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Cu-doped nickel oxide interface layer with nanoscale thickness for efficient and highly stable printable carbon-based perovskite solar cell

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A B S T R A C T

The power conversion efficiency (PCE) of hole conductor free carbon-based perovskite solar cells (PSCs) is restricted by the poor charge extraction and recombination losses at the carbon-perovskite interface. For the first time we successfully demonstrated incorporation of thin layer of copper doped nickel oxide (Cu:NiO_x) nanoparticles in carbon-based PSCs, which helps in improving the performance of these solar devices. Cu:NiO_x nanoparticles have been synthesized by a facile chemical method, and processed into a paste for screen printing. Extensive X-ray Absorption Spectroscopy (XAS) analysis elucidates the co-ordination of Cu in a NiO_x matrix and indicates the presence of around 5.4% Cu in the sample. We fabricated a monolithic perovskite module on a 100 cm² glass substrate (active area of 70 cm²) with a thin Cu:NiO_x layer (80 nm), where the champion device shows an appreciated power conversion efficiency of 12.1% under an AM 1.5G illumination. To the best of our knowledge, this is the highest reported efficiency for such a large area perovskite solar device. I-V scans show that the introduction of Cu:NiO_x mesoporous scaffold increases the photocurrent, and yields fill factor (FF) values exceeding 57% due to the better interface and increased hole extraction efficiency. Electrochemical Impedance Spectroscopy (EIS) results reinforce the above results by showing the reduction in recombination resistance (R_{rec}) of the PSCs that incorporates Cu:NiO_x interlayer. The perovskite solar modules with a Cu:NiO_x layer are stable for more than 4500h in an ambient environment (25 °C and 65% RH), with PCE degradation of less than 5% of the initial value.

1. Introduction

Significant progress has been made in the design and optimization of perovskite solar cells (PSCs), after the seminal discovery of perovskite semiconductors by [Kojima et al. \(2009\)](#). Direct band-gap, intense broad-band absorption, high carrier mobility, long diffusion lengths and solution processability make perovskite an excellent light absorbing material. ([Wehrenfennig et al., 2014](#); [Stoumpos et al., 2013](#); [Xing et al., 2013](#)) These advantages have allowed the power conversion efficiencies (PCEs) of perovskite photovoltaics to rapidly increase from 3.8% to over 22.7% ([He et al., 2017](#)).

The highly efficient PSCs adopt the device architecture of FTO/ TiO₂/Perovskite/HTL/Au. They are fabricated using spin coating and/ or vacuum deposition techniques at small lab scale (mostly with active area of less than 1 cm²) The PSCs deploy a wide variety of architectural designs from mesoporous to planar, and inverted. The choice of the hole transporting layer (HTL) is crucial in achieving high stability of the PSCs. To date, the highest PCE has been achieved using an organic hole transporting layer such as 2,2',7,7'-tetrakis (N, N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) ([Krishna and Grimsdale, 2017](#)). Organic HTLs, especially spiro-OMeTAD, constitute the bulk of fabrication cost of the PSC, and contribute to the poor stability due to the hygroscopic nature of dopants added and pinholes across the asprepared film ([Jena et al., 2018](#)).

HTL free carbon-based fully printable perovskite solar devices have shown great promise for high stability and upscaling of the solar modules ([Mei et al., 2014](#); [Priyadarshi et al., 2016](#); [Li et al., 2015](#);

[Priyadarshi et al., 2017](#); [Grancini et al., 2017](#); [Ku et al., 2013](#); [Rong et al., 2014](#); [Zhang et al., 2015](#)). The perovskite module architecture reported in this manuscript comprised of a glass-FTO/blocking layer (compact-TiO₂)/mesoporous-TiO₂/ZrO₂/Carbon (mixture of carbon black and graphite), in which all the layers can be screen printed. The perovskite solution is infiltrated from top of carbon layer by manual means or through a slot die coater. The nature of this fabrication technique is highly scalable, which makes it interesting in terms of industrial development. High abundance, low cost and hydrophobic nature makes carbon an excellent counter electrode material. However, the poor interface charge transfer limits the performance of carbonbased PSCs. In addition, the charge carrier extraction by carbon electrode alone is not as efficient as conventional HTL ([Li et al., 2016](#)). Inorganic materials like NiO; CuI, CuOx, CuSCN, and CuGaO₂ have been reported to be the promising materials to replace organic hole transport layer in spin coated PSCs ([Yu and Sun, 2017](#); [Cao et al., 2017](#); [Zeng et al., 2017](#)). Therefore, high mobility hole conductors such as NiO_x ([Liu et al., 2015](#); [Liu et al., 2015](#); [Xu et al., 2015](#)) and spinel Co₃O₄ ([Bashir et al., 2018](#)) have been introduced between the carbon and perovskite interface to improve the hole extraction. NiO_x appears promising because of its intrinsic p-type semiconducting nature, high optical transmittance, deep-lying valence band (5.4 eV) and good stability ([Cao et al., 2017](#)). Despite the beneficial advantages of using a NiO_x layer, the performance of NiO_x based PSCs is still not satisfactory due to its high series resistance (R_s) which is caused by the low intrinsic conductivity of the NiO_x films ([Kim et al., 2015](#)). The partial doping

of metals such as copper (Cu) can mitigate such losses in FF and J_{sc} through its increased p-type conductivity (Kim et al., 2015; Yao et al., 2017; Liu et al., 2016). Cu doping of NiO_x shows significantly enhanced electrical conductivity of the HTL, improving the efficiency of planar heterojunction (PHJ) devices from 8.9% to 15.4% (Liu et al., 2015). In addition, the incorporation of other metals such as magnesium (Mg) and lithium (Li) in a NiO_x matrix can also tune its valence band, which further enhances the hole extraction efficiency (Wu et al., 2016; Chen et al., 2015). Hence it is of significance to study the effect of Cu: NiO_x system on fully printable PSCs with carbon electrodes.

Here, we report a fully printable carbon based perovskite solar module architecture with a thin layer of Cu: NiO_x , which we have deployed as an interfacial structure engineered to improve charge transport from perovskite material to carbon electrode. In this work, we have synthesized high-quality Cu doped NiO_x nanoparticles, and screen printable paste that was synthesized by mixing the nanoparticles with terpineol and ethyl cellulose. The Cu: NiO_x nanoparticles are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray Absorption Spectroscopy (XAS) to elucidate the coordination of Cu in NiO_x matrix. In order to disclose the change in optical absorption behavior achieved by Cu doping, electronic structure calculations based on density functional theory (DFT) formalism are performed using the Vienna Ab-initio Simulation Package (VASP) (Kresse and Furthmüller, 1996; Kresse and Hafner, 1993). The charge extraction property of the screen-printed Cu: NiO_x layer has been investigated using photoluminescence (PL) quenching and Time Resolved PL (TRPL) experiments. We have also fabricated carbon based large area perovskite solar modules (70 cm^2) using a low-cost and robust screen printing technique with a 80 nm thin Cu: NiO_x layer and its performance is evaluated using a Solar

simulator. Electronic impedance spectroscopy (EIS) has been conducted to understand the internal electrical processes in PSCs with Cu: NiO_x interlayer. Finally, the stability of large area solar modules is reported in ambient conditions as well as in a constant light soaking.

We compared our device performance with the device already reported in literature based on carbon counter electrode. The device parameters are listed in Table S1.

2. Results and discussion

2.1. Synthesis and structural characterization of Cu: NiO_x nanoparticles and paste

Optoelectronic properties of NiO_x and Cu: NiO_x nanoparticles depend largely on the processing method employed. (Cao et al., 2017; Jung et al., 2015; Yin et al., 2016). Here, we use a facile chemical precipitation method to prepare pristine NiO_x and 5 atomic % Cu: NiO_x nanoparticles using the procedure described by Yin et al., without any organic surfactant/template to reduce the source of impurities (Yin et al., 2016). 6.442 g of $NiCl_2 \cdot 6H_2O$ (0.271 M) and $CuCl_2 \cdot 6H_2O$ (0.01 M, 5 atomic % Cu) are dissolved in 50 mL of deionized water (DI) to obtain a dark green solution. A stoichiometric volume of NaOH (10 M) is added to the solution to adjust the pH to 10 and to allow the precipitation of the product. After 30 min of stirring, the green colloidal precipitation is allowed to settle for 1 h. The obtained green precipitate is centrifuged at 12000 rpm for 10 mins, washed thoroughly with DI water and ethanol multiple times to remove all residual impurities, followed by drying overnight at 80 °C. Prior to the paste preparation, the nanoparticles are calcined at 400 °C for 4 h to obtain the black Cu: NiO_x nanoparticle powder (Yin et al., 2016). The nanoparticles were then characterized by various techniques as described below. Fig. 1(a) shows the X-ray diffraction (XRD) pattern of NiO_x and

Cu:NiO_x nanoparticles (with 5 atomic % Cu) after annealing at 400 °C. All the Bragg reflections have indexed to the cubic structure of NiO_x (JCPDS –47–1049). Both NiO and Cu:NiO_x nanoparticles exhibit similar diffraction patterns with the characteristic peak corresponding to NiO at 37.21°, 43.23°, 62.79°, 75.40° (Jung et al., 2015; Yin et al., 2016). These peaks can be correspondingly denoted as (1 1 1), (2 0 0), (2 2 0), and (3 1 1) reflections. No other diffraction peaks corresponding to any impurities are observed, representing successful doping of Cu²⁺ ions at Ni²⁺ lattice sites. Having similar ionic radii, Ni²⁺ ions are more susceptible to be replaced by Cu²⁺ at the lattice sites. It is also reported that the Cu inclusion in a NiO_x structure is related to the Ni vacancy generation in the certain compositional range (Kim et al., 2015). This is also noticeable that the relative intensity of crystalline peaks of Cu:NiO_x nanoparticles has progressively improved and the full width at the half maximum (FWHM) of the peaks narrowed as compared to that of nondoped NiO_x nanoparticles. The average crystal size and lattice parameters which are derived from the XRD patterns are shown in Table S2. The crystallite size of NiO_x was calculated to be 12.89 nm while slight increase was observed in Cu:NiO_x with the crystallite size of 19.6 nm. A representation of the crystal structure of Cu:NiO_x is shown in Fig. 1(b) where the blue spheres, grey spheres and red spheres correspond to the Cu, Ni and Oxygen atoms, respectively.

The crystallite size is further confirmed by performing a full Rietveld refinement of the experimental pattern (0% and 5% Cu doped NiO_x). A Rietveld refinement of the experimental diffractogram suggested a crystallite size of 13.6 ± 3 nm for pristine NiO_x and 18.9 ± 3 nm for 5% Cu:NiO_x sample, which is in close agreement with the size calculated using the Scherrer formula (Table S2).

The synthesized Cu:NiO_x nanoparticles are further characterized by the X-ray absorption spectroscopy structure (XAS) at the XAFCA (Du et al., 2015)

beamline of Singapore Synchrotron Light Source (SSLS) at an energy of 8979 eV, which corresponds to the Cu K-edge. All XAS measurements are collected at a ring energy of 0.7 GeV and a ring current of ca. 200 mA. The oxidation state of Cu and Ni is determined by comparing the differences in edge position and white line intensity of the X-ray absorption near edge spectrum (XANES) of the Cu:NiO_x sample and standard reference compounds. In this case Cu₂O (Cu¹⁺) and CuO (Cu²⁺) are used as standards for determining the oxidation state of Cu in Cu:NiO_x. Fig. 2(a) shows the XANES for Cu:NiO_x (blue), with Cu₂O (red), CuO (black) used as standards. The main peak positions of Cu:NiO_x are most similar to CuO, which indicates that the Cu is in the +2 oxidation state. Also, the ligand field splitting of the Cu 4p orbitals in Cu¹⁺ gives rise to additional transition around 8982 eV, which is diagnostic of Cu¹⁺ compounds (Gaur and Shrivastava, 2012). This peak becomes less pronounced as it shifts from Cu¹⁺ to Cu²⁺, which is an additional evidence that the Cu in Cu:NiO_x is in 2+ oxidation state as no visible second peak around 8982 eV is observed.

Fig. 2(b) shows the XANES for Cu:NiO_x (red), NiO_x (blue) and NiO (black). Here, NiO (Ni²⁺) is used as a reference for finding the oxidation states of Ni in NiO_x and Cu:NiO_x. The XANES spectra show that the main peak energy of Cu:NiO_x is similar to NiO which means that Ni in Cu:NiO_x has oxidation state of 2+. While for NiO_x, there is a little shift in the peak position toward higher energy. Therefore, it is apparent that the average oxidation state of Ni in NiO_x is higher than 2+. The edge positions of Cu:NiO_x and NiO_x are closer to NiO, suggesting the majority of Ni in an oxidation state of 2+ with a small percentage of the Ni possibly in the 3+ oxidation state. Table S3 shows the edge energies obtained from XANES analysis and gives a clear depiction of how close the oxidation states of Cu:NiO_x are with respect to its copper and nickel standards.

Fig. 1. (a) XRD pattern of NiO_x and Cu:NiO_x nanoparticles, (b) Crystal structure of Cu:NiO where the blue atoms represent Cu; grey atoms represent Ni and the red dots correspond to oxygen atoms.

A first shell analysis of the Cu:NiO_x sample is investigated (Fig. 2(c,d)) to determine the bond length changes in NiO that could be resulted from the insertion of Cu into the structure. Data have been processed with a k-weight of 2 and k-range of 3.5–9.1 $\text{\AA}^{-1}$. From the XANES analysis, since the oxidation states of both Cu and Ni are majorly found to be at 2+, (Extended x-ray absorption fine structure) EXAFS fitting is first done with CuO and NiO standards to find the ratio of CuO and NiO in the sample. During the experiment, around 5% of Cu is doped into NiO matrix, while EXAFS analysis indicates the presence of around 5.4% Cu in the sample, which is within the experimental uncertainty limit. CuO bond length is typically found in the range of 1.88–1.96 $\text{\AA}$ (Ching et al., 1989; Heinemann et al., 2013) while NiO bond length is approximately 2.07 $\text{\AA}$ (Mansour and Melendres, 1998). Table 1 shows the bond lengths obtained from the first shell analysis of Cu:NiO_x w.r.t the crystallographic file extracted from the DFT calculations. For both Cu and Ni, bond lengths are found to be decreased when compared to the crystal reference file. Ni is found to be coordinated to 6 oxygen atoms with bond lengths ranging from 1.91 to 2.09 $\text{\AA}$, which is in the range of previously reported NiO bond length. Cu^{2+} is found to

Fig. 2. (a) XANES spectra of the Cu K-edge of Cu:NiO_x (blue) in comparison with Cu_2O (red) and CuO (black) standards. (b) XANES spectra of the Ni K-edge of Cu:NiO_x (red) and NiO_x (blue) in comparison with NiO standard (black), (c) First shell analysis of Cu:NiO_x w.r.t Cu k-edge, (d) First shell analysis of Cu:NiO_x w.r.t Ni k-edge.

Table 1

Data obtained from analysis of XAS parameters based on Cu and Ni K-edge of Cu:NiO_x .

Bond	CN	S02	σ^2 ($\text{\AA}^2$)	Delr ($\text{\AA}^\circ$)	Reff ($\text{\AA}^\circ$)	R($\text{\AA}^\circ$)
Cu-O1	2	0.621	0.003	−0.255	2.081	1.825
Cu-O2	4	0.621	0.001	−0.447	2.227	1.780
Ni-O1	2	0.940	0.015	−0.084	1.991	1.906
Ni-O2	2	0.940	0.015	−0.084	2.081	1.996
Ni-O3	2	0.940	0.001	−0.045	2.134	2.089

CN co-ordination number, S02 amplitude factor, σ^2 EXAFS

Debye–Waller factor or disorder factor, R – bond distance.

be at a symmetric coordination with 4 planar and 2 axially coordinated oxygen atoms. It is well known that the Jahn–Teller effect (JT) is responsible for the distortion of CuO_6 octahedra, which results in a compressed Cu^{2+} octahedral structure and there is a possibility of the same JT effect resulting in the shortening of the NiO bonds as well (Veidis et al., 1969).

The structural feature and surface morphology of synthesized nanoparticles are analyzed using SEM and representative images as shown in Fig. 3 (a, b). The results indicate that the particles are almost spherical in shape, but an agglomeration of particles has occurred. It is noticeable that agglomeration is less in case of pristine NiO_x nanoparticles as compared to the Cu:NiO_x . This is possibly due to the Cu:NiO_x nanostructures having higher surface energy and surface tension as compared to pristine NiO_x , which would increase the tendency to agglomerate (Rahdar et al., 2014). A typical nanoparticle size of less than 100 nm is visible in Fig. 3 (a, b) in both the samples.

To further confirm the composition of synthesized nanoparticles, Energy-dispersive X-ray spectroscopy (EDS) is conducted. Copper (Cu), nickel (Ni) and oxygen (O) are detected (Fig. S1), and the relative concentration of Ni and Cu are determined to be 47.0% and 3%, respectively. The atomic ratio of Ni to Cu is close to 16:1, in good agreement with the

stoichiometric ratio of Cu in NiO . The elemental mapping of synthesized Cu:NiO_x is shown in Fig. 3(c-e).

The respective nanoparticles are mixed with terpineol and ethyl cellulose to prepare a paste for screen-printing on the glass substrate (details in experimental section). The prepared films are characterized using XRD, SEM, UV-Vis spectroscopy and four-point probe measurements to understand the effect of doping on the electrical and optical properties of NiO_x nanoparticles, as well as to monitor any changes in morphology during the thermal annealing process.

The top-view SEM images of the screen-printed films on a glass substrate are represented in Fig. 3(f, g). The films showed mesoporous morphology with agglomerated spherical nanoparticles of pristine NiO_x and Cu:NiO_x nanoparticles, which is required for the perovskite solution infiltration. It is clear from Fig. 3 (f, g) that there is an increase in agglomeration and particle size with the addition of Cu in the sample.

Fig. 3. Top view SEM image of synthesized nanoparticles, (a) NiO_x , (b) Cu:NiO_x , (c-e) EDS mapping for Ni, O and Cu, (f, g) Top view SEM image of screen-printed film, (f) NiO , (g) Cu:NiO_x (inset shows the color of screen printed films with and without the Cu doping).

Fig. 4. (a) Absorption spectra of NiO_x and Cu:NiO_x on glass (thickness = 500 nm), (b) calculated band gap of NiO_x and Cu:NiO_x, (c) Optical Absorption Cross section for NiO_x and 5% Cu:NiO_x, (d) The structures of pristine NiO_x and Cu:NiO_x calculated from Hellman-Feynman forces.

The XRD pattern of screen printed film (Fig. S1) reveals that the crystal structure remains unchanged for the printed Cu:NiO_x film. The diffraction pattern of nanoparticles and screen-printed film are in good agreement including the peak position and intensity.

Fig. 4 (a) shows the optical absorption spectra of screen printed pristine NiO_x and Cu:NiO_x films on glass. The data are recorded in the wavelength range of 300–900 nm. It is observed that the absorption decreases with an increase in wavelength. Rapid decrement can be observed from 300 to 550 nm while at the higher wavelength decrement in absorption is relatively lower. The absorbance is found to increase with an addition of copper in the sample, which could be due to the increase in grain size. The absorption

band gap energy can be determined from absorption spectra using below equation:

$$(\alpha h\nu)^n = B(h\nu - E_g)$$

Here, the $h\nu$ is the photon energy (eV), B' is the constant relative to the material, E_g is the band gap, α is absorption coefficient and exponent n has different values depending on the electronic transitions in the material (2 for the direct allowed transitions, $\frac{1}{2}$ for indirect allowed transition and $\frac{2}{3}$ for direct forbidden transitions). (Makhlouf et al., 2013) Fig. 4 (b) shows the variation of $(\alpha h\nu)^2$ versus $(h\nu)$ for screen printed NiO_x and Cu:NiO_x films on glass. The optical band gap energy has decreased from 3.25 eV (Pristine NiO_x) to 3.12 eV (Cu:NiO_x).

Fig. 4(c, d) shows electronic structure calculations based on DFT framework using Vienna Ab-initio Simulation Package to understand the optical response of Cu:NiO_x. To mimic the experimental conditions, we have maintained the doping concentration of Cu in NiO_x as 5%, where the doping has been introduced in substitutional manner. For the exchange-correlation corresponding to our model systems, we have used generalized gradient approximation (GGA) of the type PerdewBurke-Ernzerhof (PBE) functional (Perdew et al., 1996). The structures of pristine and Cu:NiO_x have been optimized until the calculated Hellman-Feynman forces are smaller than 0.001 eV/Å (Fig. 4(d)). After obtaining the optimized configurations, we have determined the optical absorption cross section of the corresponding pristine and Cu:NiO_x by considering double the number of occupied states to have adequate number of unoccupied states for the transition between valance and conduction bands (Fig. 4(c)). The optical absorption spectra can be extracted as the imaginary part of the frequency dependent dielectric function based on the Fermi's Golden Rule to determine the oscillator strength. We have observed differences in the optical response in the visible range for both pristine and Cu:NiO_x systems (Fig. 4(c)); Cu:NiO_x system shows enhancement of optical response compared to the pristine NiO_x system. This also supports the experimental outcome of the comparative optical response between pristine and Cu:NiO_x system, where the similar enhancement in optical response has been observed with the introduction of Cu dopant in NiO_x.

To explore the influence of Cu doping on the electrical conductivity of NiO_x, we measured the resistivity of pristine NiO_x and Cu:NiO_x films on glass by four-point probe as depicted in Table 2.

Table.2

Sample	Sheet Resistance Ω/cm)	Conductivity S/cm
NiO _x /glass	1.0×10^6	2E-3
Cu:NiO _x /glass	1.0×10^3	0.20
Carbon/glass	10.15	0.76

The sheet resistance is reduced significantly when 5% Cu ions are embedded into NiO_x matrix. Reduction in sheet resistance of NiO_x is mainly due to the increase in the carrier concentration with copper doping as reported in literature (Chen et al., 2011). Generally, the main cause of p-type conductivity of NiO_x could be ascribed to the excess oxygen (or metal deficit) within the lattice site (substitutional or interstitial). The excess oxygen would create vacancies in the normally occupied Ni sites. To preserve overall electrical neutrality, two Ni⁺² ions will be converted to Ni⁺³ for every Ni vacancy site. As Ni⁺³ ion is not stable, it will change from one Ni⁺² site to another. The process looks as if positive holes are moving. Ni⁺³ site acts as impurity level above the filled band and the excitation of electrons to these sites leaves mobile holes in the band (Yang et al., 2011; Sasi et al., 2002). It is reported in the literature that the substitutional doping of the material with an appropriate dopant is an effective method to increase the conductivity of p-type metal oxides (Yang et al., 2011). It seems that the dopant Cu on Ni site increases the concentration of holes thus the film conductivity be enhanced. According to the Kroger-Vink notation (Kröger and Vink, 1956), the defect reaction in Cu:NiO_x films could be presented by equation Scheme S1 (supporting information).

To investigate the photo-generated charge separation efficiency of NiO_x and Cu:NiO_x we conducted steady state photoluminescence (PL) and time-resolved PL (TrPL). Fig. 5(a) shows the steady state PL of ZrO₂, ZrO₂/C, ZrO₂/NiO_x/C, and ZrO₂/Cu:NiO_x/C films with infiltration of MAPbI₃. The steady state PL shows a significant quenching with carbon as contact. The maximum PL quenching

is observed with the use of Cu:NiO_x interlayer between ZrO₂ and C. TRPL measurement as shown in Fig. 5(b) was performed with excitation at 400 nm and detection on the all emission band. ZrO₂ acts as reference as its conduction band is not suitable for hole injection. The decay curve is fitted with bi-exponential decay function. The PL decay of MAPbI₃ infiltrated in ZrO₂ film exhibits a time constant of 8.4 ns whereas, for MAPbI₃/ZrO₂/C, MAPbI₃/ZrO₂/NiO_x/C and MAPbI₃/ZrO₂/Cu:NiO_x/C are 5.4, 4.2 and 2.09 ns, respectively. Thus, steady-state and time resolved PL quenching confirms the improved charge transfer due to a thin interlayer of Cu:NiO_x.

2.2. Perovskite solar cell fabrication and photovoltaic performance

The device architecture is similar to our previous report on carbon based perovskite solar cells with the addition of a thin interlayer of NiO_x or Cu:NiO_x between ZrO₂ and C. (Priyadarshi et al., 2016) The details of the device fabrication are provided in the experimental section. Fig. 6(a) shows the schematic of the perovskite solar cells which consist of glass/FTO/C-TiO₂/m-TiO₂/ZrO₂/Cu:NiO_x/C. The band diagram for the device architecture in Fig. 6(b) shows the valance band position of NiO_x (−5.5 eV); Cu:NiO_x (−5.4 eV) matches closely with the valence band of perovskite (−5.4 eV) (Jung et al., 2015; Weber et al., 2018). Fig. 6(c, d) shows cross-sectional SEM images of the perovskite solar cell with Cu:NiO_x film.

The device performance has been optimized by varying the thickness of Cu:NiO_x and ZrO₂ with an device active area of 0.8 cm². The thickness of ZrO₂ and Cu:NiO_x is varied by diluting the original paste with terpineol having the thicknesses of 1.4 μm and 570 nm, respectively (See experimental section). The cross-sectional SEM images for different dilutions of Cu:NiO_x are presented in Fig. S2. Results of the

champion devices with different thicknesses of Cu:NiO and ZrO₂ are presented in Tables S4 and S5. From the results, it is clear that when Cu:NiO_x was thick (1:0, 1:3 and 1:2 dilutions) with a thick layer of ZrO₂ (1.3 μm), device has low fill factor that might be due to the high series resistance of the as shown in Table S4. On the other hand, when we applied a thin layer of ZrO₂ (500 nm, 800 nm, 1000 nm), devices showed current leakage and low shunt resistance, resulting in low open circuit voltage (V_{oc}) and fill factor (FF) as shown in Table S5. Devices with ~80 nm (1:5 dilution) thick Cu:NiO_x and 1.3 μm thick ZrO₂ showed better performance with the high fill factor (FF) and V_{oc}. Although results show a little variation, it is clear that a ~80 nm thick layer of Cu:NiO_x gives the best performance and thinner or thicker Cu:NiO_x films yield inferior device performance. The variation in FF, J_{sc}, V_{oc} and PCE with different thicknesses of Cu:NiO_x for 8 devices are displayed in Fig. S3.

The device performance is higher for samples with Cu:NiO_x interlayer as compared to devices with NiO_x and without any additional interlayer. The best device performance is presented in Fig. 7(a). PSC with Cu:NiO_x interlayer shows a high V_{oc} of 1.00 V, J_{sc} of 22.15 mA/cm² and FF of 0.57 leading to overall efficiency of 12.79% (device area = 0.8 cm²). The corresponding cell parameters for PSCs are summarized in Table 2. The enhanced performance could be due to the deep lying VB of Cu:NiO_x (−5.4 eV) forming a better ohmic contact with the perovskite layer, resulting in a large potential difference between the hole and electron transport layers and less potential losses at HTL/perovskite interface. (Jeng et al., 2014; Park et al., 2015) J-V curves at scan rate of 0.3 V/s for device containing Cu:NiO_x film measured in different scan directions (reverse and forward) are shown in Fig. 7(b). The devices exhibit negligible hysteresis with the PCEs of 12.79% (reverse scan) and 12.65% (forward scan). The average value for device performances for 10

Fig. 5. (a) Photoluminescence (PL) spectra of $\text{MAPbI}_3/\text{ZrO}_2$, $\text{MAPbI}_3/\text{ZrO}_2/\text{C}$, $\text{MAPbI}_3/\text{ZrO}_2/\text{NiO}_x/\text{C}$, and $\text{MAPbI}_3/\text{ZrO}_2/\text{Cu:NiO}_x/\text{C}$ films on glass, (b) TrPL of $\text{MAPbI}_3/\text{ZrO}_2$, $\text{MAPbI}_3/\text{ZrO}_2/\text{C}$, $\text{MAPbI}_3/\text{ZrO}_2/\text{NiO}_x/\text{C}$ and $\text{MAPbI}_3/\text{ZrO}_2/\text{Cu:NiO}_x/\text{C}$ on glass, inset: showing the zoom out peak for $\text{MAPbI}_3/\text{ZrO}_2/\text{Cu:NiO}_x/\text{C}$.

Fig. 6. (a) Schematic illustration of the device architecture, (b) Work function of different layers, (c) low magnification and, (d) high magnification cross-sectional SEM images of the perovskite/carbon solar cell with Cu:NiO_x interlayer.

Fig. 7. (a) J-V characteristics of standard carbon cell with and without Cu:NiO_x layer with an aperture area of 0.8 cm² (Forward and Reverse scan), (b) Forward and reverse scan of device with Cu:NiO_x layer with an aperture area of 0.8 cm², at scan rate of 0.3 V/s under 1 Sun (100 mW/cm²) light illumination, (c) J-V characteristics of standard carbon cell with and without Cu:NiO_x layer with an aperture area of 70 cm² (Forward and Reverse scan), (d) Forward and reverse scan of device with Cu:NiO_x layer with an aperture area of 70 cm² under 1 Sun (100 mW/cm²) light illumination, (e): IPCE spectra of devices, Standard carbon (18.01 mA/cm²), NiO_x/C (18.77 mA/cm²), and Cu:NiO_x/C (19.84 mA/cm²).

Table 3

Solar cell parameters for carbon-based cells with and without Cu:NiO_x with aperture of 0.8 cm² under 1 Sun (100 mW/cm²) light illumination.

Parameters	Standard Carbon		With NiO		With Cu:NiO	
	Reverse	Forward	Reverse	Forward	Reverse	Forward
V _{oc} (V)	0.89	0.89	0.95	0.94	1.00	0.98
J _{sc} (mA/cm ²)	21.13	21.75	22.09	21.98	22.15	22.65
FF	0.49	0.49	0.50	0.51	0.57	0.57
PCE (%)	9.21	9.48	10.49	10.53	12.79	12.65

Table 4

Solar cell parameters for PSM of 70 cm² with and without Cu:NiO_x with an active area under 1 Sun (100 mW/cm²) light illumination.

Parameters	Standard carbon		With Cu:NiO	
	Reverse	Forward	Reverse	Forward
V _{oc} (V)	8.87	8.20	9.57	9.42
I _{sc} (mA)	149.3	136.5	153.2	151.0
FF	0.51	0.54	0.59	0.58
PCE (%)	9.75	8.75	12.10	11.90

devices with and without Cu:NiO_x is shown in Table S6. The results showed high reproducibility with an average PCE of 12.03% $\pm$ 0.3 for devices with Cu:NiO_x interlayer. The distribution curve for 17 devices with Cu:NiO_x interlayer with active area of 0.8 cm² is shown in Fig. S4. The best performing perovskite solar cell with Cu:NiO_x exhibits nearly hysteresis-free performance at slow scan rates (0.15 V/s and 0.05 V/s) as shown in Fig. S5 (a, b, c).

The incident photon-to-electric current conversion efficiency (IPCE) spectra for these devices with an active area of 0.8 cm² are shown in Fig. 7(e). These experiments used the monochromatic light without applying a white-light bias. The integrated J_{sc} from IPCE spectra for devices with NiO_x, Cu:NiO_x and without HTLs was 18.77 mA/cm², 19.84 mA/cm², and 18.01 mA/cm², respectively. Integrated J_{sc} shows slightly lower value as compared to measure from J-V (Table 3). The lower current density from IPCE measurement than from the J-V scan was probably due to the dependence of J_{sc} on light intensity, which derived from the trap state in electron transport layer. As IPCE spectra were measured under monochromatic light without bias light, resulting in lower carrier density and a lower filling level of the trap state than that under one sun illumination for the J-V measurements (Ryu et al., 2017).

The effect of Cu concentration on device performance has been studied by fabricating the PSC devices with 3% Cu doped NiO_x and 10% Cu doped NiO_x. A weakening photovoltaic performance is observed with 10 atomic % Cu doped NiO_x as shown in Table S7. This may originate due to the reduction in carrier mobility caused by surface defects due to the excess Cu. This reduction in device performance when using more than 5% Cu is similar to the trend observed in inverted perovskite solar cells that employed Cu doped NiO_x as HTL. (Kim et al., 2015).

The same devices with an active area of 0.8 cm² are tested using a metal mask to give an aperture of 0.09 cm², and the resulting efficiencies are presented in Fig. S6. The best device shows an efficiency of 13.74% with V_{oc} = 0.87 V, J_{sc} = 23.70 mA/cm² and FF = 0.69.

Furthermore, to confirm the reproducibility of performance, 8 devices are fabricated for each condition and tested with an area of 0.09 cm². The corresponding average values of FF, J_{sc}, V_{oc} and PCE along with their standard deviation are presented in Table S8.

After achieving an improved efficiency with the incorporation of Cu:NiO_x on active area of 0.09 cm² and 0.8 cm², we fabricated a 100 cm² perovskite module with an active area of 70 cm². These modules are assembled using a semi-automated screen-printing process. For the modules, the perovskite infiltration is done using an automated slot-die coater. The photovoltaic parameters of the perovskite solar module (PSM) with active area of 70 cm² (containing 10 sub-cells of area 7 cm² connected in series) are shown in Fig. 7(c, d) and summarized in Table 4. All measurements are performed under standard reporting conditions (AM 1.5G) without any encapsulation. The champion module has delivered an efficiency of 12.10%, with an improved V_{oc}, J_{sc} and FF.

2.3. Analysis of device performance

We have observed an improvement in device performance when Cu:NiO_x has been used as a HTL in the carbon-based PSC.

Electrochemical impedance spectroscopy (EIS) is performed in dark and light conditions to investigate the internal charge transport and recombination resistance in the devices. Fig. 8(a, b) shows the Nyquist plot for devices with and without Cu:NiO_x at

a different bias. Only one semicircle can be observed from the Nyquist plots under dark condition (Fig. 8(a)), corresponding to the interfacial resistance between the HTL and perovskite, which provides information about the recombination resistance (R_{rec}) and charge transfer resistance (R_{ct}) (Xu et al., 2015; Bisquert et al., 2014; Gonzalez-Pedro et al., 2014). Carrier transport and dynamics in a carbon-based perovskite cell are comprised of charge transfer processes at the cathode (TiO_2 /perovskite interface), the anode (carbon/perovskite and Cu:NiO_x /perovskite interface) and recombination within the active layer. However, a single distinct semicircle corresponding to the single resistor-capacitor (RC) element is obtained in the Nyquist plot and is generally attributed to the charge-transfer/charge-recombination resistance at the carbon/perovskite interface. This is because the charge transfer-resistance/charge-recombination resistance at TiO_2 /perovskite is too small to be detected due to the fast electron injection, large contact area and better interface contact (Yang et al., 2014; Wang et al., 2005). The high frequency semicircle obtained in the Nyquist plot is fitted with the equivalent circuit to extract R_{ct} and R_{rec} . If the conductivity is high, the transport resistance is too small to be observable (Bisquert et al., 2014). Hence, the semicircle shown in Fig. 8(a) provides the information about charge recombination resistance at the perovskite/HTL interface. The impedance measurements are performed at different operating potentials and corresponding values from the individual Nyquist plots were fitted to get R_{rec} (Fig. 8(c)). R_{rec} values remained higher for $\text{Cu:NiO}_x/\text{C}$ device throughout the operational voltage window. This proves that the insertion of the Cu:NiO_x layer reduced the interfacial recombination. This was

further confirmed by the current density-voltage (J-V) curve of a device measured in darkness as shown in Fig. S7. The Cu:NiO_x based devices showed much better diode performance as compared to standard devices without Cu:NiO_x interlayer.

EIS measurements are also conducted under 1 Sun illumination over a frequency range of 1 MHz to 0.1 Hz, at different applied biases (0.1 V to 0.3 V) to study the charge transfer and recombination resistance in devices with and without Cu:NiO_x . Fig. 8(b) shows EIS Nyquist plots for devices with and without Cu:NiO_x . The semicircle in the high frequency region is assigned to the charge transfer resistance at HTL/perovskite interface, and the second semicircle in the low frequency region is attributed to the recombination resistance (R_{rec}). Similarly, by fitting the individual Nyquist plots at different applied bias using the equivalent circuit shown in Fig. 8(b), we get R_{rec} and R_{ct} (Fig. 8(d,e)). R_{ct} values remain smaller for $\text{Cu:NiO}_x/\text{C}$ cell at all values of applied potential (Fig. 8d). This indicates the better charge carrier rate and improved interface by the inclusion of Cu:NiO_x layer which resulted into an increase of FF. (Habisreutinger et al., 2014) On the contrary, the largest R_{rec} (Fig. 8(e)) in the $\text{Cu:NiO}_x/\text{C}$ device can explain the increase in the V_{oc} by C/perovskite heterojunction engineering (Ryu et al., 2017).

2.4. Device stability

Despite the fact that PSC has been comparable to silicon in terms of PCE, the stability of PSC remains as one of the main concern. Inorganic-organic MAPbI_3 perovskites are vulnerable to moisture due to their

Fig. 8. (a) Nyquist plots of different devices at different applied bias under dark, (with equivalent circuit diagram used to fit data) (b) Nyquist plots of different devices at different applied biases under 1 sun illumination, (with equivalent circuit diagram used to fit data), (c) charge transfer resistance (R_{rec}) vs potential measurement of carbon/perovskite solar cell with (Cu:NiO_x/C) and without Cu:NiO_x (Carbon) with an active area of 0.8 cm² under dark, (d) charge transfer resistance (R_{ct}) vs potential measurement of carbon/perovskite solar cell with (Cu:NiO_x/C) and without Cu:NiO_x (Carbon) with an active area of 0.8 cm² under 1 sun illumination, (e) charge recombination resistance (R_{rec}) vs potential measurement of carbon/perovskite solar cell (Cu:NiO_x/C) and without Cu:NiO_x (Carbon) with an active area of 0.8 cm² under 1 sun illumination.

Fig. 9. (a) Normalized PCE for the standard perovskite solar cell containing carbon and Cu:NiO_x HTL measured under ambient environment conditions, (b) MPPT measurement of Cu:NiO_x for 145 h.

hygroscopic nature. Therefore, a moisture resistant top contact HTL is preferred to increase the moisture stability of PSCs (Zhang et al., 2017; Tong et al., 2016). Beside behaving as a contact, carbon also proves to be a good encapsulant for PSCs which improves the device stability by protecting it from humidity. We have analyzed the performance and stability of carbon PSCs after insertion of a Cu:NiO_x HTL. Cells are exposed to the ambient environment (25 °C and 65% RH) for more than six months (4500hrs), without any encapsulation and the performance is measured under standard AM 1.5G solar spectrum illumination every week. Fig. 9(a) shows the normalized PCE of PSCs with and without Cu:NiO_x measured under standard AM 1.5G illumination. The changes in J_{sc} , FF and V_{oc} for the devices with and without Cu:NiO_x are presented in Fig. S8. The device efficiency for PSCs with a Cu:NiO_x interlayer remained remarkably unchanged for more than 6 months and the devices showed no sign of degradation. The device efficiency for PSCs with carbon alone has suffered a decrement of about 10%. Cu:NiO_x interlayer resists the moisture and provides extra stability. Maximum power point tracking (MPPT) is performed on PSC with Cu:NiO_x interlayer. The output current density is monitored at

continuous illumination with constant applied bias of 0.62 V (Fig. 9(b)) (Christians et al., 2015). The current remained above 20 mA/cm² for more than 50 h. The device with Cu:NiO_x interlayer is showing no sign of degradation for 60 h. A slight increase in the current was observed during MPPT measurement. This is commonly attributed to the interaction of perovskite layer with ambient humidity (Hashmi et al., 2017). The J-V curve of the device along with the device parameters is obtained under 1 Sun illumination which is presented in Fig. S9.

3. Conclusion

NiO_x and 5% Cu-doped NiO_x nanoparticles have been prepared by chemical precipitation method using NiCl₂·6H₂O and CuCl₂·6H₂O as the precursors. The structural, compositional, morphological, and optical properties of the prepared samples are studied using XRD, EDS, SEM, XAS, UV-visible spectroscopy and DFT. The XAS studies confirmed the co-ordination of Cu in NiO_x matrix of the prepared nanoparticles. Steady state PL and TrPL measurements confirm efficient extraction of the photo-generated carriers from a perovskite absorber with a thin interlayer of Cu:NiO_x. The conductivity

of the NiO_x film increases with 5 atomic % Cu doping. DFT and UV-vis spectroscopy show a lowering of the band gap and the absorption edge is found to increase as the Cu concentration increases. Fully printed carbon-based perovskite solar module (an active area of 70 cm^2 on 100 cm^2 substrate) with a thin Cu:NiO_x layer achieved a record PCE of 12.10% under 1 Sun illumination. The devices with Cu:NiO_x HTL show excellent stability under ambient conditions for more than 6 months without any encapsulation. These results provide a promising method toward low cost and scalable PSCs with significant long-term stability realized through a Cu:NiO_x HTL.

4. Experimental section

4.1. Materials

All the chemicals used in this study were of analytical grade and used without further purification.

4.2. Preparation of Cu:NiO_x paste for screen printing

The paste for screen-printing was prepared by mixing 1 g of nanoparticles in a 100 mL mortar pot with 26.00 g ZrO_2 beads (0.33 mm diameter), 0.33 mL ethanol, 0.16 mL acetic acid and 0.16 mL DI water. The resultant slush was ball milled at 450 rpm for 6 h. After grinding, the resultant slush was mixed with 66.60 mL of ethanol and stirred for 20 min. Then, the stirring was stopped, and the suspension began to separate. After 10 min, the supernatant colloidal solution was separated and mixed with 10.00 g ethyl cellulose and 8.00 g terpeneol. Finally, the whole colloidal solution was concentrated by rotary evaporator to obtain NiO_x and Cu:NiO_x paste for screen printing containing 10% nanoparticles, 10% ethyl cellulose and 80% terpeneol by weight. The thickness of the original paste was 570 nm, which was further diluted with terpeneol in the different

weight ratios (w/w Cu:NiO_x : terpeneol, 1:7, 1:5, 1:3) followed by stirring to get different thickness.

4.3. Solar cells fabrication

Screen printed solar cells were fabricated by our reported method (Priyadarshi et al., 2016). Briefly, the Fluorine doped tin oxide (FTO) (FTO, $\sim 14 \text{ ohm}$ per square, 2.2 mm thick) substrates were cleaned with decon soap, DI water and finally with ethanol. These substrates were then treated with 50 mM of TiCl_4 solution (Wako Pure Chemical Industries, Ltd) for 30 min at 70°C , followed by rinsing with DI water. The substrates were held at 500°C for 30 min to allow formation of TiO_2 crystals to serve as the seed layer. A compact TiO_2 layer was then printed using a screen printer (MicroTec MT320TV) followed by relaxing and annealing at 500°C for 30 min. To fill up pin-holes in the printed compact TiO_2 layer, the substrates were treated with 100 mM of TiCl_4 solution for 30 min at 70°C followed by DI water rinsing and annealing at 500°C for 30 min. Subsequently, a 500 nm thick mesoporous TiO_2 film was printed onto the substrates using TiO_2 paste (Dyesol NRD-30, diluted with terpeneol (Sigma, FG) in weight ratio 1:1.4). To improve crystallinity, sintering was done at 500°C for 30 min with gradual ramping up of temperature. A $1.4 \text{ }\mu\text{m}$ thick ZrO_2 (Solaronix, Zr-Nanoxide ZT/SP) layer was applied as a spacer layer on top of the mesoporous TiO_2 followed by annealing at 500°C for 30 min. The thickness of ZrO_2 is varied by diluting the original paste having thickness of $1.4 \text{ }\mu\text{m}$ with the different weight ratios of terpeneol (w/w, ZrO_2 : Terpeneol) followed by stirring at room temperature. The different dilutions have thickness of 1000 nm (1:0.5), 800 nm (1:1), and 500 nm (1:1.4). On top of ZrO_2 , a very thin layer (80 nm) of $\text{Cu:NiO}_x/\text{NiO}_x$ was printed as HTL, and the film was sintered at 500°C for 30 min. Finally, to complete the device stack, carbon was printed as a top electrode (13 μm). After carbon printing, the substrates were annealed at 400°C for

30 min to remove solvents and binders (ethyl cellulose, terpeneol). The active areas of the devices were 0.09 cm², 0.8 cm² and 70 cm².

The MAPbI₃ perovskite solution was made by adding equimolar quantities of MAI and PbI₂ with a small quantity of AVA-I (1:20 atomic ratio, AVA-I to MAI) in GBL solvent (γ -Butyrolactone Sigma, $\geq 99\%$), followed by heating overnight at 50 °C to complete dissolution. This solution was then drop-casted through the carbon layer.

For 70 cm² module the infiltration was done using slot die-coating. 1 M perovskite solution was prepared by dissolution of the precursors in γ -Butyrolactone (GBL). 3% molar ratio of AVAI is added to the solution, and the solution is kept on stirring on a 50 °C hot-plate overnight to ensure complete dissolution. The slot die coater used is nTact Nrad, with a coating width of 200 mm for the slot die head. The shim thickness is 75 μ m, and width is 90 mm for the dispensing of the perovskite solution. The amount of solution dispensed was 250 μ L, over a time period of 1 min. After coating, the substrate was kept on a flat surface for 15 min. Subsequently, the substrate was heated at 50 °C for 90 min, after which the temperature was increased to 60 °C for 30 min. Silver paint was used to serve as contact electrodes for IV characterization.

4.4. Characterizations

Thin film X-ray diffraction data for synthesized nanoparticles and screen-printed films were collected using a Bruker D8 Advance diffractometer using Cu K α radiation in the 2 θ range of 10° to 70°. The XRD of screen-printed films was taken without any dilution having a thickness of around 570 nm. The FE-SEM images were acquired using Jeol JSM-7600F Field Emission Scanning Electron Microscope. I-V characteristics of the devices were measured using the solar simulator (San-EI Electric, XEC-301S) equipped with a 450 W xenon lamp connected to a Keithley 2612A source meter. The

power of the simulated light was calibrated using a Si reference cell (Fraunhofer) and monitored using a power meter throughout the testing. The IPCE (PV measurements, Inc., Boulder, CO) was measured without bias light in the wavelength range of 300 nm to 800 nm. Impedance spectroscopy was performed using Autolab potentiostat (PGSTAT 302). A voltage perturbation of 20 mV was applied from 400 kHz to 1 Hz at different bias voltages. For steady state Photoluminescence (PL), the micro-PL setup is based on fiber coupled microscope system, employing a VISNIR microscope objective (10x, NA = 0.65). The samples were excited with picosecond-pulse light emitting diode at 405 nm (Picoquant P-C405B) with a 5-MHz-repetition-rate. To study the TRPL decay, the micro-PL setup used a fiber coupled microscope system, with a VIS-NIR microscope objective (10x, NA = 0.65). The samples were excited by a picosecond-pulse light emitting diode at 405 nm (Picoquant P-C-405B) with a 5-MHz repetition rate. The beam spot size was ~ 10 mm. The TRPL decays were collected with an Acton monochromator (SpectraPro 2300), fiber coupled to the microscope, and detected by Micro Photon Devices single-photon avalanche photodiode. The signal was then received by a time-correlated single photon counting card. The temporal resolution is ~ 5 picoseconds. To measure MPPT, an Autolab machine (PGSTAT302N, Software version- NOVA 1.11) was used to apply the voltage and measure the current, while the samples were illuminated with a white LED light source. UV-Vis absorption spectra were recorded for screen-printed films using a Shimadzu UV2501PC Spectrometer in wavelength range of 300–900 nm.

X-ray absorption fine structure (XAFS) characterization at the Cu Kedge (8979 eV) for Cu:NiO_x was carried out at XAFCA beamline of Singapore Synchrotron Light Source (SSLS). All XAS measurements were collected at a ring energy of 0.7 GeV and a ring current of ca. 200 mA. A Si (1

1 1) crystal monochromator was used and data were collected in fluorescence mode at ambient temperature. The X-ray energy was calibrated at the inflection point of the absorption edge of copper foil. The Ni- K-edge (8332.8 eV) of the same sample Cu:NiO_x was collected at beamline 1.1 W at Synchrotron Light Research Institute (SLRI), Thailand. A Si(1 1 1) double crystal monochromator with an energy resolution of ($\Delta E/E$) of 10^{-4} was used and data were collected in transmission mode. The XAS for copper and nickel reference samples were taken from the database of BL5.2 beamline of Synchrotron Thailand Central Lab. Data analysis was carried out with Athena and Artemis included in the Demeter package (Ravel and Newville, 2005). The powder sample was prepared into a pellet using a pelletizer of diameter 10 mm and mounted on the sample holder for XAS measurement. Usually around 7 mg of sample is mixed with 50 mg of boron nitride to make the pellet.

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References

- Bashir, A., Shukla, S., Lew, J.H., Shukla, S., Bruno, A., Gupta, D., Baikie, T., Patidar, R., Akhter, Z., Priyadarshi, A., 2018. Spinel Co_3O_4 nanomaterials for efficient and stable large area carbon-based printed perovskite solar cells. *Nanoscale*.
- Bisquert, J., Mora-Sero, I., Fabregat-Santiago, F., 2014. Diffusion–recombination impedance model for solar cells with disorder and nonlinear recombination. *ChemElectroChem* 1, 289–296.
- Cao, J., Yu, H., Zhou, S., Qin, M., Lau, T.-K., Lu, X., Zhao, N., Wong, C.-P., 2017. Low temperature solution-processed NiO_x films for air-stable perovskite solar cells. *J. Mater. Chem. A* 5, 11071–11077.
- Chen, S., Kuo, T., Lin, Y., Lin, H., 2011. Preparation and properties of p-type transparent conductive Cu-doped NiO films. *Thin Solid Films* 519, 4944–4947.
- Chen, W., Wu, Y., Yue, Y., Liu, J., Zhang, W., Yang, X., Chen, H., Bi, E., Ashraful, I., Grätzel, M., 2015. Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers. *Science* 350, 944–948.
- Ching, W., Xu, Y.-N., Wong, K., 1989. Ground-state and optical properties of Cu_2O and CuO crystals. *Phys. Rev. B* 40, 7684.
- Christians, J.A., Manser, J.S., Kamat, P.V., 2015. Best practices in perovskite solar cell efficiency measurements. Avoiding the error of making bad cells look good. ACS Publications.
- Du, Y., Zhu, Y., Xi, S., Yang, P., Moser, H.O., Breese, M.B., Borgna, A., 2015. XAFCA: a new XAFS beamline for catalysis research. *J. Synchrotron Rad.* 22, 839–843.
- Gaur, A., Shrivastava, B., 2012. A comparative study of the methods of speciation using X-ray absorption fine structure. *Acta Physica Polonica A* 121.
- Gonzalez-Pedro, V., Juarez-Perez, E.J., Arsyad, W.-S., Barea, E.M., Fabregat-Santiago, F., Mora-Sero, I., Bisquert, J., 2014. General working principles of $\text{CH}_3\text{NH}_3\text{PbX}_3$ perovskite solar cells. *Nano Lett.* 14, 888–893.
- Grancini, G., Roldan-Carmona, C., Zimmermann, I., Mosconi, E., Lee, X., Martineau, D., Nabey, S., Oswald, F., De Angelis, F., Graetzel, M., Nazeeruddin, M.K., 2017. One-Year stable perovskite solar cells by 2D/3D interface engineering. *Nat. Commun.* 8, 15684.
- Habisreutinger, S.N., Leijtens, T., Eperon, G.E., Stranks, S.D., Nicholas, R.J., Snaith, H.J., 2014. Enhanced hole extraction in perovskite solar cells through carbon nanotubes. *J. Phys. Chem. Lett.* 5, 4207–4212.
- Hashmi, S.G., Martineau, D., Dar, M.I., Myllymäki, T.T.T., Sarikka, T., Ulla, V., Zakeeruddin, S.M., Grätzel, M., 2017. High performance carbon-based printed perovskite solar cells with humidity assisted thermal treatment. *J. Mater. Chem. A* 5, 12060–12067.
- He, Q., Yao, K., Wang, X., Xia, X., Leng, S., Li, F., 2017. Room-Temperature and Solution Processable Cu-Doped Nickel Oxide Nanoparticles for Efficient Hole-Transport Layers of Flexible Large-Area Perovskite Solar Cells. *ACS Appl. Mater. Interfaces* 9, 41887–41897.
- Heinemann, M., Eifert, B., Heiliger, C., 2013. Band structure and phase stability of the copper oxides Cu_2O , CuO , and Cu_4O_3 . *Phys. Rev. B* 87, 115111.
- Jena, A.K., Numata, Y., Ikegami, M., Miyasaka, T., 2018. Notorious Role of SpiroOMeTAD in Performance Deterioration of Perovskite Solar Cells at High Temperature and Reuse of the Perovskite Films to Avoid Pb-waste. *J. Mater. Chem. A*.
- Jeng, J.Y., Chen, K.C., Chiang, T.Y., Lin, P.Y., Tsai, T.D., Chang, Y.C., Guo, T.F., Chen, P., Wen, T.C., Hsu, Y.J., 2014. Nickel oxide electrode interlayer in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite/PCBM planar-heterojunction hybrid solar cells. *Adv. Mater.* 26, 4107–4113.
- Jung, J.W., Chueh, C.C., Jen, A.K.Y., Low-Temperature, A., 2015. Solution-processable, copper-doped nickel oxide hole-transporting layer via the

- combustion method for high performance thin-film perovskite solar cells. *Adv. Mater.* 27, 7874–7880.
- Kim, J.H., Liang, P.W., Williams, S.T., Cho, N., Chueh, C.C., Glaz, M.S., Ginger, D.S., Jen, A.K.Y., 2015. High-performance and environmentally stable planar heterojunction perovskite solar cells based on a solution-processed copper-doped nickel oxide holetransporting layer. *Adv. Mater.* 27, 695–701.
- Kojima, A., Teshima, K., Shirai, Y., Miyasaka, T., 2009. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J. Am. Chem. Soc.* 131, 6050–6051.
- Kresse, G., Furthmüller, J., 1996. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 54, 11169.
- Kresse, G., Hafner, J., 1993. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* 47, 558.
- Krishna, A., Grimsdale, A.C., 2017. Hole transporting materials for mesoscopic perovskite solar cells—towards a rational design? *J. Mater. Chem. A* 5, 16446–16466.
- Kröger, F., Vink, H., 1956. Relations between the concentrations of imperfections in crystalline solids. *Solid State Phys.* 307–435.
- Ku, Z., Rong, Y., Xu, M., Liu, T., Han, H., 2013. Full printable processed mesoscopic $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ heterojunction solar cells with carbon counter electrode. *Sci. Rep.* 3, 3132.
- Li, J., Niu, G., Li, W., Cao, K., Wang, M., Wang, L., 2016. Insight into the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{C}$ interface in hole-conductor-free mesoscopic perovskite solar cells. *Nanoscale* 8, 14163–14170.
- Li, X., Tschumi, M., Han, H., Babkair, S.S., Alzubaydi, R.A., Ansari, A.A., Habib, S.S., Nazeeruddin, M.K., Zakeeruddin, S.M., Grätzel, M., 2015. Outdoor performance and stability under elevated temperatures and long-term light soaking of triple-layer mesoporous perovskite photovoltaics. *Energy Technol.* 3, 551–555.
- Liu, Z., Zhang, M., Xu, X., Cai, F., Yuan, H., Bu, L., Li, W., Zhu, A., Zhao, Z., Wang, M., 2015. NiO nanosheets as efficient top hole transporters for carbon counter electrode based perovskite solar cells. *J. Mater. Chem. A* 3, 24121–24127.
- Liu, Z., Zhang, M., Xu, X., Bu, L., Zhang, W., Li, W., Zhao, Z., Wang, M., Cheng, Y.-B., He, H., 2015. p-Type mesoscopic NiO as an active interfacial layer for carbon counter electrode based perovskite solar cells. *Dalton Trans.* 44, 3967–3973.
- Liu, M.-H., Zhou, Z.-J., Zhang, P.-P., Tian, Q.-W., Zhou, W.-H., Kou, D.-X., Wu, S.-X., 2016. p-type Li, Cu-codoped NiOx hole-transporting layer for efficient planar perovskite solar cells. *Opt. Express* 24, A1349–A1359.
- Makhlouf, S.A., Bakr, Z.H., Aly, K.I., Moustafa, M., 2013. Structural, electrical and optical properties of Co_3O_4 nanoparticles. *Superlatt. Microstruct.* 64, 107–117.
- Mansour, A., Melendres, C., 1998. Analysis of X-ray absorption spectra of some nickel oxycompounds using theoretical standards. *J. Phys. Chem. A* 102, 65–81.
- Mei, A., Li, X., Liu, L., Ku, Z., Liu, T., Rong, Y., Xu, M., Hu, M., Chen, J., Yang, Y., 2014. A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability. *Science* 345, 295–298.
- Park, J.H., Seo, J., Park, S., Shin, S.S., Kim, Y.C., Jeon, N.J., Shin, H.W., Ahn, T.K., Noh, J.H., Yoon, S.C., 2015. Efficient $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells employing nanostructured p-type NiO electrode formed by a pulsed laser deposition. *Adv. Mater.* 27, 4013–4019.
- Perdew, J.P., Burke, K., Ernzerhof, M., 1996. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 77, 3865.
- Priyadarshi, A., Haur, L.J., Murray, P., Fu, D., Kulkarni, S., Xing, G., Sum, T.C., Mathews, N., Mhaisalkar, S.G., 2016. A large area (70 cm²) monolithic perovskite solar module with a high efficiency and stability. *Energy Environ. Sci.* 9, 3687–3692.
- Priyadarshi, A., Bashir, A., Gunawan, J.T., Haur, L.J., Bruno, A., Akhter, Z., Mathews, N.,

- Mhaisalkar, S.G., 2017. Simplified architecture of a fully printable perovskite solar cell using a thick zirconia layer. *Energy Technol.* 5, 1866–1872.
- Rahdar, A., Aliahmad, M., Azizi, Y., 2014. Synthesis of Cu Doped NiO nanoparticles by chemical method. *J. Nanostruct.* 4, 145–152.
- Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Rad.* 12, 537–541.
- Rong, Y., Ku, Z., Mei, A., Liu, T., Xu, M., Ko, S., Li, X., Han, H., 2014. Hole-conductor-free mesoscopic $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ heterojunction solar cells based on anatase nanosheets and carbon counter electrodes. *J. Phys. Chem. Lett.* 5, 2160–2164.
- Ryu, J., Lee, K., Yun, J., Yu, H., Lee, J., Jang, J., 2017. Paintable carbon-based perovskite solar cells with engineered perovskite/carbon interface using carbon nanotubes dripping method. *Small* 13.
- Sasi, B., Gopchandran, K., Manoj, P., Koshy, P., Rao, P.P., Vaidyan, V., 2002. Preparation of transparent and semiconducting NiO films. *Vacuum* 68, 149–154.
- Stoumpos, C.C., Malliakas, C.D., Kanatzidis, M.G., 2013. Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and nearinfrared photoluminescent properties. *Inorg. Chem.* 52, 9019–9038.
- Tong, X., Lin, F., Wu, J., Wang, Z.M., 2016. High performance perovskite solar cells. *Adv. Sci.* 3, 1500201.
- Veidis, M., Schreiber, G., Gough, T., Palenik, G.J., 1969. Jahn-Teller distortions in octahedral copper (II) complexes. *J. Am. Chem. Soc.* 91, 1859–1860.
- Wang, Q., Moser, J.-E., Grätzel, M., 2005. Electrochemical impedance spectroscopic analysis of dye-sensitized solar cells. *J. Phys. Chem. B* 109, 14945–14953.
- Weber, S., Rath, T., Mangalam, J., Kunert, B., Coclite, A.M., Bauch, M., Dimopoulos, T., Trimmel, G., 2018. Investigation of NiO x-hole transport layers in triple cation perovskite solar cells. *J. Mater. Sci.: Mater. Electron.* 29, 1847–1855.
- Wehrenfennig, C., Eperon, G.E., Johnston, M.B., Snaith, H.J., Herz, L.M., 2014. High charge carrier mobilities and lifetimes in organolead trihalide perovskites. *Adv. Mater.* 26, 1584–1589.
- Wu, Y., Yang, X., Chen, W., Yue, Y., Cai, M., Xie, F., Bi, E., Islam, A., Han, L., 2016. Perovskite solar cells with 18.21% efficiency and area over 1 cm² fabricated by heterojunction engineering. *Nat. Energy* 1, 16148.
- Xing, G., Mathews, N., Sun, S., Lim, S.S., Lam, Y.M., Grätzel, M., Mhaisalkar, S., Sum, T.C., 2013. Long-range balanced electron-and hole-transport lengths in organic-inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Science* 342, 344–347.
- Xu, X., Liu, Z., Zuo, Z., Zhang, M., Zhao, Z., Shen, Y., Zhou, H., Chen, Q., Yang, Y., Wang, M., 2015. Hole selective NiO contact for efficient perovskite solar cells with carbon electrode. *Nano Letters* 15, 2402–2408.
- Yang, M., Shi, Z., Feng, J., Pu, H., Li, G., Zhou, J., Zhang, Q., 2011. Copper doped nickel oxide transparent p-type conductive thin films deposited by pulsed plasma deposition. *Thin Solid Films* 519, 3021–3025.
- Yang, Y., Xiao, J., Wei, H., Zhu, L., Li, D., Luo, Y., Wu, H., Meng, Q., 2014. An all-carbon counter electrode for highly efficient hole-conductor-free organo-metal perovskite solar cells. *Rsc Adv.* 4, 52825–52830.
- Yao, K., Li, F., He, Q., Wang, X., Jiang, Y., Huang, H., Jen, A.K.-Y., 2017. A copper-doped nickel oxide bilayer for enhancing efficiency and stability of hysteresis-free inverted mesoporous perovskite solar cells. *Nano Energy* 40, 155–162.
- Yin, X., Chen, P., Que, M., Xing, Y., Que, W., Niu, C., Shao, J., 2016. Highly efficient flexible perovskite solar cells using solution-derived NiO x hole contacts. *ACS Nano* 10, 3630–3636.
- Yu, Z., Sun, L., 2017. Inorganic hole-transporting materials for perovskite solar cells.

Small Methods.

Zeng, X., Zhou, T., Leng, C., Zang, Z., Wang, M., Hu, W., Tang, X., Lu, S., Fang, L., Zhou, M., 2017. Performance improvement of perovskite solar cells by employing a CdSe quantum dot/PCBM composite as an electron transport layer. *J. Mater. Chem. A* 5, 17499–17505.

Zhang, L., Liu, T., Liu, L., Hu, M., Yang, Y., Mei, A., Han, H., 2015. The effect of carbon counter electrodes on fully printable mesoscopic perovskite solar cells. *J. Mater. Chem. A* 3, 9165–9170.

Zhang, P., Wu, J., Wang, Y., Sarvari, H., Liu, D., Chen, Z.D., Li, S., 2017. Enhanced efficiency and environmental stability of planar perovskite solar cells by suppressing photocatalytic decomposition. *J. Mater. Chem. A* 5, 17368–17378.