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Short Communication

Low-temperature processed inorganic hole transport layer for efficient and stable mixed Pb-Sn low-bandgap perovskite solar cells

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Metal halide perovskite solar cells (PSCs) have attracted tremendous attention as an emerging photovoltaic technology due to their high efficiency, low cost and ease of fabrication from earth-abundant materials [1,2]. The power conversion efficiencies (PCEs) have been rapidly boosted from 3.8% in the pioneer's work to a certified 24.2% nowadays in just ten years [3]. The PCE breakthroughs in PSCs have mostly adopted full lead-based perovskites ($APbX_3$) with bandgaps of 1.5–1.6 eV.

By mixing Pb and Sn cations, lower bandgaps down to 1.18 eV can be achieved in mixed Pb-Sn halide perovskites [4]. According to Shockley-Queisser (S-Q) limit, perovskites with a lower bandgap (1.1–1.3 eV) will give a higher efficiency than Pb-based perovskites due to the extension of absorption region. Furthermore, low-bandgap perovskites ($E_g \sim 1.2$ eV) also enable highly efficient all-perovskite tandem solar cells which could exceed the S-Q limit [5]. Mixed Pb-Sn low-bandgap PSCs have demonstrated PCEs exceeding 20% by engineering the perovskite composition and device interfaces. So far, PCEs of 25% and 23.1% have been reported for 4-terminal and 2-terminal all-perovskite tandem solar cells, respectively [6,7].

High-efficiency mixed Pb-Sn low-bandgap perovskite solar cells have exclusively used poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as the hole transport layer [7,8]. However, PEDOT:PSS layers lead to poor stability in solar cells due to their hygroscopic and acidic characteristics [9,10]. It is therefore urgent and necessary to develop robust hole transport materials that can make efficient and stable mixed Pb-Sn low-bandgap PSCs. As demonstrated in Pb-based PSCs, inorganic hole transport materials typically lead to better device stability than the organic counterparts. Among various inorganic hole transport layers (HTLs), nickel oxide (NiO_x) has attracted enormous attention due to its excellent stability and high PCEs achieved in Pb-based PSCs [11]. Using high temperature (at 300 °C) processed NiO_x as HTL, Chi et al. [12] reported 17.2%-efficient $FAPb_{0.75}Sn_{0.25}I_3$ (E_g = 1.36 eV) mixed perovskite solar cells, and better thermal stability than EPDOT:PSS has been demonstrated.

Here we report, for the first time, the low-temperature solution processed NiO_x film as the hole transport layer for mixed Pb-Sn low-bandgap perovskite solar cells. We achieve a high PCE of 17.6% (stabilized 17.0%) and a high short-circuit current density (J_{sc}) over 31 mA/cm^2. Devices with this robust inorganic HTL exhibit superior stability and retain 95% of their initial performance after 102 days storage.

We synthesized NiO_x nanocrystals according to a previous report with minor modifications [13]. Fig. S1a (online) presents the X-ray diffraction patterns of NiO_x nanocrystals powder. The diffraction peaks at 37.2°, 43.2°, 62.8°, 75.4°, and 79.4° are assigned to (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) of cubic rock salt structured NiO (PDF#47-1049), respectively. No other crystalline phase is observed in the calcinated NiO_x powders. The sharp and intense signals indicate a high crystallinity for the as-synthesized NiO_x nanocrystals. The nanocrystals are uniform in size and have an average diameter of ~8 nm (Fig. S1b online). The high-resolution transmission electron microscopy (inset in Fig. S1b online) indicates an interplanar spacing of 0.21 nm, which corresponds to the (2 0 0) plane of cubic rock salt structured NiO. Like many other transitional metal oxides, NiO_x nanocrystals are often non-stoichiometric; this non-stoichiometric nature is indicated by their

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black color (Fig. S2 online). We used X-ray photoelectron spectroscopy (XPS) to characterize the oxidation states of Ni element (Fig. S1c online). There are two peaks at 853.8 and 855.7 eV, which are attributed to Ni^{2+} associated with the Ni-O octahedral bonding of cubic rock salt NiO [14,15] and vacancy-induced Ni^{3+} ions [16], respectively. The ratio of Ni^{2+}/Ni^{3+} is estimated to 1.67. The corresponding O 1s spectrum further confirms the existence of Ni^{2+} and Ni^{3+} states (Fig. S1d online).

We fabricated mixed Pb-Sn low-bandgap perovskite solar cells using NiO_x as HTL with a planar device structure of glass/ITO/NiO_x/perovskite/C_{60}/BCP/Cu (Fig. 1a). The NiO_x films were obtained by spin-coating of aqueous solution, and they are smooth and pinhole-free, with a low surface roughness of 3.4 nm (Fig. S3a, b online). The NiO_x film has an optical bandgap of 3.92 eV (Fig. S3c online) and exhibits high transparency over the whole spectral range for Pb-Sn perovskite solar cells from 350 to 1,100 nm (Fig. S3d online). The negligible parasitic absorption by NiO_x is beneficial for achieving high photocurrents in solar cells. We used ultraviolet photoelectron spectroscopy (UPS) to investigate the electronic structure and surface work function of NiO_x film (Fig. S4 online). The film shows a work function of 4.72 eV and a valence band level of 5.17 eV, in good alignment with that of mixed Pb-Sn perovskite.

The polycrystalline mixed Pb-Sn perovskite films formed on NiO_x are smooth and pinhole-free with large grains (Fig. S5a online). The X-ray diffraction (XRD) patterns show pseudo-cubic perovskite structure; neither obvious PbI_2 nor other non-perovskite phase is detectable (Fig. S5b online). The perovskite films exhibit preferential growth orientation along ⟨1 0 0⟩, and the grains are mostly grown perpendicular with the substrate plane (Fig. 1b), which is beneficial for the charge transport in devices.

We firstly optimized the thickness of NiO_x film via varying the solution concentration and achieved the best performance at the concentration of 25 mg/mL (Table S1 online). Unless otherwise stated, we will use this optimal thickness in our devices. Fig. 1c presents the *J-V* curves of the champion device. The device exhibits high PCEs of 17.6% and 17.5% under reverse and forward scans, respectively. The efficiency is comparable to previously reported values where PEDOT:PSS was deployed as HTL and processing additive was not used in the precursor solution [17]. It is worth mentioning that the perovskite solar cells with NiO_x have a remarkably high J_{sc} above 31 mA/cm^2. The integrated J_{sc} value from EQE spectra (30.9 mA/cm^2, Fig. 1d) matches well with that from *J-V* measurement (31.1 mA/cm^2). The high EQE values and thus high J_{sc} are mainly ascribed to the low surface reflection in the visible-NIR spectral region for the NiO_x based solar cells (Fig. S6 online). The

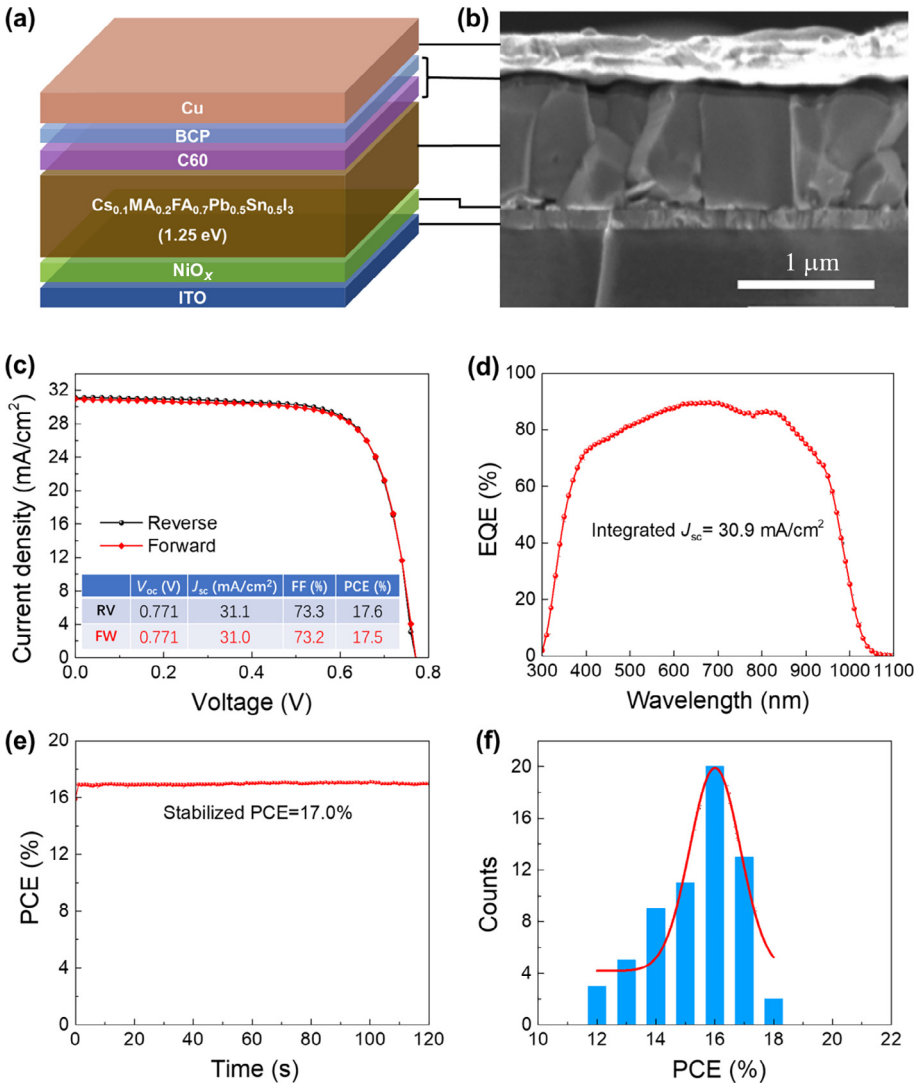

Fig. 1. (Color online) Device structure and photovoltaic performance of mixed Pb-Sn perovskite solar cells with NiO_x. FF: fill factor. (a) Device structure and (b) cross-sectional scanning electron microscope (SEM) image of solar cells. (c) *J-V* curves, (d) EQE spectrum, and (e) steady-state efficiency of the best-performing device. (f) Efficiency distribution of 60 devices processed over several batches.

steady-state PCE of our champion device tracked at the maximum power point is approaching 17.0% (Fig. 1e), in good agreement with the *J-V* characterization. The PCE histogram of 60 devices processed over several batches is shown in Fig. 1f. The average PCE is 16%, and the relatively narrow PCE distribution indicates a good reproducibility for solar cells using NiO_x as HTL.

We then examined the long-term stability of the mixed Pb-Sn perovskite solar cells with NiO_x under dark storage in a N_2-filled glovebox (Fig. S7 online). All photovoltaic parameters (V_{oc}, J_{sc}, FF, and PCE) show no obvious decay and the PCE retained 95% of their initial performance after 102 days. The detailed performance parameters are summarized in Table S2 (online). We also tested the device thermal stability by keeping the solar cells at 85 °C and tracked the performance evolution. The devices exhibit negligible decay after heating for over 3 h (Fig. S8 online).

In summary, we used low-temperature processed NiO_x film as the inorganic HTL for mixed Pb-Sn low-bandgap ($E_g \sim 1.2$ eV) perovskite solar cells. We obtained a high PCE of 17.6% (stabilized 17.0%) and a high photocurrent density over 31 mA/cm^2 in low-bandgap solar cells. We showed that low-bandgap perovskite solar cells with NiO_x have excellent stability and can maintain 95% of their initial efficiency after storage for 102 days. Our results indicate that NiO_x is a promising HTL for mixed Pb-Sn low-bandgap perovskite solar cells, which sheds light on fabricating highly efficient and stable all-perovskite tandem solar cells.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Q. Han, Y. Wei and R. Lin performed the experiments. Z. Fang, K. Xiao, X. Luo, S. Gu, J. Zhu and L. Ding participated in the discussion on experimental results. H. Tan directed this project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scib.2019.08.002.

References

[1] Tan H, Jain A, Voznyy O, et al. Efficient and stable solution-processed planar perovskite solar cells via contact passivation. Science 2017;355:722–6.
[2] Fang Z, Liu L, Zhang Z, et al. $CsPbI_{2.25}Br_{0.75}$ solar cells with 15.9% efficiency. Sci Bull 2019;64:507–10.
[3] Green MA, Dunlop ED, Levi DH, et al. Solar cell efficiency tables (version 54). Prog Photovolt Res Appl 2019;27:565–75.
[4] Hao F, Stoumpos CC, Chang RPH, et al. Anomalous band gap behavior in mixed Sn and Pb perovskites enables broadening of absorption spectrum in solar cells. J Am Chem Soc 2014;136:8094–9.
[5] Zeng Q, Liu L, Xiao Z, et al. A two-terminal all-inorganic perovskite/organic tandem solar cell. Sci Bull 2019;64:885–7.
[6] Palmstrom AF, Eperon GE, Leijtens T, et al. Enabling flexible all-perovskite tandem solar cells. Joule 2019;3:1–12.
[7] Tong J, Song Z, Kim DH, et al. Carrier lifetimes of >1 μs in Sn-Pb perovskites enable efficient all-perovskite tandem solar cells. Science 2019;364:475–9.
[8] Zhao D, Chen C, Wang C, et al. Efficient two-terminal all-perovskite tandem solar cells enabled by high-quality low-bandgap absorber layers. Nat Energy 2018;3:1093–100.
[9] You J, Meng L, Song T-B, et al. Improved air stability of perovskite solar cells via solution-processed metal oxide transport layers. Nat Nanotechnol 2015;11:75–81.
[10] De Jong MP, Van Ijzendoorn LJ, De Voigt MJA. Stability of the interface between indium-tin-oxide and poly(3,4-ethylenedioxythiophene)/poly (styrenesulfonate) in polymer light-emitting diodes. Appl Phys Lett 2000;77:2255–7.
[11] Bai S, Da P, Li C, et al. Planar perovskite solar cells with long-term stability using ionic liquid additives. Nature 2019;571:245–50.
[12] Chi D, Huang S, Zhang M, et al. Composition and interface engineering for efficient and thermally stable Pb-Sn mixed low-bandgap perovskite solar cells. Adv Funct Mater 2018;28:1804603.
[13] Yin X, Chen P, Que M, et al. Highly efficient flexible perovskite solar cells using solution-derived NiO_x hole contacts. ACS Nano 2016;10:3630–6.
[14] Zhang H, Cheng J, Lin F, et al. Pinhole-free and surface-nanostructured NiO_x film by room-temperature solution process for high-performance flexible perovskite solar cells with good stability and reproducibility. ACS Nano 2016;10:1503–11.
[15] He J, Bi E, Tang W, et al. Ligand-free, highly dispersed NiO_x nanocrystal for efficient, stable, low-temperature processable perovskite solar cells. Sol RRL 2018;2:1800004.
[16] Sajid S, Elseman AM, Huang H, et al. Breakthroughs in NiO_x-HTMs towards stable, low-cost and efficient perovskite solar cells. Nano Energy 2018;51:408–24.
[17] Zhao D, Yu Y, Wang C, et al. Low-bandgap mixed tin–lead iodide perovskite absorbers with long carrier lifetimes for all-perovskite tandem solar cells. Nat Energy 2017;2:17018.

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