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Volume: 41
Issue: 1
Year: 2022
Pages: 96-105
ISSN: 1001-0521

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Trivalent Ni oxidation controlled through regulating lithium content to minimize perovskite interfacial recombination

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Received: 26 February 2021 / Revised: 23 April 2021 / Accepted: 13 May 2021 / Published online: 28 August 2021
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Abstract Organic–inorganic hybrid perovskite solar cells, one of the most promising photovoltaic devices, have made great progress in their efficiency and preparation technology. In this study, uniform, highly conductive LiₙNiOₓ (0 ≤ n ≤ 1; 0 < x ≤ 3) films were prepared by electrochemical deposition for a range of Li concentration. Photovoltaic performance for the perovskite solar cells was enhanced through incorporation of the ion pair of Ni³⁺ ↔ Ni²⁺ as the interfacial passivation. Depending on the amount of lithium doping, controlled interfacial oxidation was induced by Ni³⁺. The Li₀.₃₂NiOₓ inhibited charge recombination, reduced the defect density, and enhanced the photocurrent density. A maximum power conversion efficiency of 20.44% was obtained by Li₀.₃₂NiOₓ. Further, in the long-term, in-air stabilities of unencapsulated LiₙNiOₓ perovskite solar cells were demonstrated.

Keywords Lithium ions; Ni³⁺; Oxidized defect; Photocurrent; Perovskite solar cells

1 Introduction

Perovskite electronic devices have been attracted considerable attentions for wearable, intelligent, and scalable development [1, 2], due to their high light absorption coefficient, long carrier life, high carrier mobility, and tunable bandgap [1, 3]. Regulation of oxidized perovskite has been conducted to improve the power conversion efficiency (PCE) and device’s long-term durability [4, 5]. Environmental illumination/heating accelerates the degradation of perovskite layers, causing oxidation of I⁻ to I⁰ [5] and Pb²⁺ reduction to metallic Pb⁰ [6–8]. Zhou et al. showed that the europium ion pair Eu³⁺–Eu²⁺ acted as the “redox shuttle” that selectively oxidized Pb⁰ and reduced I⁰ defects simultaneously in a cyclical transition [4]. Wang et al. [5] reported that I⁻ was easily oxidized to I⁰, which not only served as carrier recombination centers but also initiated chemical chain reactions to accelerate the degradation of perovskite layers. Several attempts have been devoted to eliminating either Pb⁰ or I⁰ defects, including optimizing film processing [9] and additive engineering [4, 10]. To date, these additives are mostly sacrificial
reported that HTL electrical conductivity was enhanced by Li pulse laser deposited on NiO$_2$ films. To uniformly distribute nano-sized Li onto NiO$_2$, electrochemical deposition enables the reduction of metal precursors within a very short time period ($\sim$ 0.1 s), thus allowing the formation of nano-sized metallic Li clusters without large aggregation at low potential [29]. The electrochemical deposition method exhibits the advantages of uniformity and high quality in NiO$_2$ hole transport film fabrication [30–32]. However, the accurate elemental doping proportions in hole transfer layer (HTL) have been overlooked to date. The accurate Li$^+$ doping in the hole transport layer and the Ni$^{3+}$ contents on oxidation was rarely investigated for PSCs.

We demonstrate that accurate trivalent Ni$^{3+}$ ratio in NiO$_2$ hole transfer layer by controlled lithium doping leads to exceptional photocurrent improvement and high PCE through incorporation of the ion pair of Ni$^{3+}$ $\rightarrow$ Ni$^{2+}$ as the interfacial passivation. Depending on the amount of lithium doping, controlled interfacial oxidation could be achieved. The Li$_{0.32}$NiO$_2$ doping inhibited charge recombination, reduced the defect density, and enhanced the photocurrent density.

2 Experimental

2.1 Materials

Nickel nitrate hexahydrate (Ni(NO$_3$)$_2$.6H$_2$O) (98%), anisole (99.7%), and isopropyl alcohol (IPA) (99.5%) were purchased from Aladdin. Lithium acetate CH$_3$COOLi (99.95%), N,N-dimethylformamide (DMF) (99.8%), and dimethyl sulfoxide (DMSO) (99.9%) were purchased from Sigma-Aldrich. HC(NH$_2$)$_2$ (FAI) (99.5%) and CH$_3$NH$_2$Br (MABr) (99.5%) were purchased from Lucte Co. (Taiwan, China). CsI (99.98%) was purchased from Alfa Aesar. PbI$_2$ (>99.99%), PbBr$_2$ (>99.99%), [6,6]-phenyl-C61-butyric acid methyl ester (PC$_61$BM) (99.5%), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (99%) were purchased from Xi’an Polymer Light Technology Corp. Ethyl alcohol and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. Fluorine-doped tin oxide (FTO) glass with a sheet resistance of 7 $\Omega$-square$^{-1}$ was purchased from Advanced Election Technology Co., Ltd. Ag (99.99%) was purchased from Mat-cn.

2.2 Li$_n$NiO$_2$ fabrication

FTO glass substrates were rinsed by sequential ultrasonic treatment in detergent, deionized water, anhydrous ethanol, acetone, and isopropyl alcohol for 20 min and then dried with a nitrogen stream. Then, the substrates were treated with UV-ozone for 20 min in plasma cleaner. Li$_n$NiO$_2$ was
electrochemically deposited using a constant current mode of three-electrode CHI 660a electrochemical workstation. The three electrodes were FTO glass as the working electrode, the Ag/AgCl electrode as the reference electrode, and the platinum electrode as the counter electrode. 3 mmol of nickel nitrate hexahydrate and lithium acetate in different proportions was dissolved in 30 ml deionized water as deposition solution. The deposition current density was controlled in the range of 0.05–0.50 mA·cm⁻². After the deposition, the Li₉NiO₃ film was rinsed with deionized water and absolute ethanol and then annealed at 300 °C for 1 h at ambient pressure.

2.3 Perovskite solar cell fabrication

The Li₉NiO₃ (n = 0, 0.13, 0.24, 0.32, 0.38) film doped with different ratios of lithium was transferred into a glove box filled with N₂ to complete the following processes. Precursor solution of Cs₀.₀₅FA₀.₈₁MA₀.₁₄Pb₂.₅₅Br₀.₄₅ (CsFAMA) was prepared in two steps: First, 1.211 mol·L⁻¹ FAI and 1.275 mol·L⁻¹ PbI₂ were dissolved in a 1:4 volume ratio of DMSO/DMF as Solution (I), 1.425 mol·L⁻¹ MABr and 1.5 mol·L⁻¹ PbBr₂ were dissolved in a 1:4 volume ratio of DMSO/DMF as Solution (II), and 0.75 mol·L⁻¹ CsI was dissolved in DMSO as Solution (III). Then, 440 μl Solution (I), 66 μl Solution (II), and 44 μl Solution (III) were mixed and stirred for 12 h at room temperature. The perovskite precursor solution was spin-coated onto glass/FTO/Li₉NiO₃ (n = 0, 0.13, 0.24, 0.32, 0.38) substrate under 1000 r·min⁻¹ for 10 s and 4000 r·min⁻¹ for 60 s. 68 μl anisole was jetted onto the spinning substrate for 30 s, and then, the spin coating of the film was annealed. The perovskite precursor solution was spin-coated onto glass/FTO/Li₉NiO₃ substrate. The electron transport layer PC₅₇BM (0.02 mol·L⁻¹ PC₅₇BM dissolved in anisole) was spin-coated at 4000 r·min⁻¹ for 30 s and annealed at 70 °C for 10 min, and BCP layer (3.5 mol·L⁻¹ BCP dissolved in isopropanol) was spin-coated at 5000 r·min⁻¹ for 30 s. And 70–80 nm Ag was thermally evaporated under high vacuum onto BCP as top electrode.

2.4 Characterization

X-ray diffractometer (XRD) patterns were obtained using D8 Advance diffractometer with Cu Kα radiation (40 kV and 40 mA) under the scanning rate of 4 (°)-min⁻¹ for a wide-angle test over the Bragg angle range of 10°–90°. Scanning electron microscopy (SEM) measurements were performed using a Hitachi-SU8010 electron microscope operated at an acceleration voltage of 5 kV. X-ray photoelectron spectroscopy (XPS) data were measured using Thermo Fisher’s ESCALAB250Xi instrument. The steady-state photoluminescence (PL) spectra were measured by the fluorescence spectrometer at Shanghai Anting Electronic Instrument Factory. The photocurrent–voltage (J–V) characteristics of the solar cells were measured using a Keithley 2400. The source was under the illumination of simulated sunlight (AM1.5, 100 mW·cm⁻²) provided by a solar simulator (Newport 69907) with an AM 1.5 filter. Light intensity was adjusted using an NREL-calibrated Si solar cell with a KG-2 filter for approximating 1 sunlight intensity. While measuring current and voltage, the cell was covered with a black mask having an aperture of 0.026 cm². Measurement of inductively coupled plasma-optical emission spectroscopy (ICP-OES) for Li₉NiO₃ films was performed by an Agilent ICP-OES730i instrument. The ultraviolet–visible spectroscopy (UV–Vis) absorption and transmission curves were determined with a Hitachi U-4100. Transmission electron microscopy (TEM) was performed at room temperature with JEOL’s JEM-F200 at 200 kV. The time-resolved photoluminescence spectroscopy (TRPL) spectra were recorded with FIs-800 spectrometers.

3 Results and discussion

The electrochemical fabrication process of lithium-doped nickel oxide film (abbreviated as Li₉NiO₃, 0 ≤ n ≤ 1; 0 < x ≤ 3) is schematically shown in Fig. 1. To uniformly deposit Li₉NiO₃ film on a fluorine-doped tin oxide (FTO) substrate, the deposition mode of a constant current of 1 × 10⁻⁴ A is operated in Fig. S1a. The preparation process is as following:

\[
\text{H}_2\text{O}^+(aq) + \text{NO}_3^-(aq) + 2e^- \rightarrow 2\text{OH}^-(aq) + \text{NO}_2^-(aq) \quad (1)
\]

which placed the hydroxyl ions on FTO surface [31, 33].

\[
n\text{Li}^+(aq) + \text{Ni}^{2+}(aq) + (x + n)\text{OH}^-(aq) \\rightarrow n\text{Li(OH)}(s) + \text{Ni(OH)}_x(s) \rightarrow \text{Li}_x\text{NiO}_y \quad (2)
\]

in which lithium nickel hydroxide reacted lithium/nickel ions with hydroxyl ions, prior to annealing the product to form lithium nickelate.

The perovskite Cs₀.₀₅FA₀.₈₁MA₀.₁₄Pb₂.₅₅Br₀.₄₅ (denoted as CsFAMA), electron transfer layer (PC₅₇BM/BCP), and electrode were sequentially fabricated on the hole-transfer layer of Li₉NiO₃, thereby constructing the glass/FTO/Li₉NiO₃/CsFAMA/PC₅₇BM/BCP/Ag solar cell.

Figure 2a shows X-ray diffraction (XRD) patterns of Li₉NiO₃ (0 < x ≤ 3) layers as a function of Li content (n = 0, 0.13, 0.24, 0.32, 0.38, respectively). Diffraction peaks at 37.78° and 61.63° can be seen in XRD pattern in Fig. 2a, indicating (retrieved PDF No. 47-1049 and PDF No. 26-1175) the (111) crystal plane of NiO (0 < x ≤ 3, orthorhombic unit cell) [34] and the (006) crystal plane of
Fig. 1 Schematics Illustrating Li$_n$NiO$_x$ (0 ≤ n ≤ 1; 0 < x ≤ 3) electrochemical device structure of glass/FTO/Li$_n$NiO$_x$/CsFAMA/PC$_{61}$BM/BCP/Ag formation process

![Diagram of device structure]

Fig. 2 a XRD patterns of Li$_n$NiO$_x$ (n = 0, 0.13, 0.24, 0.32, 0.38; 0 < x ≤ 3) film on FTO glass and enlarged peaks of (006) lattice plane in right segment; b HRTEM images and SAED pattern of Li$_{0.32}$NiO$_x$ nanocrystals

Li$_n$NiO$_x$ (0 ≤ n ≤ 1; 0 < x ≤ 3; cubic unit cell) [35], respectively. The intensity and position of the (111) peaks are almost identical for both NiO$_x$ and Li$_n$NiO$_x$ [36]. The ionic radius of Li (0.072–0.076 nm) is close to Ni (0.069–0.074 nm) [24, 25, 37, 38], which explains why the (111) peak intensity of XRD pattern is not obviously shifted. The 2θ value for the (006) diffraction peak of Li$_n$NiO$_x$ (0 ≤ n ≤ 1; 0 < x ≤ 3) films in Fig. 2a shifted from 61.63° to 61.76° as the Li proportion increased from n = 0.32 to 0.38. The full width at half maximum (FWHM) of XRD peak at 60°–63° and corresponding (006) crystal plane spacing are displayed in Fig. S1b.

FWHM for Li$_{0.32}$NiO$_x$ (1.18°) is 0.09° and 0.52° smaller than that of Li$_{0.24}$NiO$_x$ (1.27°) and Li$_{0.38}$NiO$_x$ (1.70°), respectively. The corresponding crystal plane (006) spacing of 0.15110 nm of Li$_{0.32}$NiO$_x$ is maximum, comparative to 0.15086 nm of Li$_{0.24}$NiO$_x$ and 0.15078 nm of Li$_{0.38}$NiO$_x$. The smaller FWHM and enlarged lattice parameters improve the crystallinity [34]. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements showed that the lithium was doped in the nickel oxide successfully, as indicated in Table S1. The crystal plane spacings of (006) and (111) of Li$_{0.32}$NiO$_x$ were determined from high-resolution transmission electron microscopy (HRTEM) image and selected area electron diffraction (SAED) pattern, as shown in Fig. 2b, and the crystal plane spacing was calculated as the strong diffraction fringes matched well with XRD pattern shown in Fig. 2a, indicating that Li ions were successfully and controllably inserted into NiO$_x$ (0 < x ≤ 3).

Enhanced photovoltaic performance for the representative perovskite solar cell with Li$_n$NiO$_x$ (n = 0, 0.13, 0.24, 0.32, 0.38; 0 < x ≤ 3) as HTL is shown in Figs. 3a, S2 and Table S2. With the lithium content increasing to 0.32, the current density (J$_{SC}$) and PCE reached the highest values of 26.53 mA·cm$^{-2}$ and 20.44%, respectively. As the lithium content increased to 0.38 in Li$_{0.38}$NiO$_x$ (0 < x ≤ 3), the PCE of Li$_{0.38}$NiO$_x$ decreased. To verify the performance stability and high J$_{SC}$ repeatability, the 10 groups of statistic best PCE and J$_{SC}$ for the Li$_{0.32}$NiO$_x$-based PSC are shown in Fig. 3b and Table S3. The average PCE and J$_{SC}$ are 19.4% ± 1.04% and (26.205 ± 1.14) mA·cm$^{-2}$, respectively. The average photovoltaic parameters of NiO$_x$, Li$_{0.13}$NiO$_x$, Li$_{0.32}$NiO$_x$ and Li$_{0.38}$NiO$_x$ are displayed in Tables S4-S7, respectively. The long-term air stabilities of unencapsulated Li$_{0.32}$NiO$_x$-based PSC are illustrated in Fig. 3c. The Li$_{0.32}$NiO$_x$-based device maintained average 75%, 90%, 80% and 98% of its initial PCE, J$_{SC}$, fill factor (FF), and open circuit voltage (V$_{oc}$),
Fig. 3 a Current–density versus voltage (J–V) curves of PSC; b 10 groups of statistic champion PCE and Jsc for \( \mathrm{Li}_{0.32}\mathrm{NiO}_x \)-based PSC; c stability testing of photovoltaic performance for unencapsulated perovskite solar devices employing \( \mathrm{Li}_{0.32}\mathrm{NiO}_x \) as hole-transfer materials respectively, after 1656 h (69 days), suggesting the high stability of \( V_{OC} \) and \( J_{SC} \).

Scanning electron microscopy (SEM) images of \( \mathrm{Li}_x\mathrm{NiO}_y \) \( (n = 0, 0.13, 0.24, 0.32, 0.38; 0 < x \leq 3) \) films and corresponding perovskite films are shown in Figs. 4, S3 and S4. The average pore size of a hierarchical porous \( \mathrm{Li}_{0.32}\mathrm{NiO}_x \) film (\( \sim 86.7 \) nm) was smaller than that of \( \mathrm{NiO}_x \) (\( \sim 224.5 \) nm); nevertheless, the thickness of \( \mathrm{Li}_{0.32}\mathrm{NiO}_x \) film (\( \sim 152.9 \) nm) is thicker than that of \( \mathrm{NiO}_x \) film (\( \sim 149.3 \) nm) fabricated by the electrochemical deposition method, as shown in SEM images in Figs. 4, S4. The doping of lithium ions increases the film thickness and decreases the pore sizes constructed by growing interplanar spacing, in accordance with XRD pattern in Fig. 2a. The modal particle size (consisting of 33.3% of the particles) of perovskite film of \( \mathrm{Li}_{0.32}\mathrm{NiO}_x \) ranging from 300 to 350 nm is shown in Fig. 4c, which is larger than that of pure \( \mathrm{NiO}_x \) substrate (250–300 nm) shown in Fig. 4f. SEM image in Fig. 4d and cross-sectional SEM image in Fig. 4e show the flower-shaped \( \mathrm{NiO}_x \) film with a thickness of \( \sim 100 \) nm. The uniform perovskite distribution in the \( \mathrm{Li}_{0.32}\mathrm{NiO}_x \) HTM improved the interfacial binding and enhanced photovoltaic performance, such as the fill factor which increased from 65.02% (\( \mathrm{NiO}_x \)) to 74.44% in Table S2. However, the 0.13, 0.24 and 0.38 lithium levels in the \( \mathrm{Li}_x\mathrm{NiO}_y \) films displayed large number of micro-cracks and defects, which reduced the charge carrier collection and suppressed the short-circuit current, in agreement with conductivity investigated by series resistance (\( R_s \)) and shunt resistance (\( R_{sh} \)) in the J–V measurement in Fig. S2 and Table S2.

The effective photovoltaic exciton-quenching was performed by steady-state photoluminescence (PL) in Figs. 5a, S6a. The ultraviolet–visible spectrum and the corresponding bandgaps for perovskite films on \( \mathrm{Li}_{0.32}\mathrm{NiO}_x \) and \( \mathrm{NiO}_x \) (0 < \( x \) \leq 3) substrate are shown in Figs. 5b, S5. The perovskite layer on \( \mathrm{Li}_{0.32}\mathrm{NiO}_x \) exhibits a higher quenching

Fig. 4 Morphology of electrochemical deposition of hole transport layer: a SEM image and pore-size distribution, b cross-sectional SEM image of \( \mathrm{Li}_{0.32}\mathrm{NiO}_x \) (0 < \( x \) \leq 3), and c SEM image of perovskite nanocrystals on \( \mathrm{Li}_{0.32}\mathrm{NiO}_x \) film and grain-size distribution, d SEM image and pore-size distribution, e cross-sectional SEM image of \( \mathrm{NiO}_x \), and f SEM image of perovskite nanocrystals on \( \mathrm{NiO}_x \) film and grain-size distribution.
rate than other HTLs with Li fractions of 0, 0.13, 0.24 and 0.38, as shown in Figs. 5a, S5a. The peak of PL intensity of Li\textsubscript{0.32}Ni\textsubscript{0.68}O\textsubscript{3} is ~789.60 nm in accordance with its UV–Vis spectrum. The abnormal PL peak of perovskite on NiO\textsubscript{x} HTL in Fig. 5a results from the MA migration [39]. The bandgap of perovskite can be tuned from 1.551 to 1.563 eV by changing Li content (n) in Li\textsubscript{n}NiO\textsubscript{x}, suggesting that the lower bandgap is conducive to photovoltaics.

The light absorbance of perovskite on Li\textsubscript{0.32}Ni\textsubscript{0.68}O\textsubscript{3} film in Figs. 5b, S5b is lower than that of NiO\textsubscript{x} film. This difference suggests that by sacrificing the light absorbance, a larger exciton-quenching as well as highly efficient PSC can be achieved. As shown in Figs. 5c, S6a, thanks to the Li\textsubscript{0.32}Ni\textsubscript{0.68}O\textsubscript{3} hole-transfer layer, the Li\textsubscript{0.32}Ni\textsubscript{0.68}O\textsubscript{3} device obtained the highest PCE of 20.44% in Figs. 3, S2 and Table S2.

To consolidate our analysis, time-resolved photoluminescence (TRPL) spectroscopy was further employed to investigate the early interfacial charge separation kinetics of the Li\textsubscript{0.32}Ni\textsubscript{0.68}O\textsubscript{3} hole-transfer layer and perovskite layer. The TRPL responses obtained by exciting at 400 nm shown in Figs. 5c, S6b for perovskite films on NiO\textsubscript{x} hole transport layer with and without lithium can be fitted using a bi-exponential equation [40]:

$$f(t) = \sum A_i \exp(-t/\tau_i) + C$$

where $A_i$ is the decay amplitude, $t$ is time, $\tau_i$ is the decay time constant, and $C$ is a constant for the baseline offset.

Table S8 lists all the parameters obtained from the analysis, showing a fast-decay component ($\tau_1$) and a slow-decay component ($\tau_2$), with a weighted average:

$$\tau_{\text{ave}} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$

The perovskite film on NiO\textsubscript{x} HTL had an average decay time of 7.09 ns. The decay time was significantly reduced (by 86.6%) to 0.95 ns when the perovskite film was coated on the Li\textsubscript{0.32}Ni\textsubscript{0.68}O\textsubscript{3} substrate, implying faster charge transfer from perovskite film coated on Li\textsubscript{0.32}Ni\textsubscript{0.68}O\textsubscript{3}. The decay amplitude $A_2$ and longer decay time constant $\tau_2$ of perovskite on the Li\textsubscript{0.32}Ni\textsubscript{0.68}O\textsubscript{3} substrate were 16.45% and 10.22 ns, respectively, in contrast with $A_1$ and $\tau_1$ of 83.55% and 0.90 ns, as shown in Table S8. The radiative recombination (16.45%) of perovskite film on Li\textsubscript{0.32}Ni\textsubscript{0.68}O\textsubscript{3} substrate is lower than nonradiative recombination (83.55%), suggesting the low interfacial trap density. This is beneficial for short-circuit current ($I_{SC}$) and is consistent with device performance results in Fig. 3a. The intrinsic hole mobility was studied by measuring the space-charge-limited-current testing (SCLC) [41], using the dark current–voltage characteristics for a hole-only device structure with FTO/Li\textsubscript{0.32}Ni\textsubscript{0.68}O\textsubscript{3}/perovskite/Spiro-OMTAD/Ag, as shown in Figs. 5d, S7. On the log–log plot, the first-order linear relationships represent the ohmic response of the devices at low bias voltages. At higher voltages, the current increased nonlinearly and transferred to the trap-filled limit (TFL) at the kink point. It could be concluded
that all the available trap states were completely filled by the injected carriers, and the kink point is defined as the TFL voltage ($V_{TFL}$). The trap density ($N_t$) is expressed by Eq. (5) [42]:

$$N_t = \frac{2\varepsilon_0 V_{TFL}}{eL^2}$$

where $\varepsilon$ is the dielectric constant of perovskite (\(\varepsilon = 28.8\)) [43], $\varepsilon_0$ is the vacuum permittivity (\(\varepsilon_0 = 8.854 \times 10^{-12}\) F-m$^{-1}$), $L$ is the thickness of perovskite film ($L = 500$ nm, as shown in the cross-sectional SEM image of the device in Fig. S4f), and $e$ is the elementary electronic charge ($e = 1.6 \times 10^{-19}$ C) [44]. The kink point in the dark $J-V$ curves is defined as the TFL voltage ($V_{TFL}$). The $V_{TFL}$ values illustrated in Figs. 5d, S7 are 0.72 V for NiO$_x$, 0.55 V for Li$_{0.32}$NiO$_x$, and 0.91 V for Li$_{0.38}$NiO$_x$, respectively, and the corresponding hole trap densities are $9.18 \times 10^{15}$ cm$^{-3}$ for NiO$_x$, $7.01 \times 10^{15}$ cm$^{-3}$ for Li$_{0.32}$NiO$_x$, and $11.60 \times 10^{15}$ cm$^{-3}$ for Li$_{0.38}$NiO$_x$, respectively. The drift carrier mobility ($8.60 \times 10^{-2}$ cm$^2$ V$^{-1}$ S$^{-1}$) for Li$_{0.32}$NiO$_x$ is the largest in contrast to that of NiO$_x$ ($2.20 \times 10^{-3}$ cm$^2$ V$^{-1}$ S$^{-1}$), Li$_{0.33}$NiO$_x$ ($1.14 \times 10^{-2}$ cm$^2$ V$^{-1}$ S$^{-1}$), Li$_{0.24}$NiO$_x$ ($2.69 \times 10^{-2}$ cm$^2$ V$^{-1}$ S$^{-1}$), and Li$_{0.38}$NiO$_x$ ($7.15 \times 10^{-2}$ cm$^2$ V$^{-1}$ S$^{-1}$), as shown in Table S9. These results indicate that the mean trap density of the HTL/perovskite interface can be significantly reduced by doping $n = 0.32$ in Li$_x$NiO$_x$ HTL, which is expected to inhibit carrier recombination and promote $J_{SC}$ in the corresponding solar cells, consistent with the results obtained from the fluorescence spectrum analysis shown in Fig. 5a, c. As a result, proper amount of Li additives improves the HTL/perovskite interfacial conductivity and leads to lower defect densities [21, 45, 46].

To investigate the influences of Ni valence states on the perovskite degradation, Ni$^{2+}$/Ni$^{3+}$ ratios in Li$_x$NiO$_x$ ($n = 0, 0.13, 0.24, 0.32, 0.38; 0 < x \leq 3$) were investigated by X-ray photoelectron spectroscopy (XPS), as shown in Figs. 5e, f, S8 and Table S10. As exhibited in Ni 2p$_{3/2}$ XPS spectra in Fig. 5e, f, four curves are in good agreement with the experimental results: NiO$_x$ peaks at 854.90 and 872.50 eV, and Li$_{0.32}$NiO$_x$ peaks at 855.00 and 872.40 eV. The coexistence of Ni$^{3+}$ and Ni$^{2+}$ indicates that NiO$_x$ film serves as a chemical metrology. In Li$_x$NiO$_x$, when Li content ($n$) increases from 0 to 0.38, the x on behalf of Ni valent state changes accordingly, as summarized in Table S10. From XPS measurements, the Ni 2p$_{3/2}$ core level peak has an unambiguous shift of $\approx 0.10$ eV, after the doping of Li ($n = 0.32$), decreasing from 872.50 to 872.40 eV (Fig. 5e, f). Li doping can significantly shift the valence band of NiO$_x$ downward, suggesting occurrence of electron transfer and in agreement with the phenomena of a valence band shift [47]. No additional or new chemical components were detected by XPS except the Li signal shown in Fig. S8a and ICP-OES in Table S1, and the schematic band diagrams of the NiO/perovskite interface in the PSCs are illustrated in Fig. 6.

Ni$^{2+}$ and Ni$^{3+}$ concentration analysis of Li$_x$NiO$_x$ from XPS spectra is summarized in Table S10. Ni$^{3+}$/Ni$^{2+}$

Fig. 6 Schematic illustration of energy band diagram of FTO/Li$_{0.32}$NiO$_x$/CsFAMA/PC$_{61}$BM/BCP/Ag perovskite solar cells

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Ni$^{3+\text{+}}$ molar ratio of Li$_{0.32}$NiO$_x$, Li$_{0.38}$NiO$_x$, Li$_{0.24}$NiO$_x$ and NiO$_x$ is 0.25, 0.31, 0.29 and 0.29, respectively. Ni$^{3+\text{+}}$ content of Li$_{0.32}$NiO$_x$ is 24% and 16% lower than that of Li$_{0.38}$NiO$_x$ and Li$_{0.24}$NiO$_x$, respectively, suggesting that Li$_{0.32}$NiO$_x$ exhibits the lowest Ni$^{3+\text{+}}$ content. In this redox transition, Γ defects could be oxidized by Ni$^{3+\text{+}}$, while Γ$^0$ defects could be produced by Ni$^{3+\text{+}}$ simultaneously through the reactions [48]:

$$\text{Ni}^{3+\text{+}} + e^- \rightarrow \text{Ni}^{2+\text{+}}$$ (6)

$$\text{Ni}^{3+\text{+}} + \Gamma^0 \rightarrow \text{Ni}^{2+\text{+}} + \Gamma^0$$ (7)

For Reaction (7), $\Delta G_m (298.15 \text{ K}) = \Delta G_m (\text{Ni}^{2+\text{+}}, 298.15 \text{ K}) + \Delta G_m (\Gamma^0, 298.15 \text{ K}) - [\Delta G_m (\text{Ni}^{3+\text{+}}, 298.15 \text{ K}) + \Delta G_m (\Gamma^0, 298.15 \text{ K})] = -(196.05 \pm 26) \text{ kJ mol}^{-1} < 0$, in which $\Delta G_m$ is standard molar reaction Gibbs free energy change; $\Delta G_m$ represents the standard molar Gibbs energy of formation [49]; $\Delta G_m (\text{Ni}^{2+\text{+}}, 298.15 \text{ K}) = -(45.77 \pm 0.77) \text{ kJ mol}^{-1}$; $\Delta G_m (\text{Ni}^{3+\text{+}}, 298.15 \text{ K}) = (202 \pm 26) \text{ kJ mol}^{-1}$; $\Delta G_m (\Gamma^0, 298.15 \text{ K}) = -(51.72 \pm 1.12) \text{ kJ mol}^{-1}$; and $\Delta G_m (\Gamma^0, 298.15 \text{ K}) = 0 \text{ kJ mol}^{-1}$. Scientific spontaneity means that the Gibbs free energy change of the reaction is negative [50]. The Gibbs energy change $\Delta G_m (298.15 \text{ K})$ of Reaction (5) is $-(45.77 + 0 - 202 + 51.72) = -196.05 \text{ kJ mol}^{-1} < 0$, suggesting that Reaction (5) occurs spontaneously, and Ni$^{3+\text{+}}$ oxidation of Γ$^0$ leads to the degradation of perovskite. Low Ni$^{3+\text{+}}$ proportion in Li$_x$NiO$_x$ HTL diminishes the detrimental effects of halide in perovskite film.

The best photovoltaic performance using Li$_{0.32}$NiO$_x$ as HTL can be attributed to the high-quality Li$_{0.32}$NiO$_x$/perovskite interface and high charge carrier transport. The highest photocurrent and efficiency with perovskite on Li$_{0.32}$NiO$_x$ film manifest as follows: (1) The lattice constant is increased by Li atom substituting Ni vacancy in NiO$_x$ framework, and Li$_{0.32}$NiO$_x$ pattern displays the highest crystallinity, as shown in XRD patterns. (2) The photo-generated excitons (electron hole pair) in Li$_{0.32}$NiO$_x$/perovskite interface can be separated effectively, and excellent electrical conductivity of Li$_{0.32}$NiO$_x$ ensured the high-speed carriers transport, as exhibited in PL and TRPL spectra. (3) The Li$_{0.32}$NiO$_x$ hole trap density is the lowest as investigated in SCLC. (4) Compared to Li$_{0.38}$NiO$_x$ and Li$_{0.24}$NiO$_x$, the lower ratio of Ni$^{3+\text{+}}$ in Li$_{0.32}$NiO$_x$ reduces the oxidation of Γ$^0$. The low trap density and high photocurrent suggest that decreasing Ni$^{3+\text{+}}$ content reduces the oxidation and degradation of the perovskite in the HTL/perovskite interface [39]. Overall, through the electrochemical deposition method, Li$_{0.32}$NiO$_x$ is constructed with uniform 90-nm pore-size structure, high crystallinity, tunable Ni oxidation, and excellent photocurrent properties.

4 Conclusion

Trivalent Ni oxidation in Li$_x$NiO$_x$ can be readily and accurately controlled by electrochemical regulating Li concentration. The Ni$^{2+\text{+}}$/Ni$^{3+\text{+}}$ ratio of Li$_{0.32}$NiO$_x$ is the highest in Li$_x$NiO$_x$ by XPS spectra, and the Ni$^{3+\text{+}}$ proportion is the least in Li$_{0.32}$NiO$_x$. The Li$_{0.32}$NiO$_x$ film as hole transport layer enabled the perovskite solar cells to acquire the best efficiency of 20.44%, attributing to the decreased oxidation, low trap density, and excitons lifetime in the HTL/perovskite interface.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (No. 11772207), the Natural Science Foundation of Hebei Province (Nos. A2019210204 and E2019210292), the Special Project of Hebei Provincial Central Government Guiding Local Science and Technology Development (No. 211Z4302G), the Youth Top-notch Talents Supporting Plan of Hebei Province and the support of State Key Laboratory of Mechanics and Control of Mechanical Structures, Nanjing University of Aeronautics and Astronautics (No. MCMS-E-051904).

Declarations

Conflicts of interests The authors declare that they have no conflict of interests.

References


