NH}_3\text{PbI}_3\text{Cl}_x \)/PCBM/Ag Cells

<table>
<thead>
<tr>
<th>hole transport material</th>
<th>( J_{SC} ) (mA/cm(^2))</th>
<th>( V_{OC} ) (mV)</th>
<th>fill factor (FF)</th>
<th>PCE % (( \eta ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>nickel oxide (NiO)</td>
<td>champion</td>
<td>14.2</td>
<td>786</td>
<td>0.65</td>
</tr>
<tr>
<td>mean ± SD</td>
<td>9.6 ± 3.2</td>
<td>784 ± 50</td>
<td>0.62 ± 0.07</td>
<td>4.7 ± 1.7</td>
</tr>
<tr>
<td>maximum</td>
<td>14.9</td>
<td>936</td>
<td>0.75</td>
<td>7.26</td>
</tr>
</tbody>
</table>

\(^a\)The mean values and standard deviations are calculated from a batch of 24 cells and a summary of their distribution is given in Figure SI 1 (Supporting Information).
MATERIALS REQUIRED

Fluorine-doped tin oxide coated glass (Pilkington, TEC-8), nickel nitrate hexahydrate (Merck, 98%), copper sulfate pentahydrate (Merck, 98%), Titriplex III (ethylenedinitrilote-triacetic acid disodium salt dihydrate) (Merck, >99%), potassium thiocyanate (Fisher Scientific, 97%), methylamine (Merck, 40% solution in water), hydriodic acid (57 wt % in water), lead chloride (Aldrich, 98%), [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) (Aldrich, 99%), (1,3)-dimethyl-2-phenyl-(2,3)-dihydro-1H-benzimidazole (DMBI) (Aldrich, 97%), silver metal (Parekh Industries, 99.99%), and chlorobenzene (Sigma-Aldrich, 99.9%) were used as supplied without further processing.

Substrate Preparation. FTO substrates were cut to a 3 × 1 cm size and cleaned with Alconox solution followed by rinsing with double-distilled water. Then the substrates were subjected to ultrasonication in Alconox solution, followed by isopropanol, acetone, and Millipore water for a period of 30 min each. The cleaned substrates were then dried in a dry air stream.

Electrodeposition of NiO Films. Nickel oxide films were deposited on top of the FTO substrates (working electrode) by galvanostatic electrodeposition in a three-electrode system with a platinum rod counter electrode and Ag/AgCl reference electrode. A thin layer of Ni(OH)₂ was initially deposited in a 0.02 M aqueous NiNO₃ bath with a constant current density of ~0.25 mA/cm² for 2 min. The Ni(OH)₂ thin films were then dried and annealed at 350 °C for 1 h in air in a muffle furnace to form NiO films of approximately 100 nm thickness. The films appeared nonporous but with high surface roughness. Annealing at a temperature higher than 400 °C resulted in a highly resistive NiO layer, whereas only partial conversion could be achieved if annealed at temperatures below 250 °C. Before deposition of the absorber layer on top of the NiO electrode, the sample was subjected to UV light treatment for approximately 20 min.

Electrodeposition of CuSCN Films. Orthorhombic CuSCN films were deposited by potentiostatic electrodeposition31 at ~0.4 V with respect to the Ag/AgCl reference electrode, with a platinum rod counter electrode and FTO-coated glass as working electrode. The composition of the deposition bath was 0.04 M CuSO₄, 0.04 M Titriplex (C₁₀H₁₄N₂Na₂O₈.2H₂O), and 0.02 M KSCN in aqueous solution, and the pH of this solution was at 1.8. No postdeposition annealing was employed. The deposition conditions were chosen to deposit nonporous films rather than a 3D architecture.

Synthesis of Methylammonium Iodide. Methylammonium iodide was synthesized by reacting 27.86 mL of methylamine (40% solution in water) in 100 mL of ethanol with 30 mL of hydriodic acid (57 wt % in water) in a round-bottom flask. The reaction was stirred in an ice bath for a period of 2 h.15 Then, the solvent was evaporated using a rotary evaporator and the product recrystallized from a mixture of ethanol and diethyl ether (1:1 by volume). The crystallized methylammonium iodide was washed repeatedly twice with diethyl ether and dried in vacuum at 60 °C for 20 h. The sample was then stored in a dark atmosphere and used over a period of no more than 2 weeks.

Coevaporation of CH₃NH₃PbI₃·Clₓ. The mixed halide perovskite absorber was deposited via dual source vacuum evaporation by evaporating PbCl₂ and CH₃NH₃I precursors simultaneously. For the thin film monitor, the density of PbCl₂ was set to be 5.85 g/cm³ and that of CH₃NH₃I 1.0 g/cm³ as reported earlier,17 and the boiling factors calculated accordingly. The PbCl₂ was evaporated at a rate of 0.95 ± 0.15 A/s and the CH₃NH₃I at 8.5 ± 1.5 A/s, resulting in a PbCl₂:CH₃NH₃I molar ratio of 1:5.4. The substrate temperature was held at a higher temperature than ambient (ca. 50

with the perovskite materials in a normal (hole conductor deposited on the perovskite) structure. Though the absolute conversion efficiencies reported here are well below those of state-of-the-art perovskite cells, they represent a promising step toward further development. It is important to mention that all the device syntheses were performed under ambient conditions where the average humidity was higher than that normally encountered. Although we have not carried out stability studies so far, the use of inorganic layers for both electron and hole transport layers might protect the moisture-sensitive perovskite absorber better than organic materials (the latter often are also oxygen sensitive).

EXPERIMENTAL SECTION

MATERIALS REQUIRED

Figure 4. Light and dark J–V characteristics of a FTO/CuSCN/CH₃NH₃PbI₃·Clₓ/PCBM/Au cell.

Figure 5. Dark I–V characteristics of FTO/NiO(100 nm)/Au and FTO/CuSCN/Au (100, 250, and 600 nm thick CuSCN).

Table 2. Series and Shunt Resistance Values Extracted from the J–V Characteristics of Figure 5

<table>
<thead>
<tr>
<th>device structure</th>
<th>Rₛ (Ω cm²)</th>
<th>RₛH (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO/NiO(100 nm)/Au</td>
<td>1.46</td>
<td>2510</td>
</tr>
<tr>
<td>FTO/CuSCN(100 nm)/Au</td>
<td>92.2</td>
<td>480</td>
</tr>
<tr>
<td>FTO/CuSCN(250 nm)/Au</td>
<td>218</td>
<td>500</td>
</tr>
<tr>
<td>FTO/CuSCN(600 nm)/Au</td>
<td>230</td>
<td>62,000</td>
</tr>
</tbody>
</table>

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(°C) during the entire deposition process. The base pressure in the evaporation chamber was 7 × 10⁻⁶ mbar. The evaporation time was optimized for the best performing devices to be 24 and 18 min for NiO and CuSCN substrates, respectively, resulting in an absorber thickness varying between 250 and 500 nm. The films were then annealed in ambient at 90 °C for 60 min and the samples were subsequently subjected to deposition of PCBM followed by evaporation of silver contacts.

Spin Coating of PCBM. The PCBM precursor was prepared by dissolving 13 mg of [6,6]-phenyl-C61-butryric acid methyl ester (PCBM) in 1 mL of chlorobenzene. After stirring the solution for 5 min, 0.26 mg of (1,3-dimethyl-2-phenyl-(2,3)-dihydro-1H-benzimidazole (DMBI) was added to the solution, and then the solution stirred continuously for 4 h. This precursor solution was then spin-coated at 3200 rpm on top of the FTO—(NiO/CuSCN)—CH₃NH₃PbI₃−ₓClₓ substrates for 30 s, and the samples were annealed at 80 °C in air for 5 min.

Silver Evaporation. The device fabrication was completed by thermally evaporating a 100 nm silver contact on top of the PCBM layer. A shadow mask with a 3 mm diameter was used. The deposition rate was 0.07 cm² was illuminated by employing a metal mask. The cross field emission electron gun.

**REFERENCES**


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Figure SI 1. Photovoltaic parameter distribution of a batch of 24 cells based on NiO hole selective contacts.
Figure SI 2. SEM cross section of FTO/CuSCN/CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$/PCBM structure. The Ag contact is not shown here.