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ARTICLE

Efficacious multifunction codoping strategy on the room-temperature solution-processed hole transport layer for realizing high-performance perovskite solar cells

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The multifunctional carrier transport layer favoring outstanding carrier extraction, high-quality active layer formation, and facile low-temperature process for efficient and large-scale perovskite solar cells (PSCs) is highly desirable. While co-doping approaches have recently become a hot topic in carrier transport layers to address the negative effects and limitations of typical single doping and further boosting the carrier extraction properties and thus device performances, high-temperature, high power, and multi-steps processes/ treatments are required which hinder their applications and potentially damage underneath structures particularly in emerging flexible electronics. In this work, we demonstrate the first kind of room-temperature solution-processed and post-treatment-free Li and Cu codoped NiO_x nanoparticle-based hole transport layer (HTL). Simultaneously, the Li and Cu codoped NiO_x HTLs show the interesting and critical features of (1) improved electrical conductivity and optical transmittance, (2) high quality (pin-hole/crack free, compact and uniform) film morphology, (3) favoring large grain-size perovskite film formation, and (4) wide-range thermal stability up to 250 °C. With these interesting multifunctions, PSCs with Li and Cu codoped NiO_x HTL achieve 20.8% and 18.2% for rigid and flexible PSCs, respectively. This work contributes to a promising route for realizing highly efficient and stable rigid and flexible PSCs using abundant low-cost inorganic HTLs.

1. Introduction

The rapidly developed perovskite solar cells (PSCs) have aroused tremendous interest owing to their excellent optoelectronic properties (such as broad absorption range, intense extinction coefficient, and high charge carrier mobility), long charge-carrier lifetime, low-temperature solution processability, and relatively low-cost fabrication¹⁻⁴. The power conversion efficiency (PCE) of PSCs has been swiftly raised from ~3.8%⁵ to recent certified 25%⁶, showing the great commercial potential of this cell technology. In PSCs, carrier transport layers (CTLs) is crucial not only for achieving better energy alignment and carrier transport but also for obtaining improved stability, and tremendous efforts have been devoted to exploring effective CTLs featuring low resistance, good optical transparency, superior charge extraction/transport ability, as well as excellent stability. Among various CTL materials, inorganic CTLs are of particular interest due to their decent carrier mobility, very low cost of raw materials and synthesis, and good stability⁷⁻¹⁵.

Recently, the modification in carrier transport materials by codoping has become a hot and attractive topic for increasing the efficiency of photovoltaic devices due to the advantages of

compensating the negative effects of single doping or further enlarged the regulating range of carrier mobility, Fermi level, and etc.¹⁶⁻²⁰. By combing the effect of Mg on bandgap and Er on light absorption and emission, the co-doped Er, Mg TiO_2 electron transport layer (ETL) under 500 °C hydrothermal treatment and effectively improve the device efficiency¹⁷. Sm^{3+} , Eu^{3+} co-doped TiO_2 ETL was also demonstrated via pulse laser deposition method and the PSCs exhibited a PCE of 19.01% with good ultraviolet (UV) light stability²¹. The improvement of device performance was explained by the UV light utilization due to the down-conversion dopant Eu^{3+} , which can be enhanced by further doping with Sm^{3+} . By doping Zr and F in SnO_2 to increase the conduction band and electrical conductivity, the PSCs with suitable annealing and UV-ozone treatment could achieve over 19% PCE with low hysteresis²². Moreover, co-doping also has been adopted in commonly used NiO_x hole transport layer (HTL) for modifying the electrical properties by increasing the dopant solubility, the activation rate by lowering the ionization energy of Ni vacancies, as well as the carrier mobility^{20, 23-25}. For instance, high-temperature sol-gel processed Pb, Li and Ag, Li co-doped NiO_x thin films have been fabricated and served as HTL in PSCs, which exhibited a PCE of 17.02% and 19.24%, respectively²³⁻²⁵. Mg and Li co-doped NiO_x HTL formed by spray technique also achieved a PCE of 18.3% in inverted PSCs^[24]. However, all the above cases require high temperatures (>200 °C) during deposition and/or annealing treatment for realizing the expected electrical performance of co-doping materials, which not only increases the complexity and cost of device fabrication but also limits the

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possibility of PSCs application on flexible plastic substrates. It is highly desirable to explore room-temperature solution-processed codoped NiO_x HTL for flexible PSCs, featuring with efficient hole extraction capabilities and uniform morphologies. To the best of our knowledge, there is no report on room-temperature solution-processed co-doped NiO_x HTL for demonstrating highly efficient rigid and flexible PSCs.

Herein, we demonstrate a room-temperature solution-processed and post-treatment-free Li,Cu-codoped NiO_x (hereafter named as (Li,Cu): NiO_x) nanoparticles (NPs) based HTL for high-performance rigid and flexible inverted planar PSCs. The (Li,Cu): NiO_x film exhibits not only simultaneously enhanced electrical conduction and optical transmittance, but also improved morphology uniformity on various substrates such as rigid indium tin oxide (ITO)/glass and flexible ITO/polyethylene terephthalate (PET). Besides, the co-doped NiO_x HTL can promote the large grain perovskite film formation. The simultaneous interesting features result in the improvement of PCE by 15% as compared to the case of pristine NiO_x to the value of 20.8% and 18.2% for inverted PSCs on the rigid and flexible, respectively. While the effective co-doped (Li,Cu): NiO_x HTL is formed at room temperature, the high performance can sustain with annealing temperature up to 250 °C. Moreover, the PSCs based on (Li,Cu): NiO_x showed decent stability, with 95% of the original efficiency remaining after 60 days of storage in inert conditions. This work provides a promising route to realize highly efficient and stable inverted planar PSCs both on rigid and flexible substrate using abundant and low-cost inorganic HTLs, which favor the development of large-scale perovskite optoelectronic device.

2. Experimental section

2.1 Materials

All chemicals with analytical reagent grade were used as received unless otherwise noted. Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 97%), Lead (II) iodide (PbI_2 , 99%), Lead (II) chloride (PbCl_2 , 99%), Zirconium (IV) acetylacetonate (ZrAcac, 98%) were purchased from Sigma-Aldrich. Lithium nitrate (LiNO_3 , 99%), Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 98%) was purchased from JK Science. Dimethylformamide (DMF, extra dry, 99%), 1, 2-Dichlorobenzene (DCB, extra dry, 98+%), Chlorobenzene (CB, extra dry, 99.8%), isopropanol (IPA, extra dry, 99.8%) were purchased from Acros Organics. $\text{CH}_3\text{NH}_3\text{I}$ was purchased from Dyesol. PC_{61}BM and C_{60} were purchased from Solarmer Energy, Inc. Ag (99.999%) was purchased from Alfa Aesar.

2.2 Synthesis of NiO_x NPs without/with doping

NiO_x NPs were synthesized by a chemical precipitation method according to previous reports^{11,26}. Typically, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mol) was dispersed in 100 mL deionized water to obtain a green solution. Under continuous magnetic stirring, the pH of the solution was adjusted to 10 by adding a NaOH aqueous solution (10 mol L^{-1}) drop by drop. After stirring for another 5 min, the green colloidal precipitation was collected by centrifugation

and washed by DI water and ethanol two times, respectively. The obtained green powders were dried at 80 °C for 6 h and then calcined at 270 °C for 2 h to obtain a dark-black powder. For 5% Cu: NiO_x , 5% Li: NiO_x , and (Li,Cu): NiO_x NPs, 5 mol % $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were respectively replaced with 5 mol % $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 5 mol % LiNO_3 , and 5 mol % $(\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}/\text{LiNO}_3=2:1)$, and all other procedures were identical with the synthesis of undoped NiO_x NPs. The as-prepared NiO_x and doped NiO_x NPs were dispersed in deionized water at a certain concentration range with ultrasonication for 10 min.

2.3 Device fabrication

ITO-coated glass substrates ($\sim 15 \Omega \text{ sq}^{-1}$) were cleaned sequential ultra-sonication in detergent water, deionized water, acetone, and ethanol for 15 min, respectively, and then ultraviolet-ozone treated for 15 min. The HTLs were deposited by spin-coating the corresponding NiO_x or (Li,Cu): NiO_x aqueous solution (20 mg mL^{-1}) at 2000 rpm for 50 s. All of the above procedures were carried out at room temperature and without any post-treatment. The average thickness of NiO_x and doped NiO_x films was about 20 nm. After transferring samples into the nitrogen-filled glovebox, the $\text{MAPbI}_{3-x}\text{Cl}_x$ perovskite films were deposited onto the HTLs according to our previous report¹². Afterward, a total concentration of 20 mg mL^{-1} mix solution of $\text{PC}_{61}\text{BM}/\text{C}_{60}$ (weight ratio, 2:3) in dichlorobenzene was spin-coated on top of the perovskite layer at 700 rpm for 60 s and then 4000 rpm for 60 s, followed by spin-coating ZrAcac (2 mg/mL in isopropanol) at 4000 rpm. Finally, 100 nm thick Ag electrode was thermally evaporated on top of the device under a base pressure of 10^{-4} Pa with a device area of 0.06 cm^2 .

2.4 Characterization and measurement

The crystal phase of the samples was identified by X-ray powder diffraction with Cu K α radiation under λ of 1.54056 Å (XRD, Bruker D2 Phaser). The nanoparticle morphology and lattice spacing were examined by tapping mode atomic force microscope (AFM, NT-MDT NTEGRA), transmission electron microscopy (TEM, Philips Tecnai G2 20 S-TWIN), and scanning electron microscope (SEM, Hitachi S-4800, and LEO 1530 FEG), respectively. The I-V measurements of the sample films were taken by conductive atomic force microscopy (c-AFM) microscope. The chemical composition of sample films on ITO was verified by X-ray photoelectron spectroscopy (XPS), which was measured in the ultrahigh vacuum environment using Physical Electronics PHI 5802 with a monochromatic Al K α X-ray source. The thickness of samples was measured by a profilometer. Optical properties of the samples were performed under a dark ambient environment using spectroscopic ellipsometry (Woollam). Ultraviolet photoelectron spectroscopy (UPS) was characterized by using a He discharged lamp (He I 21.22 eV, Kratos Analytic). Using a Keithley 2635 sourcemeter to collect the current density-voltage (*J-V*) characteristics and the solar cells were tested by using a Newport AM 1.5 G solar simulator under a light intensity of 100 mW cm^{-2} , calibrated with a standard silicon reference cell. The steady-state PCE, PCE (t) was recorded by setting the bias

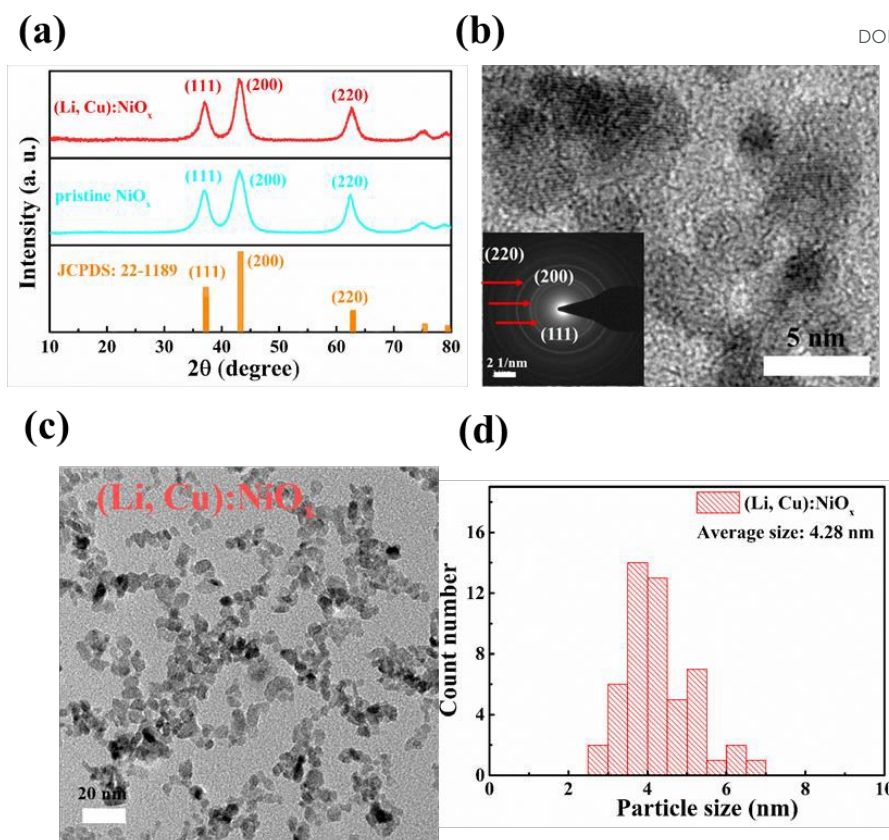


Fig. 1 (a) XRD patterns of the as-synthesized of NiO_x and (Li,Cu):NiO_x NPs. (b) HRTEM image with Indexed SAED pattern of as-synthesized (Li,Cu):NiO_x NPs. (c) TEM image and (d) size distribution of as-synthesized (Li,Cu):NiO_x NPs.

voltage to the V_{MPP} (obtained from the J - V curve) and then tracing the current density. The incident-photon-to-current conversion efficiency (IPCE) measurement was conducted by a system combining xenon lamp monochromatic chopper, and a lock-in amplifier together with a calibrated silicon photodetector (Hamamatsu mono-Si cell). Time-resolved photoluminescence (PL) spectra were performed on PicoQuanta FluoTime 300 instrument. A picosecond 375 nm pulse laser (LDH-P-C-75) with a pulse width of < 40 ps and a repetition rate of 5 MHz was used to excite the samples. The electrochemical impedance spectroscopy (EIS) analysis was measured on a CHI660C electrochemical workstation (CH Instrument, Inc.) at 0.9 voltage with the frequency ranging from 10^{-1} to 10^6 Hz.

3. Results and discussion

The undoped NiO_x and (Li,Cu):NiO_x NPs have been newly synthesized by a modified chemical coprecipitation approach^{11, 26}. Particularly, a portion of $Ni(NO_3)_2 \cdot 6H_2O$ in precursor was replaced by $Cu(NO_3)_2 \cdot 3H_2O$ and $LiNO_3$ with appropriate mole ratio which can be used to low-temperature synthesize not only Cu doped and Li doped NiO_x NPs but also the targeted co-doped (Li,Cu):NiO_x NPs, as further details in the Experimental Section.

Fig. 1(a) shows XRD patterns of NiO_x and (Li,Cu):NiO_x powders. All samples show three prominent characteristic diffraction peaks that can be respectively assigned to (111), (200), and (220) planes of the NiO phase according to JCPDS (22-

1189). The similar diffraction peaks for undoped and doped NiO_x illustrate that light doping of Cu and Li could hardly change the phase structure of NiO_x^{27, 28}. Notably, the peak shift from 62.43° to 62.60° indicates the slight increase of the lattice parameter after successfully co-doping with Cu and Li into NiO_x (**Fig. S1**), which similar to other doped NiO_x^{29, 30}. Moreover, the high-resolution TEM image and selective area electron diffraction pattern (SAED) of (Li,Cu):NiO_x nanocrystal (**Fig. 1(b)**) further verified that codoped NiO_x NPs possess good crystalline properties and pure NiO phase. TEM was applied to confirm the crystallite sizes of NiO_x and (Li,Cu):NiO_x NPs as shown in **Fig. 1(c)** and **S1**. Comparing with the pristine NiO_x (5.62 nm on average), the smaller grain size of (Li,Cu):NiO_x (4.28 nm on average, **Fig. 1(d)**) is a benefit for the formation of thin films featuring with densely packed and smooth morphology. The smaller size may be attributed to the smaller size of hydroxide intermediates.

XPS of pristine NiO_x and (Li,Cu):NiO_x samples are shown in **Fig. S2**. Both pristine and codoped NiO_x films have typical peaks including the main peak at ~ 854.1 eV, shoulder at ~ 855.5 eV, and shake-up satellite peak at ~ 861.2 eV^{31, 32}. The main peak corresponds to Ni^{2+} in the standard Ni-O octahedral bonding configuration in cubic rock salt NiO_x^{33, 34}. The shoulder peak ascribes to the Ni-vacancy induced Ni^{3+} ion³⁴⁻³⁷, nickel hydroxides and oxyhydroxides^{34, 35}, and nonlocal screening and

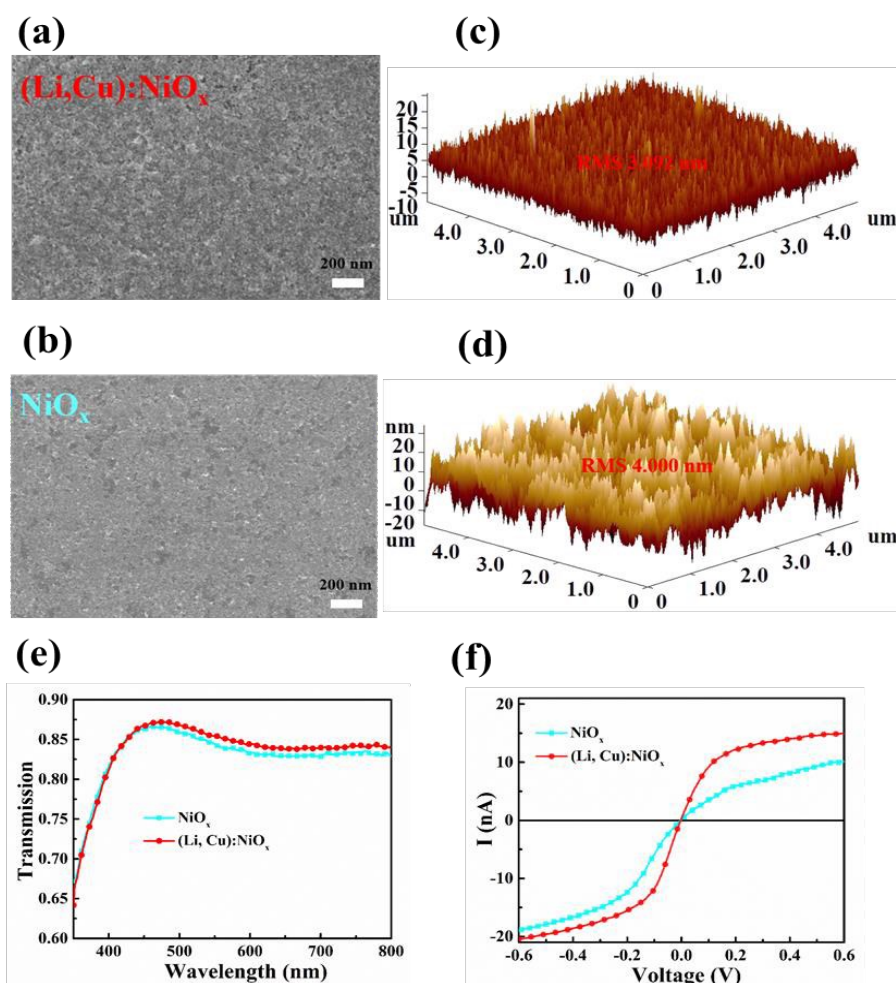


Fig. 2 SEM images of (a) (Li,Cu):NiO_x and (b) NiO_x films on ITO glass. 3D AFM images: (c) (Li,Cu):NiO_x and (d) NiO_x films. (e) The transmittance spectra of NiO_x and (Li,Cu):NiO_x films on ITO glass. (f) I-V conducting curves of NiO_x and (Li,Cu):NiO_x films measured from the c-AFM mode.

surface states³¹. Notably, in Fig. S2(b) and (c), XPS peaks corresponding to Cu 2p_{2/3} (933.6 eV), and Li 1s (55.9 eV) are clearly observed from (Li, Cu):NiO_x film, which is absent in undoped NiO_x film, revealing that Cu and Li are successfully incorporated into NiO_x³⁸. Due to the Li and Cu doping, the obtained Ni³⁺/Ni²⁺ ratio of (Li,Cu):NiO_x film (1.68) is larger than that of undoped NiO_x (1.57) which contributes to the increase of hole conductivity as further studied in later section.

The surface morphologies of undoped NiO_x and (Li,Cu):NiO_x thin films on ITO glass were determined by top-view SEM and AFM as shown in Fig. 2(a)-(d). Notably, (Li,Cu):NiO_x film consists of small-sized crystalline grains and is uniform without pin-holes (Fig. 2(a)). Moreover, 3D AFM images further confirm the closely packed and crack-free morphologies of (Li,Cu):NiO_x film with a smaller root-mean-square roughness (RMS) of 3.09 nm (Fig. 2(c)) compared to the pristine NiO_x film (4.00 nm; Fig. 2(d)). It is worth noting that the smooth and uniform surface in (Li,Cu):NiO_x film should be beneficial to the formation of high-quality perovskite films for realizing high-performance devices. Thus, the morphologies of perovskite layers on NiO_x and (Li,Cu):NiO_x thin film were characterized by SEM as shown in Fig. S3(a) and (b). It is found that all the perovskite films are homogeneous and densely packed. Notably, the perovskite

crystal grains formed on (Li,Cu):NiO_x (511 nm) show a larger grain size than that of grown on NiO_x (440 nm), displayed in Fig. S3(c) and (d). That is could because the slightly larger contact angle (inserted in Fig. S3(a) and (b)) provide a non-wetting surface, favoring to suppress heterogeneous nucleation³⁹ and promote the grain growth^{12, 40, 41}. Consequently, (Li,Cu):NiO_x based HTL favors the formation of good quality perovskite film, which is one of the interesting properties for obtaining highly efficient PSCs.

The electrical and optical properties are particularly important for realizing efficient HTL. Firstly, we investigated the optical transmittance of NiO_x and (Li,Cu):NiO_x films coated on ITO glass as shown in Fig. 2(e). Interestingly, for (Li, Cu):NiO_x thin film, the transmittance reaches 87% at 460 nm, and shows an improvement over a large wavelength range from 500 to 800 nm than that of pristine NiO_x. Furthermore, while light Li only doping does not change the transparency, the Cu doping will reduce the doping transmittance decreases as shown in Fig. S4 due to the d-d transition of Cu²⁺ in the crystalline environment of NiO_x, which agrees with the report^{34, 42, 43}.

We further study the effect of Li and Cu co-doping on the electrical conductivity of NiO_x films by performing c-AFM measurements, as described in Fig. 2(f). From the I-V curves, it

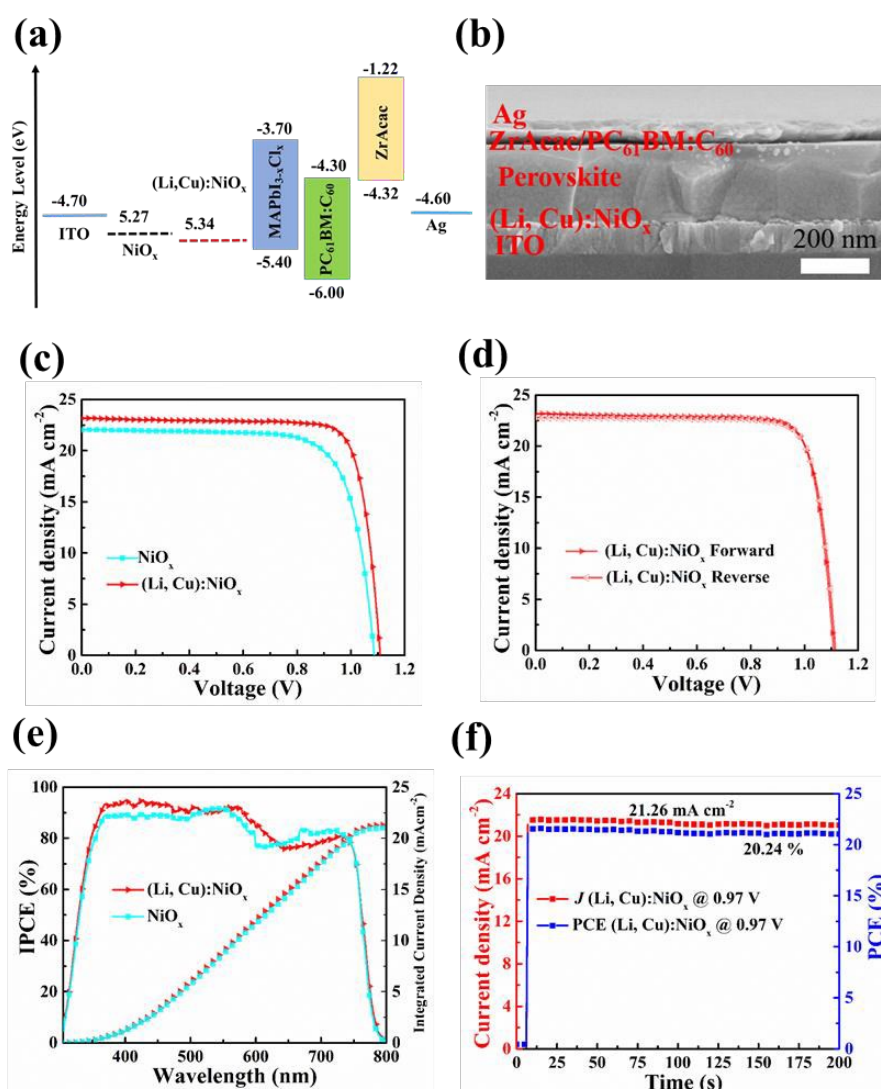


Fig. 3 (a) Energy band level diagram of the various layers in the inverted PSCs. (b) Cross-sectional SEM image of a complete perovskite device with (Li,Cu):NiO_x films as HTL. (c) J-V characteristics of the best NiO_x and (Li,Cu):NiO_x based PSCs measured under AM 1.5 G 100 mW cm^{-2} illumination. (d) J-V characteristics of (Li,Cu):NiO_x based devices extracted from forward and reverse sweeping. (e) IPCE spectra and integrated J_{sc} curves of the best NiO_x and (Li,Cu):NiO_x based PSCs (f) Steady-state photocurrent output at the maximum power point of (Li,Cu):NiO_x-based PSCs under continuous simulated AM 1.5G illumination for 200 s.

is clearly observed that a significantly higher current in (Li,Cu):NiO_x film (14.6 nA at a bias of 0.5 V), indicating a dramatically increased conductivity than the pristine NiO_x (8 nA at a bias of 0.5 V). The increased ratio of $\text{Ni}^{3+}/\text{Ni}^{2+}$ supports the successful doping by Li and Cu as well as the improved hole conductivity, which is in good agreement with others (Fig. S5) 24, 29, 34, 43–45. These results indicate the Li and Cu codoping strategy on NiO_x could achieve significantly enhanced conductivity and keep high transparency, making it more suitable as an efficient HTL for achieving high-performance PSCs.

To explore the function of the (Li,Cu):NiO_x film as the HTL, inverted PSCs with the structure of ITO/NiO_x (or (Li,Cu):NiO_x)/perovskite/ $\text{PC}_{60}\text{BM}:\text{C}_{60}$ /ZrAcac/Ag have been fabricated, where the corresponding energy level diagram was depicted at Fig. 3(a). The energy levels of ITO, perovskite, $\text{PC}_{60}\text{BM}:\text{C}_{60}$, ZrAcac, and Ag are collected from literature 12, 13, 46, and NiO_x or (Li,Cu):NiO_x are obtained from UPS. It should be

noted that zirconium acetylacetonate (ZrAcac) is inserted between the $\text{PC}_{60}\text{BM}:\text{C}_{60}$ and Ag cathode for efficiently extracting and transporting electrons. The cross-sectional view SEM image of the device configuration is shown in Fig. 3(b). Fig. 3(c) depicted the J-V curves of the champion devices based on pristine NiO_x and (Li,Cu):NiO_x under AM 1.5G illuminated. The (Li,Cu):NiO_x based PSCs with an optimized thickness of 20 nm exhibited a short circuit current density (J_{sc}) of $23.156 \text{ mA cm}^{-2}$, an open-circuit voltage (V_{oc}) of 1.11 V, and a fill factor (FF) of 0.81 to yield the best PCE of 20.83%, clearly outperforming the PSCs based on pristine NiO_x as HTL (Table S4 and S5). The best-performing reference cell using pristine NiO_x as HTL gave a J_{sc} of 22.02 mA cm^{-2} , V_{oc} of 1.09 V, FF of 0.75, and PCE of 17.91%. These values are comparable with those of a previous report on devices with the same structure 47. Thanks to the simultaneously enlarged transmittance and conductivity of the codoped HTL and the high-quality perovskite film with larger grain size, the inverted PSCs displayed significantly enhanced

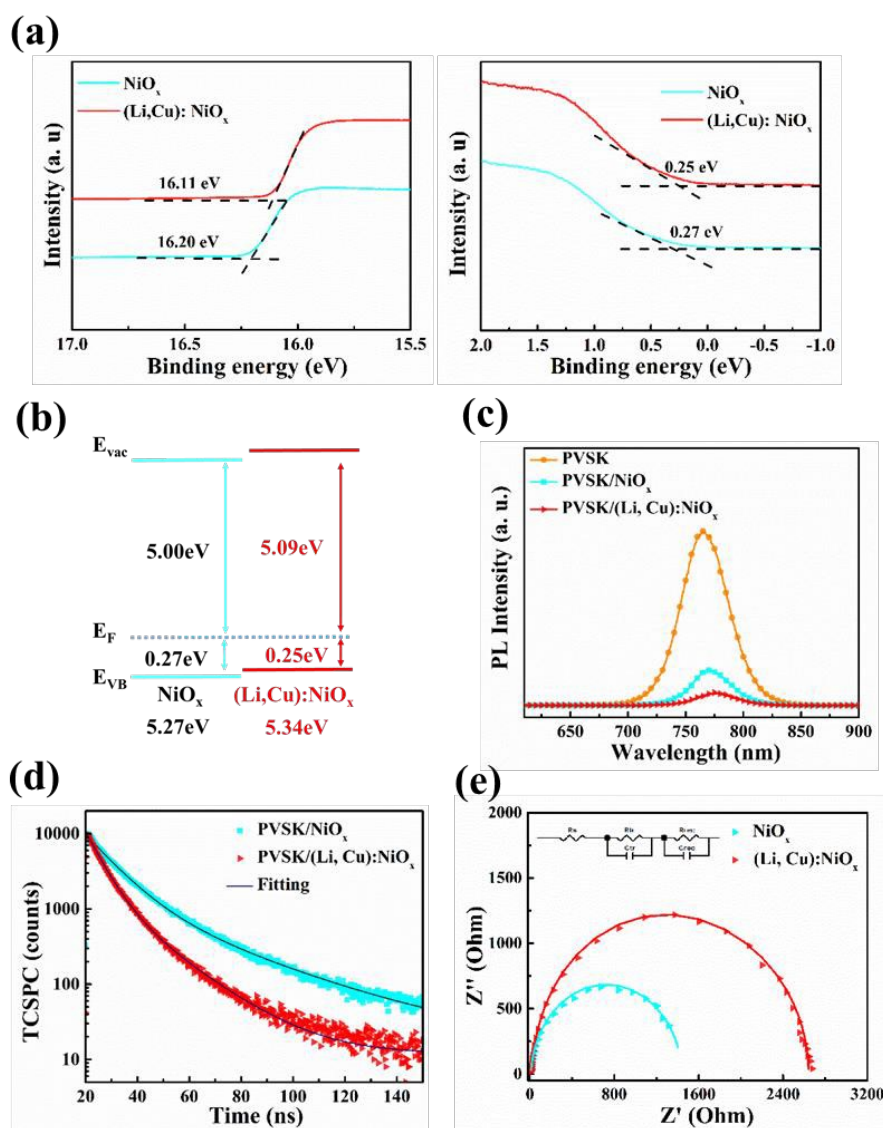


Fig. 4 (a) UPS of the NiO_x and (Li,Cu):NiO_x film on ITO glass. (b) Energy level diagrams of the NiO_x and (Li,Cu):NiO_x film. (c) PL spectra for perovskite films on different substrates: glass (orange), pristine NiO_x (black), (Li,Cu):NiO_x (red), respectively. (d) Time-resolved PL spectra of perovskite film on NiO_x and (Li,Cu):NiO_x, respectively. (e) Nyquist plots of EIS spectra for the device with NiO_x and (Li,Cu):NiO_x as HTL, respectively.

J_{SC} , FF, and PCE, which is also excellent among the reported NiO_x based inverted PSCs, as shown in **Table S1**. Additionally, the PSCs based on (Li,Cu):NiO_x HTLs showed negligible J - V hysteresis in Fig. 3(d), which is better than that of NiO_x based PSCs (**Fig. S6**). The narrow distributions of the statistical photovoltaic parameters (J_{SC} , V_{OC} , FF, and PCEs) from 30 devices further confirm the reliability of performance improvement of (Li,Cu):NiO_x-based PSCs (**Fig. S7**). Fig. 3(e) shows the IPCE spectra of the champion devices based on NiO_x and (Li,Cu):NiO_x, where the integrated J_{SC} from the IPCE over an AM 1.5 G spectrum approximately agrees with those obtained from J - V curves. In addition, the steady-state photocurrent output at the maximum power point over 200 s has been measured by siting a bias of 0.97, as shown in Fig. 3(f). There is no performance degradation under long illumination and exhibited a stable PCE of 20.24% for (Li,Cu):NiO_x based PSCs, which is consistent with that of J - V measurement.

In order to exploit the reasons for the improved performance by codoping with Li and Cu, we first compared the work function (WF) of NiO_x and (Li,Cu):NiO_x films by Kelvin-Probe measurement. For each sample, 500 points are collected, as shown in **Fig. S8**. The measured WF values are collected in **Table S2**. WF of the pristine NiO_x film is determined to be 4.99 eV, and shifted to 5.12 eV of (Li,Cu):NiO_x. From the UPS and the corresponding energy level diagram in **Fig. 4(a) and (b)**, Cu and Li codoping can cause energy band shifts and increase the work function⁴⁸, resulting in a favorable energy level alignment with the perovskite layer (-5.4 eV, Fig. 3(a)) and an enhanced hole extraction ability. In addition, the valence band (VB) shifted by about 0.02 eV closer to the Fermi energy level after Li and Cu codoping (Fig. 4(b)), showing an enhanced p-type property and improved film conductivity, which is consistent with the previous discussion.

To verify the charge extraction ability at the interface of HTL/perovskite, the PL (Fig. 4(c)) and time-resolved PL (Fig. 4(d)) measurement of the perovskite layers deposited on NiO_x , and (Li,Cu): NiO_x films were conducted, respectively. It can clearly be observed that the (Li,Cu): NiO_x HTL exhibits efficient PL quenching compared to that of the pristine NiO_x , illustrating a more favorable ohmic contact with the perovskite layer and obvious improvement of the hole extraction efficiency. Meanwhile, the TRPL profiles are shown in Fig. 4(d), where the PL lifetime is fitted by two-exponential decay^{29, 49}. There is a decrease in the average PL lifetime for (Li,Cu): NiO_x /perovskite (13 ns) as compared to the pristine NiO_x /perovskite (20 ns), which further validated that faster and more efficient hole extraction and transporting ability at the (Li,Cu): NiO_x /perovskite interface. Compared to NiO_x , the more effective hole extraction and transport by (Li,Cu): NiO_x HTL from perovskite active layer could be ascribed to the higher conductivity and increased work function, which would contribute to the high J_{sc} and FF values for (Li,Cu): NiO_x based PSCs.

Charge transport and recombination ability can also be studied from EIS measurement, where it is performed at a bias voltage of 0.9 V under a dark condition (Fig. 4(e)). The only one semicircle in the obtained Nyquist plot will be more likely related to the recombination resistance at the interface of the HTL/perovskite layer, where the larger the diameter is, the less hole recombination at the interface. Comparing to that of pristine NiO_x based devices (1.3 K Ω), (Li,Cu): NiO_x HTL based PSCs exhibit a larger charge recombination resistance (2.6 K Ω), illustrating less carrier recombination, which results in the increased J_{sc} and enhanced FF in the (Li,Cu): NiO_x HTL based PSCs. As shown in the dark current-voltage curves of Fig. S9, the lower dark current under negative bias in the (Li,Cu): NiO_x HTL based PSCs illustrates that those PSCs based on (Li,Cu): NiO_x HTL exhibited a lower leakage current, reducing leakage-induced

month storage in a nitrogen-filled glovebox, as portrayed in Fig. 5. It is found that (Li,Cu): NiO_x HTL-based devices exhibited excellent stable performance, retained 95% of initial PCE after 60 days storage, implying the beneficial effect of Cu, Li in preventing the undesired oxidation process on the NiO_x surface.

To demonstrate the feasibility of post-treatment free and room-temperature processed (Li,Cu): NiO_x HTL for the application of flexible devices, we deposited (Li,Cu): NiO_x film onto ITO-PET substrate to fabricate flexible PSCs. A photograph of a typical flexible device with an area of 0.08 cm² is shown in Fig. S10(a). Fig. S10(b) illustrates the J - V curves of the champion flexible PSCs with (Li,Cu): NiO_x HTL (under AM 1.5G illumination). The device exhibited a J_{sc} of 22.02 mA cm⁻², a V_{oc} of 1.06, and a FF of 0.78, corresponding to the best PCE of 18.16%, which are comparable to those of the reported best flexible PSCs with inverted structures (Fig. S10(c)). To the best of our knowledge, 18.2% is the highest PCE value attained for NiO_x based flexible inverted PSCs. This result suggests that the (Li,Cu): NiO_x HTL without any high-temperature treatment is compatible with the flexible substrate and shows a broad application prospect for the roll-to-roll scale-up fabrication process.

Another interesting feature of the (Li,Cu): NiO_x films is that while only room temperature condition is needed for forming efficiency HTLs, the films can sustain a wide tolerance temperature for practical application of PSCs in the temperature changing environment. The J - V characteristics of PSCs using (Li,Cu): NiO_x HTL with different annealing temperatures are collected in Table S3. Our results show that all the devices show similar performances for the co-doped (Li,Cu): NiO_x HTL with annealing temperature up to 250 °C. Until the annealing temperature further increases to 300 °C, the PCE begins to decrease, which attributed to the decreased J_{sc} and V_{oc} . Our results demonstrate that the (Li,Cu): NiO_x HTL in this work can function as effective HTLs without any post-treatment, as well as offer wide temperature stability from room temperature up to 250 °C, which can contribute to the device stability during the fabrication and application of PSCs.

4. Conclusions

In this work, we have successfully demonstrated efficient HTL by a simple room-temperature solution process without any treatment for high performance rigid and flexible PSCs. Particularly, the co-doped (Li,Cu): NiO_x film simultaneously exhibits several interesting features of (1) improved electrical conductivity, (2) enhanced optical transmittance, (3) high quality (compact and uniform) film, and (4) favoring large grain-size perovskite film formation. The PCE of PSCs based on (Li,Cu): NiO_x HTL improved by 15% as compared to the case of pristine NiO_x and reach a promising value of 20.8% on rigid substrates and 18.2% on flexible substrates. While the effective co-doped (Li,Cu): NiO_x HTL is formed at room temperature, the high performance can sustain with annealing temperature up to 250°C. Meanwhile, the PSCs exhibit excellent stability, with 95% of the original efficiency remaining after 1000 h of storage in ambient conditions. This work provides a promising route to

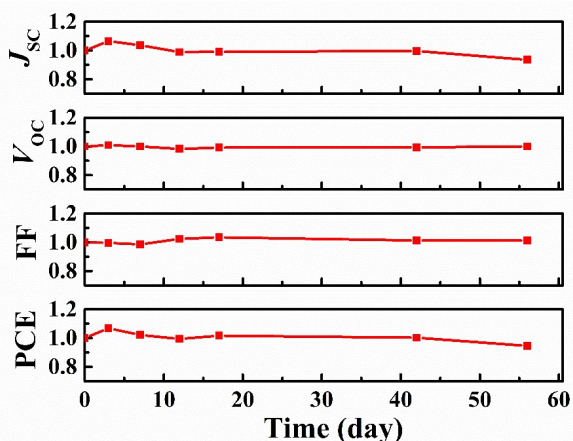


Fig. 5 Photovoltaic performance parameter (J_{sc} , V_{oc} , FF, PCE) of (Li,Cu): NiO_x based PSCs as a function of storage time under inert environment almost 60 days. All devices were encapsulated and stored at the glove box.

recombination that would improve the V_{oc} .

Regarding the stability and reversibility of PSCs, the PCE of (Li,Cu): NiO_x HTL based PSCs were characterized after one-

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realize highly efficient and stable rigid and flexible PSCs using abundant low-cost inorganic HTLs.

Conflicts of interest

The authors declare no competing financial interests.

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A simple room-temperature solution-based and post-treatment-free processed (Li,Cu):NiO_x HTL is successfully demonstrated for high-performance rigid and flexible perovskite solar cells.

Efficacious multifunction codoping strategy on the room-temperature solution-processed hole transport layer for realizing high-performance perovskite solar cells

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Keyword: Codoping, Nanoparticle, Solution-processed, Hole transport layer, Perovskite solar cells

