Tailoring electrical property of the low-temperature processed SnO₂ for high-performance perovskite solar cells

Jing Liu^{1,2}, Nan Li¹, Qingshun Dong¹, Jiangwei Li¹, Chao Qin² and Liduo Wang^{1*}

ABSTRACT Herein, we for the first time doped Nb⁵⁺ into the low-temperature (<100°C) SnO₂ sol-gel route to tailor the electrical property of SnO₂ layers and the band alignment between SnO₂ and the normally used mixed perovskites. The results revealed that proper Nb⁵⁺ doping increased the conductivity of the SnO₂ electron transport layer (ETL), and the conduction band (CB) level of the SnO₂ ETL was shifted down to approach the CB level of perovskites, which facilitated the electron injection from perovskite to SnO₂, accelerated the charge transport, and reduced the non-radiative recombination, leading to improved power conversion efficiency from 18.06% to 19.38%. The Nb⁵⁺ doping process provided an efficient route for fabricating high-efficiency perovskite solar cells (PSCs) at a temperature lower than 100°C, and promoted the commercialization progress of PSCs.

Keywords: SnO₂, niobium doping, band alignment, perovskite solar cells, photo-stability

INTRODUCTION

Metal halide perovskites have stirred researchers' great interests in the photovoltaic field and achieved rapid development in the recent decade due to the high absorption coefficient, tunable band gaps, long carrier diffusion length, and low trap density [1–6]. Perovskite solar cells (PSCs), as the star candidates of photovoltaic devices, have realized a power conversion efficiency (PCE) up to 22.7%, comparable with conventional CdTe or CIGS analogues [7]. The solution processability of perovskites contributes to low-cost fabricating and potential industrial application of PSCs.

Titanium dioxide (TiO₂) has been widely employed as

the electron transport layer (ETL) in both the mesoporous and the planar n-i-p PSCs architectures, since it owns proper conduction band (CB) and electron mobility, which are responsible for effective electron injection and transport [8–11]. However, high-quality TiO₂ films are always sintered at a high temperature over 450°C, which limits the low-temperature fabricating for lower cost and the compatibility with flexible substrates. Besides, the charge accumulation at the TiO₂/perovskite interface is apt to aggravate the hysteresis [12–15]. Moreover, the generated holes in TiO₂ under ultraviolet would cause severe degradation of perovskites, leading to the decay of photovoltaic performances [16–18]. Recently, tin oxide (SnO₂) has been exploited as an efficient ETL due to its high optical transmittance, superior mobility (100 times over that of TiO₂), low-temperature (<200°C) processing and strong resistance to ultraviolet light [19,20]. Atomic layer deposited SnO₂ was once utilized by Anders Hagfeldt's group to fabricate efficient planar n-i-p devices, but the cost for the atomic layer deposition was disadvantageous for commercial application [21]. Most reported solution processes for SnO₂ preparation employed organic sols [22,23], purchased nanoparticles dilutions [24], or SnCl₄/SnCl₂·2H₂O precursors [20,25,26], which were operated under 150°C–200°C. In our recent work, we explored a sol-gel route for fabricating crystallized SnO₂ ETL below 80°C, which significantly advanced the low temperature fabrication of PSCs and the development of flexible photovoltaic devices [27].

Elemental doping in semiconducting metal oxide was found to efficiently improve the electronic properties

¹ Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China

² Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun 130024, China

* Corresponding author (email: chldwang@mail.tsinghua.edu.cn)

[28], reduce the trap-state density [29], as well as modify the CB position [30,31]. Herein, we for the first time doped Nb^{5+} into the low-temperature SnO_2 sol-gel route (under 100°C) due to the close ionic radius of Nb^{5+} to Sn^{4+} , to tailor the electrical property of SnO_2 layers and the band alignment between SnO_2 and the normally used mixed perovskites for further improvement in charge injection and transport. It was previously reported that Nb-doping could be realized by adding niobium ethoxide or niobium chloride in the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solution, followed by a high annealing temperature ($\sim 190^\circ\text{C}$) for the crystallization of SnO_2 [32,33]. In our work, Nb-doped SnO_2 was crystallized with the refluxing (at 78°C) and aging process (at 40°C), and the temperature of the whole fabrication process was under 100°C , which would reduce the fabrication consumption and show potential application in the flexible devices. The results revealed that proper Nb^{5+} doping improved the conductivity of SnO_2 ETL, and modified the CB level, which facilitated the electron injection from perovskite CB to SnO_2 , accelerated the charge transport, and reduced the non-radiative recombination, leading to improved PCE from 18.06% to 19.38%. Through Nb^{5+} doping in the low-temperature processed SnO_2 , we realized high-efficiency PSCs fabricated at a temperature lower than 100°C , which provided an efficient route for promoting the commercialization progress of PSCs.

EXPERIMENTAL SECTION

Materials

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (ACS, 98%–103%, Alfa Aesar), PbI_2 (99.9985%, Alfa Aesar), methylammonium iodide (MAI), formamidinium iodide (FAI), methylammonium bromide (MABr) (Xi'an Polymer Light Technology Corp), PbBr_2 (99.999%, Alfa Aesar), 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9-spirobifluorene (Spiro-OMeTAD, 99.7%, Lumtec Co.), 4-*tert*-butylpyridine (TBP, 96%), bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI, 99.95%), and isopropanol alcohol (IPA, Sinopharm Chemical Reagent Co., Ltd) were used as received. Niobium ethoxide (99.95%), acetonitrile (99.9%), dimethylformamide (DMF, 99.8%), dimethylsulfoxide (DMSO, 99.9%), and chlorobenzene (99.8%) were purchased from Sigma Aldrich and used without further purification.

Preparation of the SnO_2 /doped SnO_2 collosol

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was diluted by IPA to obtain 0.1 mol L^{-1} turbid liquid, which was further heated in the water bath at 78°C with stirring and reflux for 3 h. Subsequently, the

liquid was left still for 3 h at 40°C . For doped SnO_2 , niobium ethoxide was mixed with the ready-made SnO_2 collosol with different molar ratios.

Perovskite precursor solution preparation

$(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ was prepared with the anhydrous mixture of DMF and DMSO (volume ratio was 4:1) containing FAI (1.0 mol L^{-1}), PbI_2 (1.1 mol L^{-1}), MABr (0.2 mol L^{-1}) and PbBr_2 (0.2 mol L^{-1}) by stirring at 60°C for 2 h.

Perovskite solar cells fabrication

Fluorine-tin-oxide (FTO) glasses were etched with zinc powder and 1.0 mol L^{-1} HCl to obtain the electrode pattern, and then washed with deionized water, ethanol (99.7%, Sinopharm), acetone (99.5%, Beijing Shiji) and isopropanol (99.7%, Sinopharm) sequentially. To prepare SnO_2 ETLs, the SnO_2 sol or doped SnO_2 sol was spin coated on FTO at 2,000 rpm for 30 s, and heated at 100°C for 1.5 h. Then, the as-deposited ETLs were treated with UV-ozone for 30 min. Afterward, 60 μL of the perovskite precursor solution was spin coated on the FTO/ETL substrates followed by a two-stage spin coating process (1,000 rpm for 10 s and 6,000 rpm for 30 s). During the second spin coating stage, 100 μL of chlorobenzene was poured on the spinning substrate at 5 s prior the end of the program. Finally, the substrates were annealed at 100°C for 40 min. The hole transport layer (HTL) was deposited atop the perovskite films by spin coating the precursor at 3,000 rpm for 30 s, which was prepared by dissolving 72.3 mg Spiro-OMeTAD, 29 μL TBP 17.5 μL Li-TFSI acetonitrile solution (520 mg mL^{-1}) into 1 mL chlorobenzene. 250 μL titanium (IV) isopropoxide was mixed with 2 mL ethanol and 34 μL hydrochloric acid (2 mol L^{-1}) to prepare the TiO_2 precursor solution. Then, the precursor solution was spin coated on FTO substrates at 2,000 rpm for 30 s, and heated at 500°C for 1 h to prepared the TiO_2 ETL. For the TiO_2 -based device, the perovskite and HTL layers were fabricated as the same as the SnO_2 -based devices. Finally, a 60 nm Au electrode was thermally evaporated under high vacuum ($<10^{-4} \text{ Pa}$). The active area of the device was 0.16 cm^2 , defined by the aperture area of the mask.

Characterizations

Ultraviolet photoelectron spectroscopy (UPS) characterizations were performed by monochromatized HeI radiation at 21.2 eV. The morphologies and microstructures were performed by a field-emission scanning electron microscope (FE-SEM, JEOL JSM-7401F).

Figure 1 XPS spectra of the pristine SnO_2 and doped SnO_2 films.

Transmission electron microscopy (TEM) analysis was carried out on a JEOL JEM-2100F microscope. The crystal structure and phase of the materials were characterized using a Bruker D8 ADVANCE X-ray diffractometer (XRD). The SnO_2 XRD samples were prepared through drying the SnO_2 gel in a watch glass at 50°C for 6 h in the air, then peeled off as powders. The steady-state photoluminescence spectra were measured through an F-7000 FL Spectrophotometer by exciting samples using a laser at 460 nm with repetition rates at 10 MHz. The spectrophotometer (Hitachi, Ltd., U-3900) was utilized to measure the absorption and transmission spectra of the perovskite films and ETLs. X-ray photoelectron spectroscopy (XPS) was performed by an XPS system (ULVAC-PHI, PHI Qantera SXM). The current-voltage (J - V) characteristics of the devices were measured using a Keithley 2400 digital source meter with the scan speed of 100 mV s^{-1} under Oriel Solar AAA solar simulators with AM 1.5G, and the devices were covered with a 0.096 cm^2 mask on it. Electrochemical impedance spectroscopy (EIS) spectra were measured with an electrochemical workstation (Zennium Zahner, Germany). The incident photon-to-electron conversion efficiency (IPCE) spectra were measured by a setup consisting of a xenon light source, a monochromator and a potentiostat. The steady-state output and PCE measurements of photovoltaic devices were carried out using a Keithley 2400 digital source meter under a certain bias.

RESULTS AND DISCUSSION

We successfully synthesized SnO_2 nanocrystals by the refluxing and aging process, which was confirmed by the TEM characterization, with a diameter around 2 nm and d -spacing around 0.34 nm (Fig. S1), very close to the results of our previous work [27]. The Nb-doping of SnO_2

was performed by simply adding niobium ethoxide into the SnO_2 collosol, as described in the experimental section. Firstly, we investigated the existence and states of elements in the pristine SnO_2 and doped SnO_2 films by XPS spectra. As illustrated in Fig. 1, the peaks around 494.5 and 486.1 eV were corresponding to the binding energy of Sn $3d_{3/2}$ and $3d_{5/2}$, respectively, which indicated the formation of typical Sn^{4+} [34]. The appearance of the peak at 530.3 eV proved the oxygen state as O^{2-} . Moreover, we detected additional peaks at 208.8 and 207.0 eV in the doped SnO_2 films, which were attributed to the binding energy of Nb $3d_{3/2}$ and $3d_{5/2}$, respectively, demonstrating the successful doping of Nb^{5+} in SnO_2 films [35–37]. SEM images of SnO_2 /doped SnO_2 films were carried out to study the morphological change by Nb^{5+} -doping. As shown in Fig. 2a, the doped- SnO_2 films showed densely packed distribution, similar to the pristine SnO_2 films. XRD patterns were further carried out to illustrate the crystallinity of SnO_2 before and after Nb^{5+} -doping. In Fig. 2b, the peaks around 26.5° , 34.0° and 51.9° were corresponding to the (110), (101) and (211) diffraction planes of tetragonal rutile SnO_2 (JCPDS 21-1250), respectively [38]. With the doping of Nb^{5+} , the peak slightly shifted to lower 2θ values, which indicated the lattice shrinkage due to the slightly larger radius of Nb^{5+} compared to Sn^{4+} [32]. Subsequently, the optical transmittance of the pristine SnO_2 and doped SnO_2 films was carefully studied since the light transmittance of the top perovskite light absorber. Fig. 2c revealed that with the Nb^{5+} -doping process, the SnO_2 film retained excellent transmittance over 80% in the range of 480–730 nm, showing much increased transmittance between 350 and 850 nm compared to FTO glass. To note, as illustrated in Fig. S2, the reflectance of the rough FTO was much

Figure 2 (a) Top-view SEM images, (b) XRD patterns, and (c) the optical transmittance spectra of the pristine SnO₂ and doped SnO₂ films. The scale bar in SEM images represented 1 μm .

higher than that of the FTO/SnO₂ and FTO/Nb-doped SnO₂ substrates, which increased the light reflection and reduced the transmitting probability of light. With SnO₂ or doped SnO₂ on top of FTO, the surface roughness was significantly reduced from 30.25 to 20.00 and 19.97 nm, respectively, which decreased the loss of incident light by reflectance, as proved by the reflectance spectra, further enhancing the light harvesting of the perovskite absorber on top of SnO₂ or doped SnO₂. Based on the excellent transmittance property, the Nb⁵⁺-doped SnO₂ could serve as a superior anti-reflection layer, which could decrease the optical loss and facilitate the improvement of light harvesting efficiency. Besides, we studied the morphology and crystallinity of the mixed perovskite films on different SnO₂ substrates, which could influence the exciton generation and charge transport process. Fig. S3 provided the top-view SEM images of perovskite films, which illustrated uniform and smooth morphologies both before and after the elemental doping in SnO₂ substrates. The as-prepared perovskites showed excellent optical property with absorption up to 780 nm (Fig. S4a), and XRD patterns (Fig. S4b) proved the formation of typical cubic perovskites structure with good crystallinity [39], which also manifested that the Nb⁵⁺ doping process showed negligible effect on the light absorption and crystallinity of the perovskite absorber.

Based on the as-prepared SnO₂/doped SnO₂ films, we fabricated devices with a common architecture FTO/SnO₂

(~20 nm)/(FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} (~700 nm)/Spiro-OMeTAD (~200 nm), as illustrated in the insert image of Fig. 3a and Fig. S5. *J*-*V* curves were measured at a scanning rate of 100 mV s⁻¹ under AM 1.5G illumination. The statistic performance parameters were summarized in Table S1. The PCE value of the derived devices reached a champion efficiency of 19.38% with 1% Nb⁵⁺ doping. The corresponding best-performed *J*-*V* curves of undoped-SnO₂ devices and doped-SnO₂ devices were illustrated in Fig. 3a. With the PCE increased from 18.06% to 19.38%, the *J*_{SC} increased from 22.02 to 22.72 mA cm⁻², the *V*_{OC} increased from 1.16 to 1.18 V, and the fill factor (FF) increased from 0.71 to 0.73. The corresponding photocurrent integrated from the IPCE spectra (Fig. 3b) was improved from 21.18 to 21.89 mA cm⁻², in accordance with the *J*-*V* curves. Moreover, the statistic performance parameters in Table S1 reflected good reproducibility of as-fabricated devices.

Since the Nb⁵⁺-doping process showed negligible effect on the morphology, absorption and crystallinity of perovskites, we inferred that the doping mainly influenced the charge injection and transport process. To give further investigation on the improved device performance, we gained deep study on the charge injection and transport process by analyzing the electrical property of as-prepared SnO₂ films, as well as the band alignment at the perovskite/SnO₂ interface, which might be influenced by the Nb⁵⁺ doping in SnO₂. Firstly, we tested the linear

Figure 3 (a) J - V curves and (b) IPCE spectra of the undoped- SnO_2 and doped- SnO_2 derived devices. The inset image presented the corresponding PSCs device structure.

Figure 4 (a) The linear sweep voltammetry (LSV) curves, (b) UV-vis spectra and derived Kubelka-Munk spectra, (c) UPS spectra of undoped and doped SnO_2 films, (d) the band alignment of the fabricated devices.

sweep voltammetry (LSV) curves of FTO/ SnO_2 /Au devices to measure the conductivity (σ_0) of both the undoped SnO_2 and doped SnO_2 film. As illustrated in Fig. 4a, the doping of Nb^{5+} in SnO_2 obviously improved the conductive property of SnO_2 , and according to the equation $I = \sigma_0 A D^{-1} V$ [40], in which A is the area (0.16 cm^2) and D is the thickness of the sample (50 nm), the calculated conductivity of undoped SnO_2 and doped SnO_2 was 3.62×10^{-3} and $5.72 \times 10^{-3} \text{ mS cm}^{-1}$, respectively.

The significant increase of conductivity could accelerate the charge transport in the SnO_2 ETL and reduce the probability of non-radiative recombination [36,41]. Subsequently, the bandgap of SnO_2 with and without Nb^{5+} doping was measured by UV-vis spectra. As shown in Fig. 4b, the bandgap of the doped SnO_2 calculated from the derived Kubelka-Munk spectra was 4.13 eV, as same as the pristine SnO_2 film, which was in accordance with the previous report [27]. The low-level Nb doping process

Figure 5 (a) The steady-state PL spectra of perovskite/SnO₂ films, (b) EIS spectra of devices derived from undoped and doped SnO₂ films. The inset image showed the equivalent circuit diagram.

illustrated unchanged bandgap in comparison with the pristine SnO₂ film. UPS spectra were further performed to study the energy levels of SnO₂ before and after the Nb⁵⁺ doping, as illustrated in Fig. 4c. The calculated energy levels of the valence band (E_V) and the conduction band (E_C) were summarized in Table S2. Both E_V and E_C shifted to lower values with the Nb⁵⁺ doping. As shown in Fig. 4d, the E_C of doped SnO₂ shifted from -4.19 to -4.25 eV, which approached the E_C of the mixed perovskite (-4.28 eV). The satisfactory down-shift of the doped-SnO₂ E_C decreased the charge injection barrier from perovskite E_C to the SnO₂ E_C , which could dynamically facilitate the charge injection process and reduce the undesirable accumulation of photogenerated charges at the perovskite/SnO₂ interface [21].

As illustrated in the steady-state photoluminescence (PL) spectra (Fig. 5a), compared with the pristine SnO₂, the PL quenching was obviously accelerated for the doped SnO₂, which might be attributed to the lower injection barrier from perovskite to the doped SnO₂. EIS measurements were conducted in the dark to further determine the mechanism of the electron transfer in fabricated devices. As shown in Fig. 5b, we fitted the Nyquist plot according to the built equivalent circuit, in which the R_s , R_{rec} and C_{rec} represented the series resistance, the recombination resistance and the corresponding capacity, respectively. The fitted results were summarized in Table S3, in which the R_s was reduced from 96.74 to 74.35 Ω , and R_{rec} showed an increase trend from $1,150$ to $1,879$ Ω after the Nb⁵⁺ doping in SnO₂, demonstrating the decreased charge transport resistance and reduced recombination in the fabricated devices. The retarded recombination was also manifested by the lower dark current density as illustrated in Fig. S6, which indicated that the Nb⁵⁺ doping in SnO₂ could reduce the energy loss caused by the non-radiative recombination, resulting in the enhanced FF and V_{OC} [42,43]. Thus, we

concluded two aspects responsible for the enhanced devices performance. On the one hand, the improved conductivity of SnO₂ by the Nb⁵⁺ doping accelerated the electron transport in the SnO₂ ETL. On the other hand, the down-shift of E_V decreased the electron injection barrier from perovskite to SnO₂. Both the two aspects facilitated the electron extraction, reduced the undesirable accumulation of photogenerated charges at the perovskite/SnO₂ interface, and further retarded the non-radiative recombination, leading to the promotion of J_{SC} , FF and V_{OC} of the derived devices. We further investigated the hysteresis phenomenon of as-fabricated devices. As illustrated in Fig. S7 and Table S4, the hysteresis ratio, defined as $(PCE_{reverse} - PCE_{forward})/PCE_{reverse}$, was decreased by doping 0.5% and 1% Nb in SnO₂, which was probably attributed to the accelerated charge injection and transport in the ETL, resulting in the decreased charge accumulation at perovskite/SnO₂ interface [36,41]. The photo-stability of PSCs was also studied under ultraviolet light with intensity of 80 mW cm^{-2} (Fig. S8). Compared with the TiO₂-based PSCs, the SnO₂-based devices showed much improved stability under the UV light due to the UV-resistant property of the SnO₂ ETL, which could impair the photo-catalyzed degradation of perovskites.

CONCLUSION

To conclude, we performed Nb⁵⁺ doping in the low-temperature ($<100^\circ\text{C}$) processed SnO₂ ETL by simply incorporating niobium ethoxide in the SnO₂ collosol. The characterization of the electrical property of the Nb⁵⁺-doped SnO₂ indicated that the conductivity of SnO₂ ETL was significantly increased, and the E_C shifted from -4.19 to -4.25 eV, which approached the E_C of the mixed perovskite (-4.28 eV) and reduced the electron injection barrier from perovskite to the SnO₂ ETL. The accelerated electron injection and transport resulted in the retarded

non-radiative recombination, as manifested by the PL and EIS measurements. Ultimately, a high PCE of 19.38% was achieved by the Nb⁵⁺ doping in SnO₂, meanwhile with much improved photo-stability compared with the TiO₂-based devices. Our work promoted the development of SnO₂-based PSCs with lower fabricating temperature, high photovoltaic performance and improved photo-stability, paving an energetic route for the potential commercialization of PSCs.

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Author contributions Liu J and Wang L designed the experiment. Liu J prepared the SnO₂ precursor solution, fabricated the ETL and perovskite films, and characterized the SEM, XRD, transmittance, UV-vis absorption, XPS, UPS, PL and LSV of the above films. Dong Q fabricated the PSCs, and tested the *J-V* curves, IPCE and EIS spectra. Li N prepared the manuscript. Wang L helped to revise the manuscript. The final version of the manuscript was approved by all authors.

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Supplementary information Supporting data are available in the online version of the paper.

Jing Liu graduated from Beijing University of Chemical Technology (BUCT) in 2016 with a bachelor's degree. Currently, he is a postgraduate at the Northeast Normal University, and receives united training at Tsinghua University. His research interest focuses on electron transport layers of perovskite solar cells.

Liduo Wang is a professor of the Department of Chemistry at Tsinghua University. He received his PhD degree from Nagoya University in 1995. Dr. Wang has once worked as a visiting scholar in the Department of Chemistry and as a research associate in the Department of Electrical and Electronic Engineering at Hong Kong University of Science and Technology, and as a postdoctoral researcher in the Department of Materials Science and Engineering, Tsinghua University. His current research interest includes perovskite solar cells, organic-inorganic semiconductor multilayer and its optoelectronic properties.

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刘京^{1,2}, 李楠¹, 董庆顺¹, 李江伟¹, 秦超², 王立铎^{1*}

摘要 本文中我们首次在低温(<100°C)SnO₂溶胶-凝胶中通过掺杂Nb⁵⁺调控SnO₂电学性质,使SnO₂与混合离子钙钛矿之间形成更匹配的能级。掺杂Nb⁵⁺后SnO₂电子传输层导电率明显提升,导带位置下移更加接近混合离子钙钛矿导带,有效促进了电子由SnO₂向钙钛矿层的注入,并加速了电子传输过程,二者的共同作用使非辐射复合几率降低,器件效率由18.06%提升至19.38%。Nb⁵⁺掺杂SnO₂为低温(<100°C)制备高效率钙钛矿太阳能电池提供了有效参考途径,有望进一步推动钙钛矿太阳能电池的产业化进程。