Electron transport layer assisted by nickel chloride hexahydrate for open-circuit voltage improvement in MAPbI$_3$ perovskite solar cells†

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SnO$_2$ is a promising electron transport layer (ETL) material with important applications in planar perovskite solar cells (PSCs). However, electron–hole recombination and charge extraction between SnO$_2$ and the perovskite layer necessitates further exploration. Nickel chloride hexahydrate (NiCl$_2$·6H$_2$O) was introduced into the SnO$_2$ ETL, which significantly increased the power conversion efficiency (PCE) from 15.49 to 17.36% and the open-circuit voltage ($V_{OC}$) from 1.078 to 1.104 V. The improved PCE and $V_{OC}$ were attributed to the reduced defect states and increased energy level of the conduction band minimum. This work provides new insights into optimizing the $V_{OC}$ and PCE of PSCs.

Introduction

In recent years, the perovskite solar cell (PSC) has been developed as a promising type of solar cell with outstanding advantages such as high photoelectric conversion efficiency, low cost, and simple fabrication.\(^1\)\(^-\)\(^3\) At present, PSCs have achieved a high power conversion efficiency (PCE) of 25.5%.\(^4\)\(^-\)\(^12\) The main technical approach used to improve the PCE of PSCs is through component engineering of the perovskite layer, hole transport layer (HTL), and electron transport layer (ETL).\(^13\)\(^-\)\(^18\) The other method is to optimize the interface performance by adjusting the structure or adding a buffer layer between the interlayers of PSCs.\(^19\)\(^-\)\(^28\)

The quality of the ETL plays an important role in perovskite device performance. TiO$_2$, one of the most widely used ETL materials, has deep electron trap states, which easily leads to strong electron–hole recombination. ZnO has also been used as an ETL in PSCs due to its low-temperature film preparation and higher charge mobility. However, the PSC readily decomposes owing to the polyhydroxyl groups on the surface of the ZnO. The SnO$_2$ ETL material is widely used in PSCs for high charge mobility and high perovskite compatibility.\(^29\) However, the oxygen vacancy in SnO$_2$ greatly reduces the hole blocking effect, resulting in significant carrier recombination.\(^30\) Therefore, the SnO$_2$ ETL requires modification to reduce ETL defects and improve the performance of PSCs. For example, Liu et al. incorporated EDTA into the SnO$_2$ ETL to enhance the device performance,\(^31\) whereas Yang et al. doped Ga$^{3+}$ ions into SnO$_2$ to passivate the defect state in the ETL.\(^32\)

Herein, we report a simple and effective method to passivate SnO$_2$ defects by introducing nickel chloride hexahydrate (NiCl$_2$·6H$_2$O) into a SnO$_2$ precursor solution. NiCl$_2$·6H$_2$O not only reduced the trap density, but also increased the energy level of the conduction band minimum of SnO$_2$ and caused the energy level to better match that of the perovskite. Consequently, a champion PCE of 17.36% with a $V_{OC}$ of 1.104 V was achieved, remarkably higher than the relevant reference devices which provided a PCE of 15.49% and $V_{OC}$ of 1.078 V.

Experimental section

Materials

All the materials and solvents were used as received without further purification. Fluorine-doped tin oxide (FTO) glasses (1.5 cm × 1.5 cm) were purchased from OPVtech (China). The SnO$_2$ solution (tin(Ⅱ) oxide, 15 wt% hydrocolloid dispersion) was purchased from Alfa Aesar. Lead iodide (PbI$_2$), methylammonium iodide (MAI), and 2,2',7',7'-tetракис (N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) were obtained from Xi’an Polymer Light Technology. N,N-dimethyformamide (DMF), dimethyl sulfoxide (DMSO), chlorobenzene (CB), and 4-tert-butylpyridine were acquired from J&K. Lithium bis(trifluoromethylsulfonyl) imide (Li-TFSI) and cobalt(m) FK209 were obtained from Sigma-Aldrich. Nickel dichloride hexahydrate (NiCl$_2$·6H$_2$O) and ammonium (NH$_3$·H$_2$O) were purchased from Aladdin.

Device fabrication

The FTO glass was sequentially cleaned with detergent water, deionized water, acetone, and isopropanol for 30 min in an
ultrasonic system. Plasma treatment was performed for 3 min to enhance the surface wettability before spin coating the ETL solution. The pristine SnO$_2$ precursor solution was prepared from the SnO$_2$ colloidal solution by diluting 5 times with deionized water. The sample ETL solution was prepared by adding 4, 12 and 20 mg NiCl$_2$·6H$_2$O into the 4 mL mixed solvent, which comprise of 1 mL SnO$_2$ colloidal solution, 2 mL H$_2$O and 1 mL NH$_3$·H$_2$O. Ultimately the concentration of the NiCl$_2$·6H$_2$O was 1, 3 and 5 mg mL$^{-1}$. The sample ETL (SnO$_2$–NiCl$_2$) solution was deposited on the FTO substrates at 4000 rpm for 30 s. The substrates were subsequently annealed in the air at 150 °C for 30 min to improve the electrical properties. After plasma treatment, the FTO substrates were transferred into a glove box. A perovskite precursor solution was prepared from the solution mixture of PbI$_2$ (1.67 M) and CH$_3$NH$_3$I (1.67 M) in DMF/DMSO (7:3 by volume). The perovskite solution was spin coated on the substrate at 1000 rpm for 13 s and at 5000 rpm for 25 s. Three hundred microliters of CB was dropped on the substrates during the second step after 12–15 s, and the films were then annealed on the hot plate at 100 °C for 30 min. After the substrates cooled to room temperature, a HTL was formed by spin coating the spiro-OMeTAD precursor solution onto the surface of the perovskite film at 5000 rpm for 30 s, which was prepared by dissolving 58.4 mg of spiro-OMeTAD, 23 mL of tBu, 14 mL of LiTFSI (520 mg mL$^{-1}$ acetonitrile), and 23 mL of FK209 (300 mg mL$^{-1}$ acetonitrile) in 800 μL of chlorobenzene. Finally, an 80 nm gold electrode was deposited on the surface of the HTL under high-vacuum conditions.

### Results and discussion

As shown in Fig. S1, the introduction of NiCl$_2$·6H$_2$O did not change the crystal structure of SnO$_2$. The higher transmittance of SnO$_2$–NiCl$_2$ film in the visible region indicates that NiCl$_2$·6H$_2$O could reduce the light loss when light passing through the substrate. FTO/SnO$_2$ films become smoother when the FTO substrate covered with a thin SnO$_2$ film. The smoother surface should be beneficial to the light transmission. SnO$_2$ films can improve the optical transmission properties of FTO substrates. Compared with FTO/SnO$_2$, FTO/SnO$_2$–NiCl$_2$ films were denser, and Ni$^{2+}$ had the effect of antireflection, which promoted the increase of transmittance of FTO/SnO$_2$–NiCl$_2$ films in the visible region. Fig. 1a and b show the SEM images of the SnO$_2$ films without and with NiCl$_2$, respectively. The introduction of NiCl$_2$·6H$_2$O improved surface compactness of the ETL, which can promote the formation of perovskite grains and performance of the device.

To confirm the successful introduction of nickel and chloride ions into the ETL, XPS was performed on different substrates. Fig. 1c shows the full XPS spectra of the corresponding ETls. Fig. S4 shows energy dispersive spectroscopy (EDS) characterization of SnO$_2$–NiCl$_2$ films. The results show
that the Ni, Cl, Sn, and O elements are uniformly distributed on the surface of the film. The enlarged XPS spectra are shown in Fig. S2 and S3. The XPS spectra of SnO2–NiCl2 show characteristic peaks of Ni (855 eV) and Cl (198 eV) compared with unmodified SnO2. SnO2 was deposited on FTO substrate, and it was annealed in the air at 150 °C for 30 min. In the annealing process, [Ni(NH3)6]2+ by reaction with Ni2+ and NH3 would almost loses the NH3 and H2O when heated above 140 °C. The presence of Ni 2p3/2 at 855.6 eV, based on the binding energy position of XPS Ni 2p, indicates the transformation of Ni2+ into Ni(OH)2. Ni(OH)2 cannot further lose water to form NiO during annealing at 150 °C. The photoelectron binding energy of the Sn 3d level of SnO2–NiCl2 is slightly higher than that of the unmodified SnO2, indicating an interaction between SnO2 and NiCl2. According to previous reports, the Ni2+ may play a more important role than Cl2− in improving the device performance of PSCs. We presumed that the Ni2+ from NiCl2 can interact with the hydroxyl groups (–OH) on the surface of the SnO2 film, which can lead to a trap state, causing nonradiative recombination. As shown in Fig. 1d and Table S1,† the peak at 530.46 eV was O–Sn bonds (or O2− state), and the higher binding energy at 531.70 eV corresponded to hydroxyl groups (or oxygen vacancies). After the introduction of NiCl2·6H2O, the intensity of hydroxyl (or oxygen vacancies) decreased significantly, indicating that the oxygen vacancies were effectively passivated. The reduction of oxygen vacancy defects will improve Voc. Therefore, the successful introduction of NiCl2·6H2O will considerably improve the ETL.

Further characterizations were conducted to better understand the ETL/perovskite interface. Ultraviolet photoelectron spectroscopy (UPS) was performed to investigate the band structure of SnO2 and SnO2–NiCl2. We tested the optimal concentration 3 mg mL−1. The possible energy band alignment of planar PSCs was depicted in Fig. 1e. Combining with the high binding energy cutoff (Ecuton) on the right side of Fig. 1f and the Fermi edge (E_F,edge) region on the left side of Fig. 1f, the value of E_VB could be calculated for SnO2 and SnO2–NiCl2. We further confirmed the band gaps (E_g) of ETLs by the Tauc plots of UV-vis absorption spectra (Fig. S5†). The energy levels of the conduction band (E_Cb) of SnO2 and SnO2–NiCl2 were calculated to be −3.85 and −3.80 eV, respectively. According to the relative energy levels of the different PSC parts, the EcB of the SnO2–NiCl2 ETL was higher than that of the SnO2 ETL. The Voc depends on the difference in energy between electron quasi Fermi level and hole quasi Fermi level. More appropriate energy level would make the solar cell based on SnO2–NiCl2 show higher Voc.

SEM characterization of the perovskite films prepared on SnO2 and SnO2–NiCl2 substrates was performed, and the results are shown in Fig. 2a and b. The perovskite films prepared on the SnO2–NiCl2 substrates have larger grains and are generally compact, compared with the perovskite films prepared on SnO2. In addition, cracks obviously exist on the perovskite films prepared on SnO2, which lead to the recombination of electrons and holes. The UV-vis absorption spectrum shown in Fig. 2c indicates that the bandgap of perovskite growing on the NiCl2-modified ETL has not changed. Fig. S6† presents the bandgap of perovskite grown on ETL with and without NiCl2·6H2O, and the calculated bandgap value is 1.61 eV. The UV-vis absorption spectra shown in Fig. 2d. The results show that the characteristic diffraction peaks of CH3NH3PbI3 appear near 14.1°, 24.5°, 28.5°, 31.6°, and 40.4°, which correspond to the crystal planes of (110), (202), (220), (310), and (224) of CH3NH3PbI3, respectively. These results confirm that perovskite films with good crystallinity were prepared by introducing NiCl2·6H2O.

To study the carrier transport in PSCs, steady-state fluorescence spectroscopy (PL) experiments were performed on the perovskite films on SnO2 and SnO2–NiCl2 substrates. As shown in Fig. 3a, carrier quenching was slower for the samples on the SnO2–NiCl2 substrates, which is detrimental to increasing J_sc of the solar cell. However, the transmittance of the tin dioxide layer was increased after modification by NiCl2·6H2O, the utilization rate of photons will be improved and J_sc will increase. Overall, the J_sc of the device based on SnO2–NiCl2 was a little better than that of the SnO2 solar cell. The reason of the carrier quenching was slow for the samples on he SnO2–NiCl2 substrates was the passivation of chloride ions, which suppressed the nonradiative recombination of perovskite films for the enhancing intensity and the larger perovskite grain.
In Fig. 3b, the biexponential decay behavior is evident on the TRPL spectrum. We calculated the decay times (e.g., $\tau_1$ and $\tau_2$) of the perovskite film deposited on the SnO$_2$ and SnO$_2$–NiCl$_2$ substrates; the fitting parameters are summarized in Table S2. PL decay process consists of a carrier recombination process in the bulk region, as characterized by the slow decay lifetime $\tau_2$, as well as a charge-transfer process at the interface, as characterized by the fast lifetime $\tau_1$. According to the results of the double exponential fitting in TRPL $\tau_1$ increases, show that charge extraction at a slower pace and it will cause a decline in $J_{SC}$. $\tau_2$ increases, and combining with SCLC and EIS data, shows that tin oxide layer of oxygen vacancy defects passivation, $V_{OC}$ increases. The average decay time of the SnO$_2$/perovskite film is 70.62 ns, and the perovskite film deposited on SnO$_2$–NiCl$_2$ exhibited slower fluorescence quenching with an average decay time of 107.1 ns. The results were consistent with PL conclusions.

To justify the photoelectric performance of the PSCs caused by the introduction of NiCl$_2$-6H$_2$O, SCLC analyses were performed on the SnO$_2$ and SnO$_2$–NiCl$_2$ ETLs. The results are shown in Fig. 4a and b, including the calculated density of defect states. The defect density between the interface of ETL and the perovskite layer can partially reflect the contact and matching degree between interfaces. In the SCLC analyses, there is a clear linear relationship between the current and low bias voltage, which indicates a tendency of the defect state between the ETL and the perovskite substrate; the transmission electricity of the SnO$_2$-based cell was measured. The small semicircle at high frequency corresponds to the recombination resistance ($R_{rec}$) values of the PSCs employing pristine SnO$_2$ and NiCl$_2$ modification. After further calculation obtained defect concrete values, the trap densities of perovskite film deposited on pristine SnO$_2$ and SnO$_2$–NiCl$_2$ ETL are 1.45 × 10$^{16}$ cm$^{-3}$ and 1.26 × 10$^{16}$ cm$^{-3}$.

We further elucidated the effect of NiCl$_2$ on the defects of the SnO$_2$ film by measuring the recombination dynamics, transient photovoltage (TPV), and transient photocurrent (TPC) decay. As shown in Fig. 4c, the carrier recombination lifetime of the device with SnO$_2$–NiCl$_2$ increased from 22.65 to 35.33 $\mu$s, confirming the suppressed charge recombination at the ETL and perovskite interface. For the transport time constants ($\tau_t$) measured from TPC (Fig. 4d), PSCs based on SnO$_2$–NiCl$_2$ exhibited 0.67 $\mu$s compared to that of the pristine SnO$_2$-based PSCs (0.93 $\mu$s).

To investigate the effect of SnO$_2$–NiCl$_2$ ETL on device performance, we fabricated PSCs with the FTO/ETL/MAPbI$_3$/Spiro-OMeTAD/Au (Fig. 5a) structure and investigated the doping concentration of NiCl$_2$–6H$_2$O in SnO$_2$. The devices were prepared with the concentration of SnO$_2$ precursor solution (1, 3 and 5 mg mL$^{-1}$) and annealing at 150 °C for 30 min. Electrochemical impedance spectroscopy (EIS) analyses were performed on devices composed of SnO$_2$ and SnO$_2$–NiCl$_2$ substrates, and the results are shown in Fig. 5b. In the dark state condition, within the frequency range of 0.1 to 10$^6$ Hz, the transmission electricity of the SnO$_2$-based cell was measured. By fitting the measured results, the contact resistance ($R_c$) and recombination resistance ($R_{rec}$) values of the PSCs employing pristine SnO$_2$ and SnO$_2$–NiCl$_2$ are summarized in Table S3.

The small semicircle at high frequency corresponds to the charge transfer process between perovskite and selective interfaces.
contacts while the large semicircle at low frequency demonstrates the recombination of charge carriers in the perovskite layer. Through EIS test, the results show that the transmission resistance $R_c$ and the composite resistance $R_{soc}$ increased, indicating that the charge transmission speed slowed down and the defect was effectively passivated. However, because the transmittance of the tin dioxide layer increased after modification, the utilization rate of photons will be improved and $J_{SC}$ will increase. The results were consistent with the fluorescence and efficiency data. Simultaneously, it was beneficial to improve $V_{OC}$ of the device.

The corresponding $J$-$V$ curves are shown in Fig. 5c and S7. The results show that the device performance slightly improved with SnO$_2$–NiCl$_2$ concentration of 1 mg mL$^{-1}$. The highest open-circuit voltage ($V_{OC}$), FF, and PCE values of the PSCs were obtained with SnO$_2$–NiCl$_2$ concentration of 3 mg mL$^{-1}$. When the doping NiCl$_2$·6H$_2$O amount further increased, the photoelectric performance of the device decreased, and thus the optimum concentration of SnO$_2$–NiCl$_2$ was 3 mg mL$^{-1}$.

Subsequently, the IPCE of the optimum NiCl$_2$·6H$_2$O and control devices were tested. As shown in Fig. 5d, the light absorption capacity of the NiCl$_2$-modified devices in the range of 400–700 nm was stronger than that of the SnO$_2$-based devices, corresponding to a higher current. The results show that the introduction of NiCl$_2$·6H$_2$O could effectively improve the ability of the ETL to light transmission. The integrated $J_{SC}$ value measured by IPCE was consistent with the $J_{SC}$ obtained by the $J$-$V$ curves.

The statistical distribution of PCE for PSCs based on doped ETLs of different NiCl$_2$·6H$_2$O concentrations are shown in Fig. 5e and S8. The PCE of the SnO$_2$-based devices ranged between 14%–16% and the PCE of the SnO$_2$–NiCl$_2$-based devices was in the range of 16–18%. As shown in Table 1, the modified device exhibits a PCE of 17.36% with a $J_{SC}$ of 20.59 mA cm$^{-2}$, $V_{OC}$ of 1.104 V, and FF of 76.4%. Devices based on the SnO$_2$–NiCl$_2$ ETL also exhibit greater stability than the reference devices (Fig. 5f). The SnO$_2$–NiCl$_2$-based PSCs can retain 76% of their initial efficiency after being stored for 1000 h at the room temperature (RT) of 25 °C for 1000 h. In contrast, the reference devices only retained 43% of their initial efficiency. This may be due to the larger grain size with fewer grain boundaries which offers additional protection against oxygen and moisture.

## Conclusions

In this study, we provide a simple and effective method to modify SnO$_2$ ETL with NiCl$_2$·6H$_2$O, which reduced the oxygen vacancies of SnO$_2$ and improved the energy level alignment. This modification ultimately dramatically passivated defects, which effectively improved the $V_{OC}$ and PCE. Notably, the stability of the SnO$_2$–NiCl$_2$-based PSCs increased, and was able to maintain 76% of the original PCE after 1000 h of storage, compared to 43% for the device without NiCl$_2$·6H$_2$O.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors acknowledge financial support from the National Key R&D Program of China (Grant no. 2018YFA0208701), National Natural Science Foundation of China (Grant no. 21773308), the Research Funds of Renmin University of China (Grant no. 20190320).

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