

Article

The Performance Improvement of Using Hole Transport Layer with Lithium and Cobalt for Inverted Planar Perovskite Solar Cell

Shaoxi Wang ^{1,2} , He Guan ^{1,*}, Yue Yin ¹ and Chunfu Zhang ³ 

¹ School of Microelectronics, Northeastern Polytechnical University, Xi'an 710072, China; shxwang@nwpu.edu.cn (S.W.); yinyue@nwpu.edu.cn (Y.Y.)

² Yangtze River Delta Research Institute of NPU, Taicang 215400, China

³ School of Microelectronics, Xidian University, Xi'an 710071, China; cfzhang@xidian.edu.cn

* Correspondence: he.guan@nwpu.edu.cn

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Abstract: With the continuous development of solar cells, the perovskite solar cells (PSCs), whose hole transport layer plays a vital part in collection of photogenerated carriers, have been studied by many researchers. Interface transport layers are important for efficiency and stability enhancement. In this paper, we demonstrated that lithium (Li) and cobalt (Co) codoped in the novel inorganic hole transport layer named NiO_x, which were deposited onto ITO substrates via solution methods at room temperature, can greatly enhance performance based on inverted structures of planar heterojunction PSCs. Compared to the pristine NiO_x films, doping a certain amount of Li and Co can increase optical transparency, work function, electrical conductivity and hole mobility of NiO_x film. Furthermore, experimental results certified that coating CH₃NH₃PbI₃Cl_{3-x} perovskite films on Li and Co- NiO_x electrode interlayer film can improve chemical stability and absorbing ability of sunlight than the pristine NiO_x. Consequently, the power conversion efficiency (PCE) of PSCs has a great improvement from 14.1% to 18.7% when codoped with 10% Li and 5% Co in NiO_x. Moreover, the short-circuit current density (J_{sc}) was increased from 20.09 mA/cm² to 21.7 mA/cm² and the fill factor (FF) was enhanced from 0.70 to 0.75 for the PSCs. The experiment results demonstrated that the Li and Co codoped NiO_x can be a effective dopant to improve the performance of the PSCs.

Keywords: perovskite solar cells; hole transport layer; nickel oxide; codoping; performance

1. Introduction

It is necessary to search for new energy for people. The solar cells [1], which is based on the photovoltaic effect, have been studied, from the original crystalline silicon solar cells to thin film solar cells and then to the present organometal halide perovskite solar cells (PSCs). PSCs have attracted much more attention owing to the advantages such as simple manufacturing process, low cost, high light absorption coefficient, long charge diffusion length, high charge carrier mobility, low exciton binding energy, low defect density, and its rapidly increasing efficiency [2–5]. Perovskite solar cells (PSCs) are a new type of photovoltaic devices, which are derived from dye sensitized solar cell systems [6]. And its optical absorption layer has the typical perovskite crystal structure represented by CH₃NH₃PbI₃. Nowadays, the available highest value of the power conversion efficiency (PCE) is up to 25.2% [7].

Many researchers accept mesoporous structure and planar heterojunction (PHJ). The inverted planar heterojunction with the basic structure of ITO (Indium tin oxide)/HTL (hole transport layer)/Perovskite/ETL (electronic transport layer)/Electrode [8,9] has the characteristics of low hysteresis, simple manufacturing process and low processing temperature. Hole transport layer

is used to collect many photogenerated carrier in inverted planar PSCs, which sites in the cathode and optical absorption layer of perovskite solar cells. Then it has double functions of transmitting blocking electrons and holes. With regard to content of HTL, it includes organic small molecules semiconductors, such as 2,2',7,7'-tetrakis (*N,N*-di-*p*-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD) [10,11] and H101 [12], organic polymers, such as P3HT [13,14] and PTAA [15], poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) [16], and inorganic semiconductors such as Cu [17] based materials, V_2O_5 [18], PbS [19], MoO_3 [20,21], NiO_x [22,23]. However, compared to inorganic p-type semiconductors, the organic one has worse chemical stability and lower hole migration rate [24]. Thus many researchers use inorganic p-type semiconductors to act as HTL. Compared to other inorganic semiconductors, NiO_x has better chemical stability, wider band gap and well transmittance. NiO_x plays an important roles in the heterojunction device with the function of transporting holes and blocking electrons. Moreover, NiO_x is more suitable to the perovskite layer, which is not hindered to electron blocking and hole collection. And the perovskite layer with NiO_x also shows more stability and improvement in surface smoothness compared with PEDOT:PSS [25], poly-TPD, perylene, PTAA and p-type doped spiro-OMeTAD. Also NiO_x is low cost. Although NiO_x can exactly improve the performance of PSC, the poor stability of PSCs need to be solved because of PSCs's sensitivity to water and oxygen [26].

Many reports are available about the manufacturing of the transparent layer of the Perovskite Solar Cells (PSCs). The deposition methods include gas-assisted solution deposition, pulsed laser deposition (PLD) [27], radio frequency (RF) sputtering, one-step spin coating, two step spin coating, magnetron sputtering and co-evaporation deposition [28]. We adopt two-step simple solution-based process because of the peculiarity with short preparation time, simple preparation steps and low experimental temperature. These factors will influence the film forming of perovskite layer and final performance of PSCs.

In the paper, we firstly investigated that the p-type hole transport layer of Li, Co-codoped NiO_x was used as an effective hole-extraction layer, which can significantly improve the fill factor (FF), the short-circuit current density (J_{sc}), the power conversion efficiency (PCE) [29] of PSCs and at the same time can make the membrane of the perovskite layer more smoother. The HTL films were prepared by a simple solution-based method, and they were uniform and highly reproducible. Then the material of perovskite layer was spin coated over the HTL using two steps solution method. Inverted PHJ device with Li, Co codoped NiO_x hole transport layer exhibit an optimal performance approaching 19%. The elements of Li and Co can affect the formation, absorption and charge transport of the perovskite films [30]. This paper clarified that p-type doping in HTL is an effective and low cost way to improve the performance of PSCs.

2. Experimental and Results

The configuration of the inverted PSC is comprised six layers that is ITO (Indium tin oxide, which is a transparent electrode)/HTLs (hole transport layer, NiO_x or doped NiO_x)/perovskite ($CH_3NH_3PbI_{3-x}Cl_x$)/PC₆₁BM ([6,6]-phenyl-C₆₁-butyric acid methyl ester, which is the electron transport layer)/BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline). Those can enhance charge separation and transport and improve the quality of $MAPbI_{3-x}Cl_x$ film)/Ag (the counter electrode) and schematically displayed in Figure 1a. In this paper we set the concentration of Li to 10 mg/mL. Li element can effectively change the crystallization of $MAPbI_{3-x}Cl_x$ because the small ion size of Li can easily enter into the interstitial of perovskite crystals to increase the grain size of provskite films, which would greatly improve amount of photogenerated carrier. The previous research certified that a Li doping degree over 10 mg/mL gained lower PCE [31], which maybe because of the reason that the concentration of Li exceeds 10 mg/mL. The perovskite film pinholes will be available between the large crystallites during the Li permeated into the perovskite layer, which can reduce the PCE of PSCs and lead to current leakage.

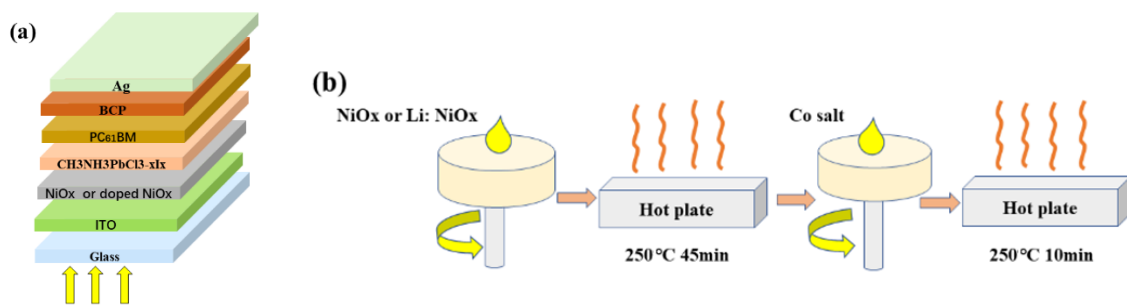


Figure 1. (a) diagram of the device for inverted planar perovskite solar cells; (b) Schematic diagram of spin coating HTLs step.

Also Co^{2+} can increase the grain of perovskite film based on the same reasons. The radius of Co element is much bigger than Li, thus the phenomenon of pinhole will be more clear when the content of Co exceeds a certain concentration. Schematic diagram of solution spin coating NiO_x HTL films at room temperature in this work is illustrated in Figure 1b. Four steps need to complete the fabrication process of the hole transport layer. The first step is that Li: NiO_x or pure Li: NiO_x solution was putted on the ITO. The second step is to anneal the above Li: NiO_x or pure Li: NiO_x layer film at 250°C for 45 min. The third step is that the Co^{2+} solution was spined over Li: NiO_x . The last step is to anneal the above film at 250°C for 10 min. The perovskite film would be deposited as-prepared films with second method and then be annealed in the condition that the temperature of the hot plate is 105°C . Heating time is 10 min (to improve the annealing effect, 40 uL IPA should be added during the annealing of the perovskite layer material).

From Figure 2a, the energy level of Li: NiO_x (or Co: NiO_x) is close to the energy level of $\text{MAIPbI}_{3-x}\text{Cl}_x$, which is quite beneficial to the transport of holes from perovskite layer to hole transport layer (HTL). The X-ray Diffraction (XRD) of perovskite layer based on the pristine NiO_x and diverse doping concentration NiO_x are showed in Figure 2b to demonstrate Li^+ and Co^{2+} doping NiO_x can affect the crystal structure of the perovskite layer. Figure 2b showed the location of the diffraction peak of $\text{MAPbI}_x\text{Cl}_{3-x}$ films that was already annealed at 100°C for 20 min. From Figure 2b, it can be observed that all the perovskite film based on different NiO_x contained the diffraction peaks including three values with 14.21° , 28.51° , and 31.88° which is relative to (110), (220), and (310) lattice planes of the tetragonal perovskite structure respectively. It also can be obtained from Figure 2b that there is no 12.8° diffraction peaks (12.8° represents the diffraction peaks of the PbI_2). The effect of the perovskite layer on film formation not only has a better quality but also the crystallinity of $\text{MAPbI}_x\text{Cl}_{3-x}$ perovskite film stable in the condition of doping the element of Li, Co based on NiO_x hole transport layer.

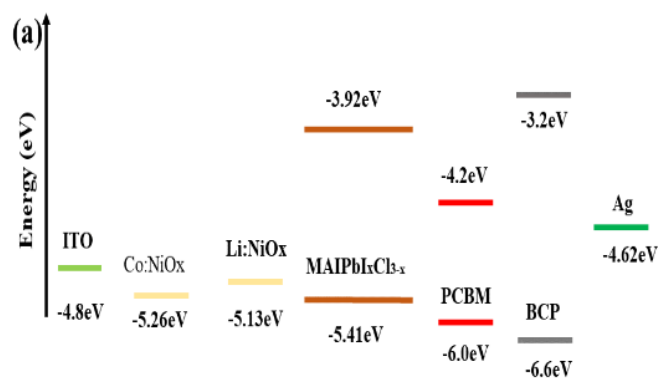


Figure 2. Cont.

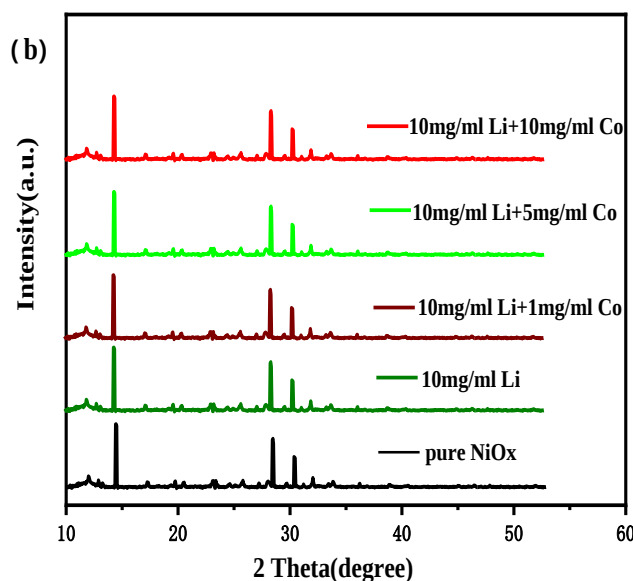


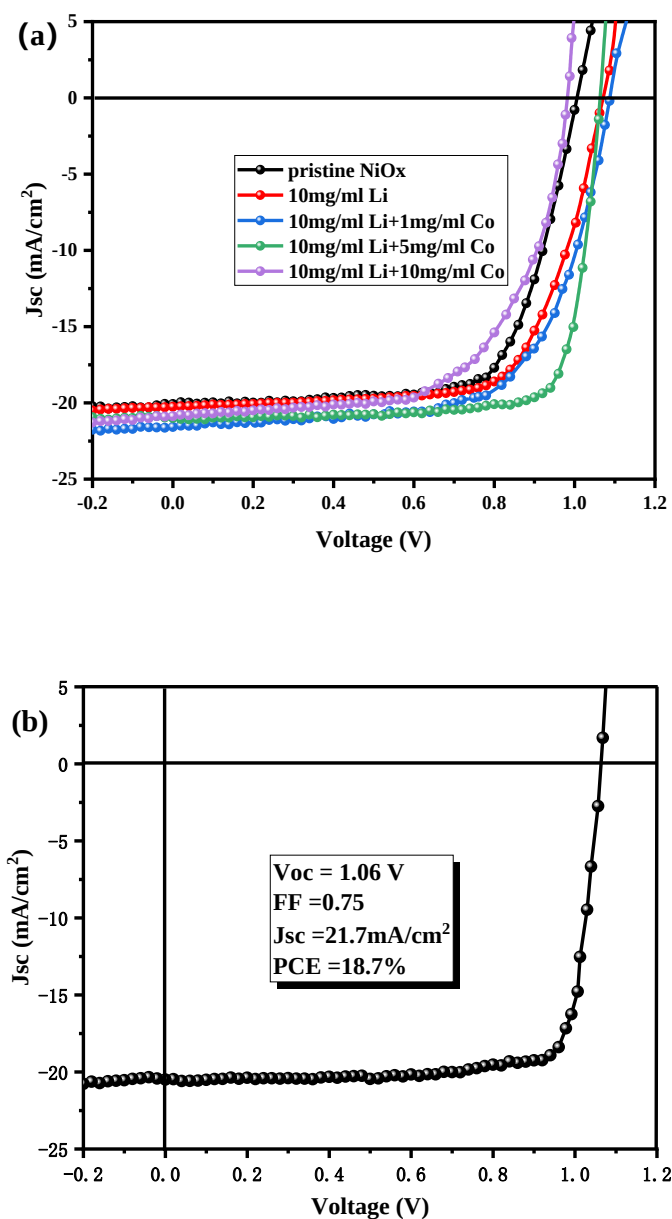
Figure 2. (a) Energy level diagram of different layers of planar heterojunction perovskite solar cells; (b) XRD curve of perovskite film based on pristine NiO_x , 10 mg/mL Li-doped NiO_x , 10 mg/mL Li, 1 mg/mL Co-codoped NiO_x , 10 mg/mL Li, 5 mg/mL Co-codoped NiO_x , 10 mg/mL Li, 10 mg/mL Co-codoped NiO_x .

Figure 3 is always showing the photo-current density–voltage (J–V) curves of the NiO_x —based perovskite solar cells with different amounts of Li^+ , Co^{2+} doping, where marks different colors to distinguish different substances. The device performance of V_{oc} , J_{sc} , FF and PCE with different Li, Co content are listed in Table 1. From J–V curve of the devices, it can be obviously obtained that doping NiO_x with Li and Cu can improve the photoelectric conversion efficiency perovskite light absorbing layer. Figure 3b demostraed that the average performance parameter of the best device is $\text{PCE} = (18.3 \pm 0.3)\%$, $V_{oc} = (1.02 \pm 0.01) \text{ V}$, $\text{FF}(\text{fill factor}) = (0.73 \pm 0.02)$ and $J_{sc} = (20.8 \pm 0.3) \text{ mA/cm}^2$ respectively, which is obtained from the device based on 10 mg/mL Li, 5 mg/mL Co codoped NiO_x . We achieved the peak PCE of 18.7% related to $V_{oc} = 1.06 \text{ V}$, $J_{sc} = 21.7 \text{ mA/cm}^2$ and $\text{FF} = 0.75$. Meanwhile, the PCE of the best solar cell devices based on pristine NiO_x is 14.1% with open-circuit voltage V_{oc} of 1.0 V, a short circuit current density J_{sc} of 20.09 mA/cm^2 and a fill factor FF of 0.7 respectively. The device with 10 mg/mL Li-doped NiO_x improved the performance of PSCs, with obtaining $\text{PCE} = 14.79\%$, $J_{sc} = 21.1 \text{ mA/cm}^2$, $V_{oc} = 0.98 \text{ V}$, and $\text{FF} = 0.71$ respectively which are the best devices performance based on 10 mg/mL Li-doped NiO_x . Similarly, the PSC device with 10 mg/mL Li, 1 mg/mL Co codoped NiO_x obviously increase the PCE to $(16.6 \pm 0.5)\%$, the J_{sc} to $(21.1 \pm 0.5) \text{ mA/cm}^2$, the V_{oc} to $(1.03 \pm 0.02) \text{ V}$, corresponding to the $\text{FF} = (0.69 \pm 0.03)$. However, with the doping concentration of NiO_x changing to 10 mg/mL Li and 5 mg/mL Co, the performance of the devices was worse with $\text{PCE} = (12.6 \pm 0.4)\%$, $J_{sc} = (18.6 \pm 0.6) \text{ mA/cm}^2$, $V_{oc} = (0.85 \pm 0.05) \text{ V}$, and $\text{FF} = (0.57 \pm 0.05)$.

Figure 4 is to experiments hysteresis in device. The results showed there were negligible hysteresis for the PSCs based on pure NiO_x , 10 mg/mL Li doped NiO_x , 10 mg/mL Li, 1 mg/mL Co codoped NiO_x , 10 mg/mL Li, 5 mg/mL Co codoped NiO_x , which demonstrated that NiO_x is a suitable and stable material of hole transport layer for perovskite solar cell. And NiO_x is less expensive with little influence on stability of the devices. However, it can be seen from Figure 4e that there is much hysteresis in perovskite layer when the codoped concentration chaged to 10 mg/mL Li, 10 mg/mL Co, which lead to increase pinhole with too much Co element adding and then leading the quality of perovskite film decreased correspondingly.

Table 1. Summarized photovoltaic performances of PSCs under AM 1.5G illumination (100 mW/cm^2).

Condition	$J_{sc} \text{ (mA/cm}^2\text{)}$	$V_{oc} \text{ (V)}$	FF	PCE (%)
pristine	19.8 ± 0.8	0.98 ± 0.03	0.64 ± 0.04	13.8 ± 0.8
Pristine (best)	20.09	1	0.7	14.1
10 mg/mL Li	20.0 ± 0.7	1.02 ± 0.02	0.66 ± 0.03	15.4 ± 0.6
10 mg/mL Li (best)	21.1	0.98	0.71	14.79
10 mg/mL Li + 1 mg/mL Co	21.1 ± 0.5	1.03 ± 0.02	0.69 ± 0.03	16.6 ± 0.5
10 mg/mL Li + 1 mg/mL Co (best)	21.5	1.06	0.73	16.7
10 mg/mL Li + 5 mg/mL Co	20.8 ± 0.3	1.02 ± 0.01	0.73 ± 0.02	18.3 ± 0.3
10 mg/mL Li + 5 mg/mL Co (best)	21.7	1.06	0.75	18.7
10 mg/mL Li + 10 mg/mL Co	18.6 ± 0.6	0.85 ± 0.05	0.57 ± 0.05	12.6 ± 0.4
10 mg/mL Li + 10 mg/mL Co (best)	18.7	0.86	0.6	12.8

**Figure 3.** (a) Current density (J_{sc})–voltage (V) characteristics of perovskite solar cells for two-step method under standard test conditions (AM 1.5G, 100 mW cm^{-2}) based on different doping content in NiO_x ; (b) J–V curve of the best device and corresponding device performance parameters.

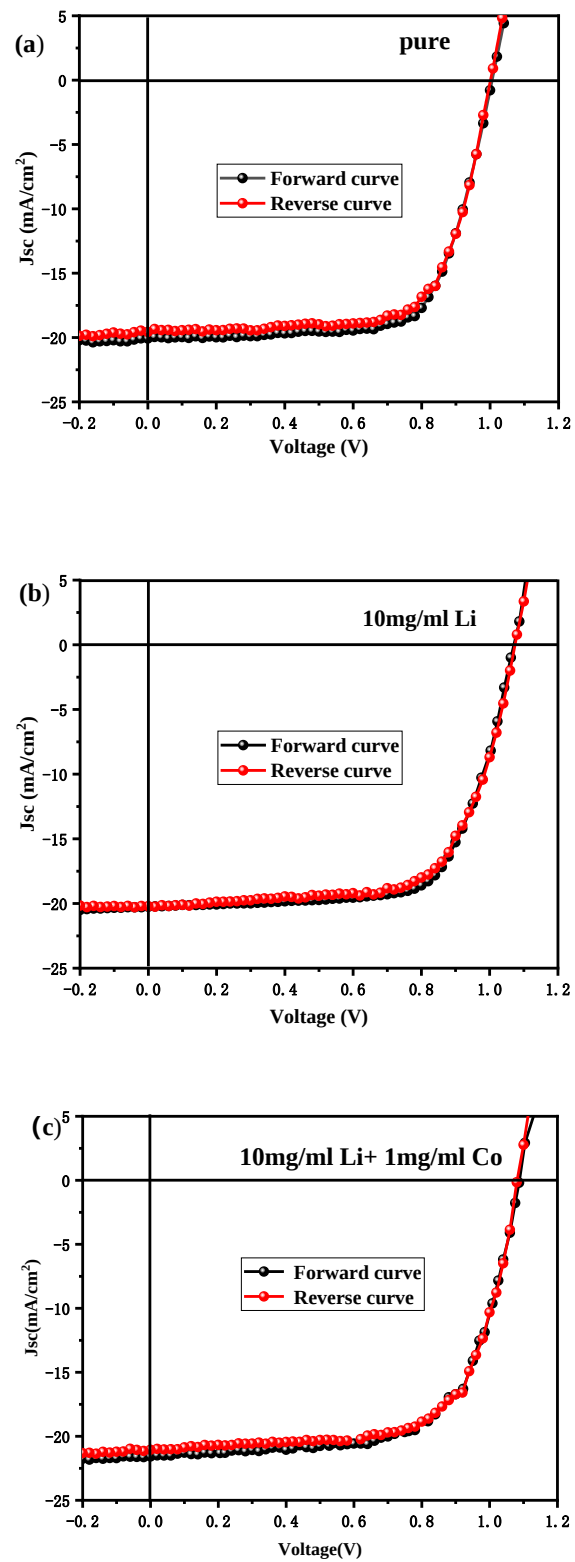


Figure 4. Cont.

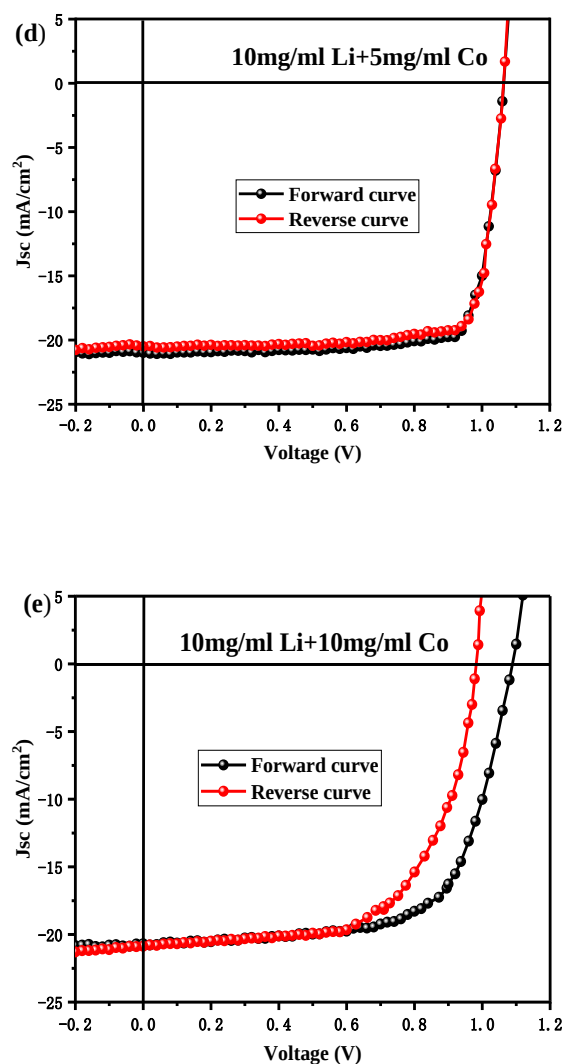


Figure 4. Forward scan ($-0.2 \text{ V} \rightarrow 1.2 \text{ V}$, step 0.08 V , delay time 500 ms) and Reverse scan ($1.2 \text{ V} \rightarrow -0.2 \text{ V}$, step 0.08 V , delay time 500 ms) of Inverted planar heterojunction perovskite solar device with different Li, Co doping content. (a) pristine NiO_x ; (b) 10 mg/mL Li doped NiO_x ; (c) 10 mg/mL Li, 1 mg/mL Co codoped NiO_x ; (d) 10 mg/mL Li, 5 mg/mL Co codoped NiO_x ; (e) 10 mg/mL Li, 10 mg/mL Co codoped NiO_x .

For investigating the perovskite layer absorption condition in the visible range, the IPCE along with the change of wavelength is depicted. From Figure 5a showed the value of IPCE (incident photon-to-electron conversion efficiency) has been improved much more with doping Li, Co into NiO_x HTLs. The absorption strength was improved with doping Li, Co, and particularly had a visible improve with the value of 10 mg/mL Li, 5 mg/mL Co codoped in HTLs. However, when the codoped concentration changed to 10 mg/mL Li, 10 mg/mL Co, it can be observed obviously that IPCE value declined drastically, which may be owing to defects increasing in perovskite light absorbing layer film. The IPCE spectrum and integrated J_{sc} of the device is showed in Figure 5b. The integrated J_{sc} is $22.1 \text{ mA}/\text{cm}^2$, which is basically consistent with the measured $J_{sc} = 21.7 \text{ mA}/\text{cm}^2$ value of the J–V curve and the corresponding IPCE has a broad plateau with a maximum value of 84.1% over essentially the entire visible range. Based on above results, the IPCE value of perovskite light absorbing layer varied a lot based on different NiO_x HTL, especially for the device with 10 mg/mL Li, 5 mg/mL Co codoped NiO_x .

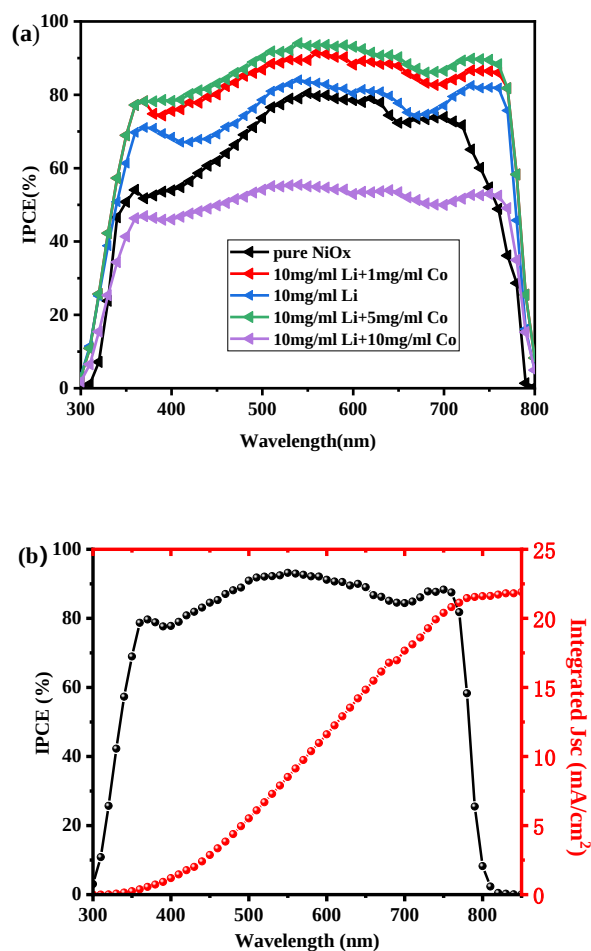


Figure 5. (a) The IPCE spectrum of MAPbI_{3-x}Cl_x perovskite film based on different HTLs; (b) The IPCE spectrum (black) and integrated J_{sc} (red) of the best device.

Because the stability of device performance is an important criterion for measuring the quality of a device, the PCE curve with time of perovskite solar device based on different NiO_x HTL was depicted in Figure 6a in an ambient environment (22 °C, 30% humidity). From the Figure 6a, compare with the PSCs based on pristine NiO_x of, doping Li⁺ or Li⁺, Co²⁺ co-doped NiO_x of PSCs showed better in stability of PSCs. The enhanced stability is for two reasons. The first is the crystal grains of perovskite film is much larger and denser in the process of Co infiltration into the perovskite layer. The second is that HTL can effectively block more the ambient air entering the perovskite layer.

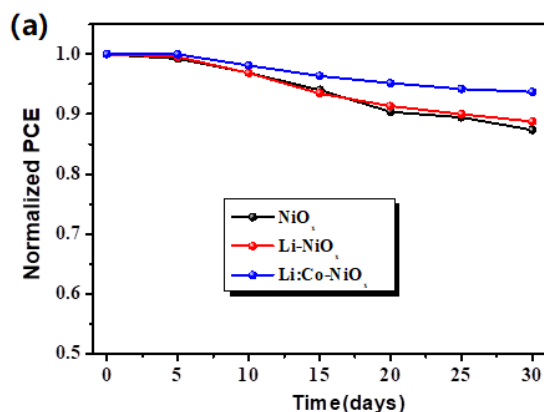


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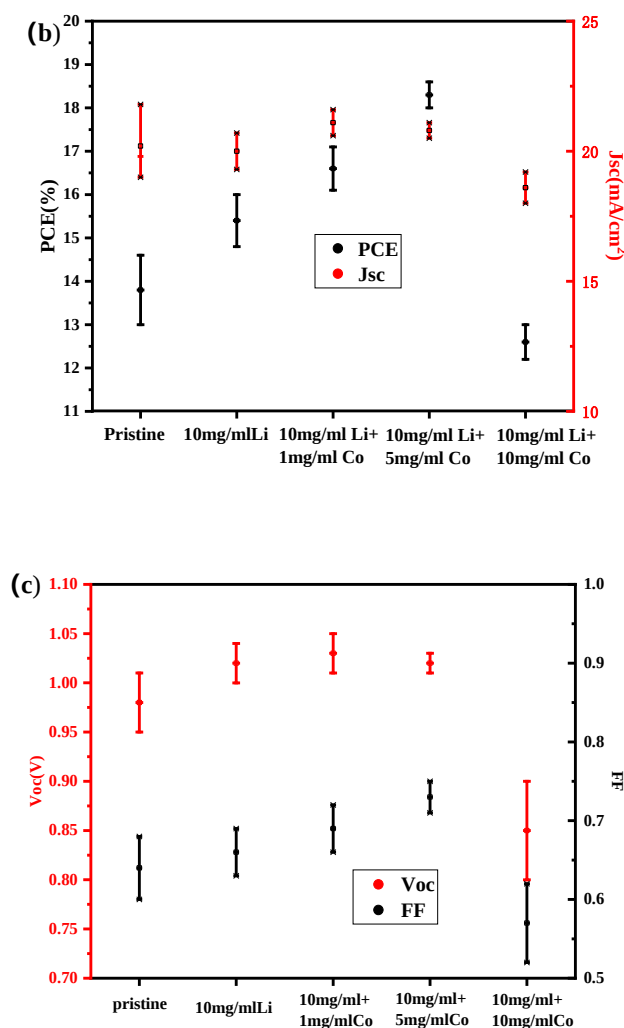


Figure 6. (a) PCE change of the best PSCs with no doping, 10 mg/mL Li doping, 10 mg/mL Li and 1 mg/mL Co codoping, 10 mg/mL Li and 5 mg/mL Co codoping, 10 mg/mL Li and 10 mg/mL Co codoping; (b) PCE and J_{sc} values of PSCs in three batches with different doping degrees; (c) Voc and FF values of PSCs in three batches with different doping degrees.

To investigate the device reproducibility, experiments were conducted for each concentration. The PSCs with pristine NiO_x had a seriously change while the PSCs based on Li^+ or Li^+ , Co^{2+} codoping NiO_x HTL appeared few distributions (Figure 6b,c).

In order to investigate the effect of Li and Co doping on the photophysics of $\text{MAPbI}_x\text{Cl}_{3-x}$, the steady-state photoluminescence (PL) measurements were included. PL measurements were adopted to analyze the extraction efficiency of photogenerated carriers from perovskite layer to NiO_x layer. Figure 7a showed that the PL quenching of $\text{MAPbI}_x\text{Cl}_{3-x}$ changed with different concentration of Li and Co doping in NiO_x substrates. The effect of PL quenching without doping was remarkable that may be ascribe to the relatively small grains of perovskite. And it was weakened after doping 10 mg/mL Li^+ in NiO_x HTL and was more obvious with Co element doping in NiO_x . Li^+ and Co^{2+} can increase charge transfer rate from photoactive layer transport layer and cut down the recombination of photogenerated carriers. The UV-vis absorption spectra (Figure 7b) manifest Li, Co codoped in NiO_x at lower concentrations cannot affect the perovskite thin film absorption (such as 10 mg/mL Li doped NiO_x , 10 mg/mL Li, 1 mg/mL Co codoped NiO_x , 10 mg/mL Li, 5 mg/mL Co codoped NiO_x), but it may produce impediment effect the perovskite thin film absorption at higher content (such as 10 mg/mL Li, 10 mg/mL Co codoped NiO_x).

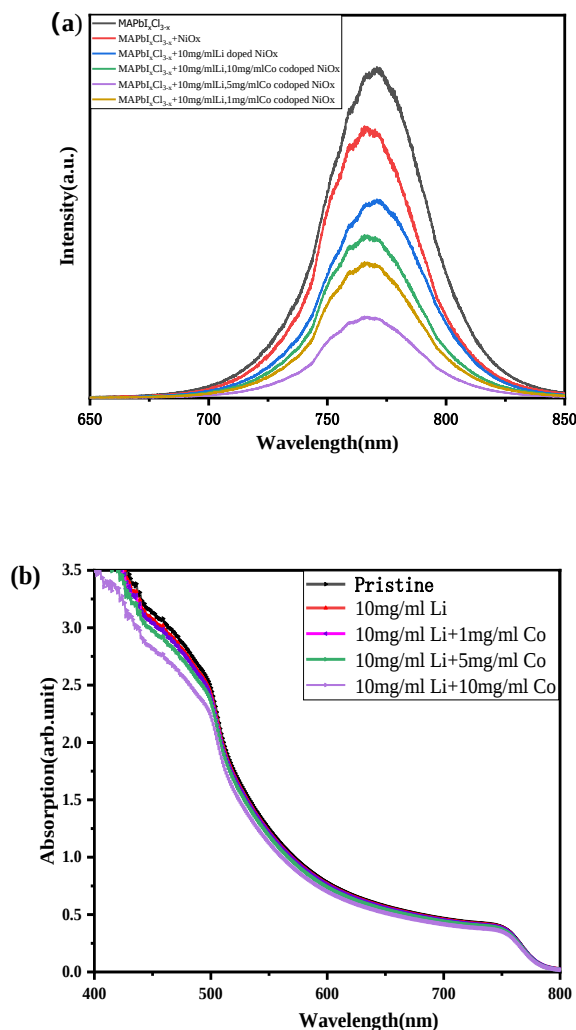


Figure 7. (a) Photoluminescence of MAPbI₃Cl_{3-x} which based on glass, pristine NiO_x, 10 mg/mL Li doped NiO_x, 10 mg/mL Li, 1 mg/mL Co codoped NiO_x, 10 mg/mL Li, 5 mg/mL Co codoped NiO_x, 10 mg/mL Li, 10 mg/mL Co codoped NiO_x; (b) UV-vis absorption spectra based on different HTL.

The steady-state photocurrent output and PCE at maximum power point diagram as a function of time for the pristine device and the best device based on 10 mg/mL Li, 5 mg/mL Co codoped NiO_x HTL were showed in Figure 8. The steady-state PCE output with 14.9% and 18.4% has been exhibited for conventional device and the best device respectively. It is demonstrated that the device performance are stable. And the absence of photocurrent hysteresis has been proved in the devices.

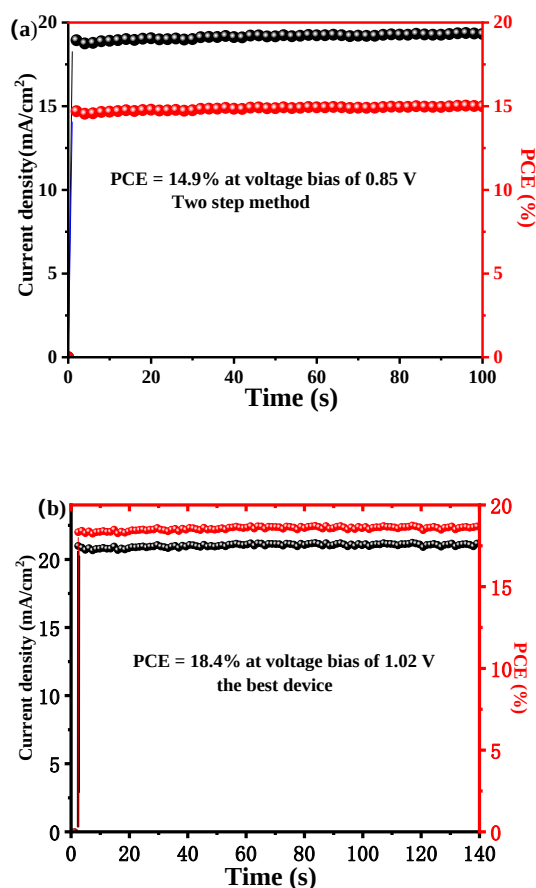


Figure 8. The steady state outputs of current density and PCE at maximum. (a) the conventional device using two step method based on pure NiO_x; (b) the best device based on 10 mg/mL Li, 5 mg/mL Co codoped NiO_x.

3. Conclusions

In conclusion, the influence of Li, Co-codoped NiO_x to the photovoltaic performance of PSSc was experimented. In this paper, one step method which is simple and effective was used and the elements of Li and Co are also non-poisonous and no impact on the stability of the PSSc. The influence of Li doping NiO_x is that can evidently improve the fill factor (FF) of PSSc while can increase the grain size of the perovskite film. The improvement of FF, which is a greatly significant characteristic of PSSc, is caused by the increased electrical conductivity. The p-type Co²⁺ was first doped into a NiO_x using spin coating at room-temperature and then was heated at a low temperature (about 250 °C) with the purpose of heating to make Co²⁺ element better to enter the perovskite layer. The film adding Co²⁺ made a great promotion of hole mobility in a way meanwhile made the surface of the perovskite layer more smoother. According to the report, a low doping degree of Li⁺ can increase the J_{sc} and FF, and increase the PCE of PSCs. Optimal doping is 10 mg/mL Li, 5 mg/mL Co, the J_{sc} increasing from 20.09 mA/cm² to 21.7 mA/cm², the FF increasing from 0.7 to 0.75, and the PCE similarly from 14.1% to 18.7%. The experimental results and mechanism analysis suggest that Li, Co doping NiO_x is really a promising way to improve the photovoltaic performance of PSCs.

All the materials including nickel acetate (Ni(CH₃COO)₂ · 4H₂O), Methylammonium iodide (CH₃NH₃I, 99.9%, Dyesol), Co(3)TFSI, LiTFSI, acetonitrile, Decon-90 cleaning agent, deionized water, acetone, alcohol, lead (II) iodide (PbI₂, 99.999%, Alfa), lead (II) chloride (PbCl₂, 99.999%, Alfa), phenyl-C61-butyric acid methyl ester (PC₆₁BM, 98%, nano-c), chlorobenzenes (99.8%, Sigma), isopropanol (99.5%, Sigma), and bathocuproine (96%, Alfa), Dimethyl sulphoxide (DMSO, 99.8%),

γ -hydroxybutyrate lactone (GBL), *N,N'*-dimethylformamide (DMF, 99.8%, Aladdin), Ag (electrode material), were used as received without further purification.

For the sol-gel-processed NiO_x , 248.8 mg $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol) with 60 μL (0.001 mmol) ethanolamine was dissolved in 2-methoxyethanol (10 mL). Then, the solution was stirred at 70 °C for 4 h.

The patterned ITO glass substrates were sequentially ultrasonic cleaned with detergent, de-ionized water, acetone, and isopropyl alcohol at 50 °C for 20 min, respectively. Inverted planar PSCs were fabricated on pre-patterned ITO glass substrates (around $2 \times 2.5 \text{ cm}^2$ in size, 10 Ω per square). Then, after a thin layer of NiO_x or Li-NiO_x was spin-coated on the substrates at 3000 rpm for 42 s and annealed at 250 °C for 35 min, the ITO substrates were dried with nitrogen gun and treated in a UV ozone oven for 15 min. After that the substrates were transferred into a nitrogen-filled glovebox. The spin-coating process of the Co(3)TFSI solution was programmed to run at 3000 rpm for 45 s and then annealed at 250 °C for 10 min. A $\text{MAPbI}_{3-x}\text{Cl}_x$ precursor solution containing 1.26 M PbI_2 , 0.14 M PbCl_2 and 1.35 M MAI was prepared in the cosolvent of DMSO:GBL (3:7 vol. ratio), and stirred for 2 h at 75 °C. The spin-coating process for the perovskite precursor solution was programmed to run at 1000 rpm for 20 s and then 4000 rpm for 40 s. When the spinning was at 50 s, 350 μL anhydrous chlorobenzene solution was injected onto the substrates that had. The perovskite films were thermally annealed on the hotplate at 100 °C for 20 min. Then, a layer of PCBM (20 mg mL^{-1} in chlorobenzene) was spin coated on the top of the perovskite layer at 2000 rpm for 40 s. After that, a thin layer of BCP (0.5 mg mL^{-1} in IPA) was spin coated on the top of the PCBM layer. The devices were achieved by thermally evaporated 100 nm Ag in high vacuum ($\leq 5 \times 10^{-4}$ Pa) through a shadow mask. All the devices had an area of 7 mm^2 .

The UV-visible absorption spectra were recorded with an UV-visible spectrophotometer (Perkin-Elmer Lambda 950) (PerkinElmer, Boston, MA, USA). The X-ray diffraction (XRD) test was conducted on Bruker D8 Advance XRD. Photovoltaic performances were measured by using a Keithley 2400 source meter under simulated sunlight from XES-70S1 solar simulator matching the AM 1.5G standard with an intensity of 100 mW/cm^2 . Incident photo-to-current conversion efficiencies (IPCEs) of PSCs were tested by the solar cell quantum efficiency measurement system (SCS10-X150, Zolix Instruments Co. Ltd., Beijing, China). The system was calibrated against a NREL certified silicon reference solar cell. All the measurements were carried under ambient atmosphere at room temperature without encapsulation. We use Tektronix D4105 (A digital oscilloscope) to record the photocurrent or photovoltage decay process with a sampling resistor of 50 Ω or 1 M Ω , respectively.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used Conceptualization, C.Z.; methodology, H.G.; software, Y.Y.; validation, Y.Y., S.W.; formal analysis, S.W.; data curation, Y.Y.; writing—original draft preparation, S.W.; writing—review and editing, S.W.; visualization, Y.Y.; supervision, H.G.; project administration, C.Z.; funding acquisition, S.W. All authors have read and agreed to the published version of the manuscript.

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