P-contact metal oxide in efficient organometal halide perovskite/fullerene hybrid solar cells

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Abstract

Applying a thin nickel oxide (NiOₓ) interlayer between glass/indium-tin-oxide (ITO) electrode and light absorbing methylammonium lead iodide (CH₃NH₃PbI₃) perovskite significantly increases the photovoltaic performance of perovskite/fullerene-derivative planar-heterojunction (PHJ) hybrid solar cells. First, NiOₓ electrode interlayer is a p-type semiconductor of high work function of 5.4 eV, which is close to the valence band edge level of CH₃NH₃PbI₃ perovskite (5.4 eV). The alignment of energy level minimizes the interfacial energy losses for the hole transfer and optimizes the photovoltage output of device. Second, CH₃NH₃PbI₃ perovskite

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films prepared by the spin-coating process on glass/ITO/NiOₓ substrate exhibit a relatively smooth morphology than those deposited on glass/ITO/poly(3,4-ethylenedioxythiophene) poly(styrene-sulfonate) (PEDOT:PSS) substrate. The conformal coverage of the perovskite film enhances the light harvesting, reduces the leakage current, increases short-circuit current (J_SC), and elevates the power conversion efficiency (PCE) of the devices. The best performing cell with the configuration of glass/ITO/NiOₓ/CH₃NH₃PbI₃ perovskite/[6,6]-phenyl C61-butyric acid methyl ester (PCBM)/bathocuproine/Al presents an open-circuit voltage (V_OC)= 0.92 V, a J_SC = 12.43 mA/cm², and a fill factor (FF) = 0.68, corresponding to a PCE of 7.8 % under standard 1 sun AM 1.5G simulated solar irradiation. The performance is much superior to the device applying PEDOT:PSS interlayer with photovoltaic parameters of V_OC = 0.62 V, J_SC = 9.39 mA/cm², and fill factor FF = 0.66, corresponding to a PCE of 3.9 %. Our findings reveal the design principle for enhancing the photovoltaic performance of CH₃NH₃PbI₃ perovskite/PCBM hybrid PHJ solar cells through the judicious selection of the metal oxide electrode interlayer.

Keywords: CH₃NH₃PbI₃, perovskite, planar heterojunction, hybrid solar cell, metal oxide, nickel oxide, electrode interlayer
Organometal halide perovskite is an ideal photovoltaic material that exhibits a direct optical band gap around 1.5 eV, a low exciton bonding energy and long diffusion length (~1 µm), a broad range of light absorption covering the visible to near-infrared spectrum (800 nm) with high extinction coefficient (~10^4 cm^{-1} at 550 nm)^1-3. Most importantly, organo-lead halide perovskites behave the ambipolar characteristics and work very well with organic carrier transport materials, such as 2,2'7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-OMeTAD)^4,5, fullerene (C_{60}) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM)^6-11, and the conjugated polymers…etc.^12-14, to form a hybrid heterojunction and generate the efficient photovoltaic effect. Organometal halide perovskite-based mesoscopic or planar heterojunction (PHJ) solar cells present the very promising photovoltaic performance. Recent reports had indicated the devices based on this material showing the high power conversion efficiency (PCE) of 12~15%^4,5,12,15,16. Several reports prospectively propose the device can achieve PCE of 20% shortly.^17,18

The hybrid PHJ perovskite-based solar cells have the advantage to be fabricated by low temperature and solution processes, and flexible devices with remarkable efficiency have been demonstrated recently.^8,9,19,20

Our previous work had successfully demonstrated the efficient hybrid solar cells made of the methylammonium lead iodide (CH_{3}NH_{3}PbI_{3})/C_{60} PHJ configuration.\(^6\) Applying C_{60} derivatives of varied lowest unoccupied molecular level (LUMO) modulates the open-circuit voltage (V_{OC}) as well as other device parameters. These results verify the photovoltaic effect yielding from CH_{3}NH_{3}PbI_{3} perovskite/C_{60} hybrid PHJ interface and reveal the difference in the energy level at junction interface would be important parameters to manipulate the device performance. The hybrid CH_{3}NH_{3}PbI_{3}/PCBM PHJ cell exhibits the decent photovoltaic performance as reported in our previous study and the photovoltaic parameters of similar device
configurations were further improved by other related works.\textsuperscript{6,8-11} First, under the illumination, the electron transfer from excited states in CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite to PCBM is very efficient. Docampo \textit{et al.} reported the quenching of the perovskite photoluminescence (PL) by PCBM is much completed, about 91\%, than that of TiO\textsubscript{2} (47\%).\textsuperscript{8} The electron transfer process as calculated by Xing \textit{et al.} is around 0.4 ns, which is faster than the transport of holes to \textit{spiro}-OMeTAD, 0.66 ns.\textsuperscript{1} Second, the match of the LUMO level of PCBM (3.7 to 3.9 eV) with the conduction band (CB) edge level of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite (3.9 eV) minimizes the energy redundancy to achieve the maximal photovoltage output of devices. These properties make PCBM an ideal electron acceptor material with CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite (donor) in a hybrid donor-acceptor PHJ. However, while considering the transfer and transport of holes from CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite to reach the positive charge collecting electrode, the mismatch 0.6 eV between the valence band level (VB) edge level of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite, 5.4 eV, with the work function of indium-tin-oxide (ITO) electrode, 4.8 eV, markedly diminishes the photovoltage output. Accordingly, introducing an electrode interlayer to adjust the mismatch of the energy level would be an applicable approach to reduce the energy loss and elevate the photovoltaic efficiency.

Poly(3,4-ethylenedioxythiophene) poly(styrene-sulfonate) (PEDOT:PSS) is a widely used electrode buffer to modify the surface properties of glass/ITO substrate for most organic electronics devices, but researchers in this society are aware of many drawbacks by using PEDOT:PSS interlayer, especially for devices under the long-term operation\textsuperscript{21-24}. Irwin \textit{et al.} first reported the replacement of PEDOT:PSS layer by a thin p-type semiconducting nickel oxide (NiO) layer in polymer bulk-heterojunction (BHJ) solar cells and got the enhanced device performance.\textsuperscript{25} Later, Steirer \textit{et al.} developed a relatively simple solution process to deposit NiO\textsubscript{x} thin interlayer on glass/ITO electrode.\textsuperscript{26} Owing to the optical transparency, the chemical
stability, the good conductivity of hole, as well as the tunable work function from 5.0 to 5.6 eV by the different O$_2$-plasma surface treatments, consequently we would regard that NiO$_x$ can be the potential electrode interlayer to work with CH$_3$NH$_3$PbI$_3$ perovskite materials. A better alignment in the work function of NiO$_x$ electrode interlayer with the VB edge level of CH$_3$NH$_3$PbI$_3$ perovskite would improve the transfer of hole and increase device photovoltage as well as other photovoltaic parameters. Actually, applying NiO$_x$ electrode interlayer to enhance $V_{OC}$ and PCE of BHJ solar cells made of low band gap conjugated materials had been reported by many researchers, due to a better match of the transfer level for hole in the highest occupied molecular orbital (HOMO) level of donor materials.$^{22,25-27}$

In this manuscript, we apply a thin NiO$_x$ electrode interlayer on the glass/ITO electrode to fabricate the efficient CH$_3$NH$_3$PbI$_3$/PCBM PHJ hybrid solar cells. Our results indicate that all photovoltaic parameters exhibit a remarkable enhancement by applying the NiO$_x$ electrode interlayer. The hybrid cell of the configuration, glass/ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$ perovskite/PCBM/bathocuproine (BCP)/Al, presents a $V_{OC} = 0.92$ V, a short-circuit current ($J_{SC}$) = 12.43 mA/cm$^2$, and a fill factor (FF) = 0.68, corresponding to a PCE of 7.8% under standard 1 sun AM 1.5G simulated solar irradiation. The photovoltaic parameters are superior to those of the hybrid cell with PEDOT:PSS interlayer of $V_{OC} = 0.62$ V, a $J_{SC}$ = 9.39 mA/cm$^2$, and a fill factor FF = 0.66, corresponding to a PCE of 3.9 %. We attribute the match of energy level for the VB edge level of CH$_3$NH$_3$PbI$_3$ perovskite with the work function of NiO$_x$ minimize the energy loss for hole and optimize the magnitude of $V_{OC}$. The higher magnitude of $J_{SC}$ and PCE also results from the better surface coverage (93%) of CH$_3$NH$_3$PbI$_3$ perovskite film on the glass/ITO/NiO$_x$ substrate. Our results point out the design principle for applying a p-type, high work function, nickel oxide electrode interlayer to fabricate CH$_3$NH$_3$PbI$_3$ perovskite/PCBM PHJ hybrid cells, which is of great
importance to future research and development in the community of next generation stable and cost-viable photovoltaics.

Figure 1 illustrates the UV-Vis spectra and the corrected PL responses of CH$_3$NH$_3$PbI$_3$ perovskite film on the glass, glass/ITO/PEDOT:PSS, and glass/ITO/NiO$_x$ substrate by a spin coating process. The magnitude of the steady-state PL response for CH$_3$NH$_3$PbI$_3$ perovskite film from 700 to 830 nm was reduced by the PEDOT:PSS and NiO$_x$ interlayer in a bilayer structure, which indicates the compatibility of charge transfer from CH$_3$NH$_3$PbI$_3$ perovskite to PEDOT:PSS and NiO$_x$ layers. The corrected PL responses of CH$_3$NH$_3$PbI$_3$ perovskite layers on the glass, glass/NiO$_x$, and glass/PEDOT:PSS substrates are normalized to the light harvesting efficiency (LHE) with the relationship of LHE =1-10$^{-Absorbance}$. The results show that the differences in PL responses are not resulted from the absorption variance of CH$_3$NH$_3$PbI$_3$ perovskite layers. This observation indicated NiO$_x$ as expected is a potential electrode interlayer for the charge transfer of hole. Docampo et al. reported the similar PL quenching effect of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite on PEDOT:PSS and NiO layers, too$^8$. However, while they applied CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite with p-type NiO electrode interlayer to fabricate the devices, Docampo et al. depicted that the devices present the very low photovoltaic performance, because of the extremely poor perovskite film formation upon the substrate and very poor surface coverage. This leads to the direct contact between PCBM n-type layer and the p-type metal oxide and generates a shunting path. They also pointed out the high series resistance of the device arising from the low conductivity of the p-type metal oxide layer is another concerning issue.

The crystal growth and aggregation of CH$_3$NH$_3$PbI$_3$ or CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite during the spin coating process coarsen the films on the substrate and markedly degrade device performance or result in device failure. To preheat a
glass/ITO/NiOₓ substrate at an elevated temperature of 60 °C for 5 min and then to immediately cast the precursor solution at a high-spinning speed of 9500 rpm ensure the solvent evaporation of solution during the perovskite film formation in a fast regime to inhibit the coarsening of the crystals⁶. Figure 2(a) to (c) illustrate the high-resolution scanning electron microscopy (HR-SEM) images at the magnification of 10,000x for CH₃NH₃PbI₃ perovskite film on the glass/ITO/PEDOT:PSS (8000 rpm), glass/ITO/NiOₓ (8000 rpm), and glass/ITO/NiOₓ (9500 rpm) substrates, respectively. In Fig. 2(a), the CH₃NH₃PbI₃ perovskite film exhibits densely interconnected crystalline strips on the glass/ITO/PEDOT:PSS substrate. The surface coverage of the film is estimated approximately 85%. Although the film looks very smooth and reflective as inspected by naked eye, there are still voids on the film, as shown in Fig. 2(d) HR-SEM image at the magnification of 50,000x, causing the shunting path of the devices. On the other hand, we observe that CH₃NH₃PbI₃ perovskite films exhibit a different surface morphology and a higher surface coverage, 89%, on glass/ITO/NiOₓ substrate as shown in Fig. 2(b). Increasing the spinning speed from 8000 rpm to 9500 rpm further improves the quality of CH₃NH₃PbI₃ perovskite film formation as illustrated in Fig. 2(c), in which the number density of void or crevice on the film is markedly reduced. The surface coverage estimated from Figs. 2(c) is estimated approximately 93%. Figs. 2(c) and (f) indicate the images of a good quality of CH₃NH₃PbI₃ perovskite film upon the flat NiOₓ surface (glass/ITO/NiOₓ substrate). Our results are very different to the observation reported by Docampo et al., probably due to the differences in the film forming and preparing condition of perovskite materials and NiOₓ layer.

The UV-Ozone treatment of glass/ITO/NiOₓ substrate for 2 minutes modifies the work function and surface wetting properties of NiOₓ electrode interlayer. Figure 3 depicts the onset (Eᵢ) and cutoff (E_cut-off) energy regions in Ultraviolet photoelectron
spectrum (UPS) (He I) of the surface measurement for the glass/ITO/PEDOT:PSS and the treated glass/ITO/NiO\textsubscript{x} substrate. The $E_i$ and $E_{\text{cut-off}}$ energy is 5.07 eV and 20.88 eV, respectively, and the work function ($\phi$) of NiO\textsubscript{x} electrode interlayer is estimated to be 5.4 eV by equation $\phi = 21.21 -(E_{\text{cut-off}} - E_i)$. In addition, UV-Ozone treatment reduces the water contact angle of the glass/ITO/NiO\textsubscript{x} substrate from 79° (untreated) to 58° (treated), in which the insets of Figure 3 show the photographs of the measurement. The decrease of the water contact angle improves the surface wetting property of NiO\textsubscript{x} electrode interlayer for precursor solution as well as the surface coverage of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite film. Figure 4(a) illustrates the device configuration of glass/ITO/NiO\textsubscript{x}/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite/PCBM/BCP/Al and Figure 4(b) diagrams the energy level of each layer. As shown in Figure 4(b), both edge level of CB (3.9 eV) and VB (5.4 eV) in CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite exhibit a good alignment with LUMO level of PCBM (3.9 eV) and the work function of NiO\textsubscript{x} (5.4 eV), respectively. Accordingly, it is anticipated that the minimal energy loss for the transfer of charge carriers (electron and hole) in the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite/PCBM and NiO\textsubscript{x}/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite heterojunction interfaces enhances the photovoltage output of the hybrid solar cells. On the other hand, NiO\textsubscript{x} is a wide band gap material with the CB edge level around -2.1 eV, which is much higher than that of perovskite around -3.9 eV, thus injection of electron into NiO\textsubscript{x} is not energetically favorable.

Figure 5(a) presents the current density-voltage ($J$-$V$) curves of hybrid organic solar cells under the standard 1 sun AM 1.5G simulated solar irradiation, made of the glass/ITO as the positive electrode, PEDOT:PSS or NiOx as the electrode interlayer, a PHJ of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite/PCBM as the active layers, a thin BCP film as hole-blocking layer (HBL), and an Al negative electrode. Table I. summarizes the photovoltaic parameters of the devices. The hybrid cell of the configuration,
glass/ITO/PEDOT:PSS/CH$_3$NH$_3$PbI$_3$ perovskite (9500 rpm)/PCBM/BCP/Al, presents a $V_{OC} = 0.62$ V, a $J_{SC} = 9.39$ mA/cm$^2$, and a fill factor FF = 0.66, corresponding to a PCE of 3.9 %. On the other hand, the hybrid cell of the configuration, glass/ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$ perovskite (9500 rpm)/PCBM/BCP/Al, presents $V_{OC} = 0.92$ V, a $J_{SC} = 12.43$ mA/cm$^2$, and a fill factor (FF) = 0.68, corresponding to a PCE of 7.8%, a superior photovoltaic performance than that of device applying PEDOT:PSS interlayer. The change of $V_{OC}$ is correlated with the work function of electrode interlayer. The work function of glass/ITO/PEDOT:PSS is estimated to be 5.1 eV, by UPS measurement. The $E_i$ and $E_{\text{cut-off}}$ energy is 4.90 eV and 21.01 eV, respectively, and the $\phi = 21.21 - (E_{\text{cut-off}} - E_i) = 5.1$. The result from UPS measurement indicates that the VB edge level (5.4 eV) of CH$_3$NH$_3$PbI$_3$ perovskite exhibits a good alignment with the work function of NiO$_x$ (5.4 eV), but there is the 0.3 eV offset in the PEDOT:PSS (5.1 eV)/CH$_3$NH$_3$PbI$_3$ perovskite (5.4 eV) junction interface. The increase in $V_{OC}$ magnitude from 0.62 V to 0.92V is related with the assumption that minimizing the energy loss for hole in NiO$_x$/CH$_3$NH$_3$PbI$_3$ perovskite junction elevates the output photovoltage. Additionally, the CH$_3$NH$_3$PbI$_3$ perovskite exhibits a better surface coverage of film morphology on glass/ITO/NiO$_x$. The better surface coverage of CH$_3$NH$_3$PbI$_3$ perovskite film on the glass/ITO/NiO$_x$ substrate reduces the shunting path of devices. This would be another dominant parameter to the enhanced magnitude of $V_{OC}$. At current stage, we cannot totally exclude the above two effects on the photovoltaic performance. The increase of $V_{OC}$ may be further fortified by analyzing Electrochemical Impedance Spectroscopy of devices, which is currently under investigation. The hybrid cell of the configuration, glass/ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$ perovskite (8000 rpm)/PCBM/BCP/Al, presents $V_{OC} = 0.88$ V, a $J_{SC} = 13.58$ mA/cm$^2$, and a FF = 0.58, corresponding to a PCE of 6.9%. The higher magnitude of $J_{SC}$ probably results from the relatively thicker CH$_3$NH$_3$PbI$_3$
perovskite film prepared at 8000 rpm. The decreases of other photovoltaic parameters are associated with the lower surface coverage of CH$_3$NH$_3$PbI$_3$ perovskite film. Additionally, the hybrid cell of the configuration, glass/ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$ perovskite (9500 rpm)/C$_{60}$/BCP/Al, is fabricated for comparison. The device presents a $V_{OC} = 0.74$ V, a $J_{SC} = 12.95$ mA/cm$^2$, and a FF = 0.60, corresponding to a PCE of 5.7%. The result indicates the energy loss for electron in CH$_3$NH$_3$PbI$_3$ perovskite/C$_{60}$ junction (C$_{60}$ of a LUMO level 4.5 eV) also degrades the output device performance.

Another parameter to modulate the photovoltaic performance is the treatment of glass/ITO/NiO$_x$ substrate by UV-Ozone for fabrication. Table I. also presents the data for the glass/ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$ perovskite (8000 rpm)/PCBM/BCP/Al cells without and with 2, or 4 minutes of UV-Ozone treatment on glass/ITO/NiO$_x$. Our results agree with the observations by Park et al. and Steirer et al. that the variation of the surface properties of NiO$_x$ film modulates the photovoltaic parameters. The hybrid cell fabricated with 2 minutes of UV-Ozone treatment exhibits the optimal condition for fabrication. By UPS measurement, the work functions of the glass/ITO/NiO$_x$ without and with 4 minutes of UV-Ozone treatment have offsets of approximately 0.07 eV smaller and 0.05 eV larger, respectively, than that of the glass/ITO/NiO$_x$ with 2 minutes of UV-Ozone treatment. It is noted that the changes in the magnitude of the work functions for the glass/ITO/NiO$_x$ substrates by UV-Ozone treatment are relatively marginal comparing with the modulations of device parameters as illustrated in Table I.. On the other hand, the water contact angles are 79° and 58° for the glass/ITO/NiO$_x$ substrates without (untreated) and with (treated) 2 minutes of UV-Ozone treatment, as the photographs of water contact angle depicted in the insets of Figure 3. Therefore, we may attribute the marked enhancement of device parameters by 2 minutes of UV-Ozone treatment on glass/ITO/NiO$_x$ to the improvement of surface wetting property, which enables the higher surface coverage.
of CH$_3$NH$_3$PbI$_3$ perovskite film. However, the prolonged 4-minute UV-Ozone treatment degrades the device parameters, which probably are associated with excess oxygen content in the NiO$_x$ film. This part of work requires further investigations in order to understand the effect of UV-Ozone treatment for the optimization of device fabrication process. In a summary, the hybrid cell, glass/ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$ perovskite (9500 rpm)/PCBM/BCP/Al exhibits the optimal device performance in this study owning to the reducing the energy loss in the charge transfer process for both hole and electron in the PHJ interfaces and the improvement of surface coverage of CH$_3$NH$_3$PbI$_3$ perovskite film upon glass/ITO/NiO$_x$ substrate. Those disclosures pose the direction to further improve the photovoltaic performance of the hybrid CH$_3$NH$_3$PbI$_3$ perovskite/PCBM solar cells by the p-type, nickel oxide electrode interlayer.

Figure 6 illustrates the incident photon to electron conversion efficiency (IPCE) spectrum and the integrated photocurrent calculated under AM 1.5G solar irradiation of the glass/ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$ perovskite (9500 rpm)/PCBM/BCP/Al cell. The hybrid solar cell exhibits the device’s spectral response from the visible to near-infrared (300 to 800 nm) region with a peak IPCE of 60~70 % at approximately 450~550 nm. The threshold for the generation of photocurrent starting at around 780 nm agrees very well with the bandgap of CH$_3$NH$_3$PbI$_3$ perovskite. The photocurrent integrated from the overlap of the IPCE spectrum with the AM 1.5G solar irradiation gives a current density of 11.35 mA/cm$^2$. The IPCE spectrum of the device is coincident with the UV-Vis spectrum of CH$_3$NH$_3$PbI$_3$ perovskite film and the magnitude of the integrated photocurrent is correlated with the results as depicted in Fig. 5.

NiO is a well-known p-type semiconductor widely used as hole selective contact for organic BHJ solar cells$^{22,25-27}$ and p-sensitization electrode for dye solar cells.$^{28-30}$
However, p-type NiO-based dye solar cells usually suffered from serious charge recombinations and markedly degraded device performance. Currently, the effective p-type selective contact materials for organometallic perovskite are mostly organic (spiro-OMeTAD, poly(3-hexylthiophene), PEDOT:PSS and other organic hole transporter). This work demonstrates the metal oxide (NiO$_x$) as a p-contact for the efficient organic-inorganic hybrid perovskite-based solar device. Alternatively, molybdenum oxide (MoO$_3$) of the work function 5.3 eV would be another possible candidate as the p-contact electrode interlayer for perovskite-based solar cells.$^{31}$ When to thermally evaporate a thin layer (5~10 nm) of MoO$_x$ on the glass/ITO substrate as the electrode interlayer to fabricate the devices, we observed the increase on $V_{OC}$ from 0.60V to 0.75V, but the decrease on $J_{SC}$, FF, and PCE, probably due the relatively high resistance of MoO$_x$ layer in our test. It is anticipated that the photovoltaic parameters can be further improved by optimizing the electrical and the surface wetting properties of MoO$_x$ interlayer. Since there are many n-type metal oxide materials (TiO$_2$, ZnO) available for perovskite-based solar cells, in future perovskite solar cells can be made of both inorganic p-type and n-type metal oxide as the electrode interlayers (p-type metal oxide/perovskite/n-type metal oxide). This device configuration replaces all the organic components by the inorganic metal oxides and would be the robust perovskite solar cells of real application. This opens up further diversities in structure designs and new paradigm for fully inorganic thin film solar cells. Our results implied that judicious selection of contact materials for the ambipolar organometallic perovskite could have critical influences on the device performance especially the photovoltage. Further development using mesoscopic p-contact electrode is expected to increase the light absorption and the final efficiency, which is under investigation in our group.

In conclusion, we have successfully integrated NiO$_x$ p-type metal oxide
semiconductor for CH$_3$NH$_3$PbI$_3$ perovskite/PCBM PHJ hybrid solar cells. A respectful solar to electrical PCE of 7.8% has been achieved with the device composed of the glass/ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$ perovskite/PCBM/BCP/Al structure. In comparison with device using PEDOT:PSS as the electrode interlayer, our experimental data showed that due to the improved wetting and better energy level alignment between light absorber (CH$_3$NH$_3$PbI$_3$ perovskite) and NiO$_x$, the photovoltage is significantly enhanced together with the overall photovoltaic parameters. We believe the significant improvements can be realized with further optimizations, such as increasing the film thickness of CH$_3$NH$_3$PbI$_3$ perovskite for the higher harvest of light. The application of p-type metal oxide material has the advantages of providing robust device and the development of fully inorganic perovskite-based thin film solar cells. We believe the rapid significant advances in the development of perovskite-based solar cells in recent years will strengthen confidence in this promising technology.

Experiments

Materials and Sample preparation: The ethylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) perovskite was prepared according to our previous work$^6$ and from other reports elsewhere.$^{3,32}$

Fabrication of CH$_3$NH$_3$PbI$_3$ perovskite/[6,6]-phenyl C61-butyric acid methyl ester (PCBM) planar-heterojunction (PHJ) hybrid solar cells: The solar cells were fabricated in a standard arrangement by sandwiching a PHJ of CH$_3$NH$_3$PbI$_3$ perovskite/PCBM structure between p-type and n-type contact. The p-type contact is made of pre-cleaned and -patterned transparent glass/indium-titanium-oxide (ITO) (RITEK Corp., 15 Ω/□) coated with poly(3,4-ethylenedioxythiophene) poly(styrene-
-sulfonate) (PEDOT:PSS) (Baytron P, Bayer AG, Germany) or nickel oxide (NiO$_x$) film electrode interlayer as the positive electrode. The n-type contact is made of bathocuproine (BCP) (Aldrich) film (as a hole-blocking layer, HBL) and aluminum (Al) as the negative electrode. Figure 4(a) illustrates the device configuration and Figure 4(b) diagrams the energy level of each layer. Prior to the device fabrication, the ITO/glass substrates were sequentially cleaned by ultrasonic treatment in detergent, de-ionized water, acetone and isopropyl alcohol. The glass/ITO/PEDOT:PSS or glass/ITO/NiO$_x$ substrates were pre-heated at 60 °C for 5 min prior to spin-casting the precursor solution at 8000 rpm or 9500 rpm, 30s. The CH$_3$NH$_3$PbI$_3$ precursor solution was prepared by mixing CH$_3$NH$_3$I and lead iodide (PbI$_2$) (Showa Chemical Inc.) at 1:1 (0.8:2.3 g) equi-molar ratio in 15.8 ml anhydrous N,N-dimethylformamide (Aldrich) (17.2 wt.% solution) at 60 °C, stirring for 12 hrs implemented inside a nitrogen-filled glove box with oxygen and moisture levels < 1 ppm. The preheating treatment of the substrate and the high spinning rate (by a customer designed spin coater of spinning rate up to 9500 rpm, accelerating rate of 30,000 rpm/sec$^2$-loaded, Model: SP-13035, IVY Semiconductor Engineering, LTD, Taiwan) for coating ensure the solvent evaporation in a fast regime to inhibit the coarsening of the crystals. The thickness of CH$_3$NH$_3$PbI$_3$ perovskite (9500 rpm) layer was approximately 60 nm as determined by the cross session images of Transmission Electron Microscopy (TEM) (JEM-2100, JEOL, USA). The UV-Vis absorbance spectra of CH$_3$NH$_3$PbI$_3$ perovskite films prepared at 8000 and 9500 rpm are illustrated in the Supporting information, Figure S1. The C$_{60}$ (30 nm) (>99.5%, Aldrich), PCBM (25 nm) (> 99.5%, Solenne, Netherlands), BCP (10 nm), and Al (100 nm) were thermally deposited on the substrate inside a vacuum chamber (10$^{-6}$ Torr). The deposition thickness was monitored by the quartz crystal monitor. The active area of the device is 0.06 cm$^2$. All the procedures are implemented inside a nitrogen-filled
glove box with oxygen and moisture levels < 1 ppm except for casting the PEDOT:PSS and NiO$_x$ electrode interlayer.

Fabrication of PEDOT:PSS and NiO$_x$ electrode interlayer: PEDOT:PSS solution was spun-cast in atmosphere at 4000 rpm for 60 seconds. Then, the substrate was post-annealed at 150 °C for 30 minutes. For the preparation of NiO$_x$ electrode interlayer, the ethylene glycol solution containing 0.5 M nickel formate dihydrate (Alfa Aesar) with 1 molar equivalents of ethylenediamine (Aldrich) was filtered with 0.45 µm nylon filters. The solution was spun-cast on glass/ITO substrate at 4000 rpm for 90 seconds. Then, the substrate was post-annealed at 300 °C in atmosphere for 60 minutes. Later, the glass/ITO/NiO$_x$ substrate was treated by a UV-Ozone cleaner (Model: 42, Jelight, USA) for 2 minutes and used immediately for fabricating devices. The thickness of PEDOT:PSS and NiO$_x$ interlayer was determined by TEM cross section image of 40 nm and 10 nm, respectively.

Characterization: Device characteristics, current density-voltage (J-V) curves, were measured in a nitrogen-filled glove box using a Keithley 2400 sourcemeter under the standard 1 sun AM 1.5G simulated solar irradiation (100 mW/cm$^2$) from an Newport 91160A 300 W Solar Simulator (Class A). The simulated solar irradiance is corrected by a Schott visible-color glass-filtered (KG5 color filter) Si diode (Hamamatsu S1133). The incident photon to electron conversion efficiency (IPCE) spectra were measured by a 300 W xenon light source (Oriel), Oriel Cornerstone 130 1/8 m monochromator, Keithley 2400 sourcemeter, a chopper (SR540, Stanford research system Inc.) and a Lock-in amplifier (SR510, Stanford research system Inc.). UV-Vis spectra were taken by a spectrometer (U4100, Hitachi). The high-resolution scanning electron microscopy (HR-SEM) images were performed by a FEI Quanta 400. The work functions were measured by Ultraviolet photoelectron spectrum (UPS)
with He source of incident energy of 21.21 eV (He I line) in National Synchrotron Radiation Research Center, Taiwan. The analysis of the surface coverage for CH$_3$NH$_3$PbI$_3$ perovskite film was done by the ImageJ software. The surface coverage for CH$_3$NH$_3$PbI$_3$ perovskite films on different substrates was estimated by the ImageJ software. The ImageJ-analyzed images are illustrated in the Supporting information, Figure S2. The sample for the steady-state photoluminescence (PL) measurement was excited by the continuous (CW) frequency-doubled diode-pumped solid state (DPSS) laser beam (focused), 473 nm, about 8 mW. A 500 nm long pass filter was applied to filter out the laser light. The spectrometer, (Ocean optics HR 4000, USA), was used to measure PL responses.

Acknowledgements

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Table I. The photovoltaic parameters of CH$_3$NH$_3$PbI$_3$/PCBM hybrid solar cells.

<table>
<thead>
<tr>
<th>PHJ structures</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS/CH$_3$NH$_3$PbI$_3$ (9500rpm)/PCBM</td>
<td>0.62</td>
<td>9.39</td>
<td>0.66</td>
<td>3.9</td>
</tr>
<tr>
<td>b)$\text{NiO}_x$/CH$_3$NH$_3$PbI$_3$ (9500rpm)/PCBM</td>
<td>0.92</td>
<td>12.43</td>
<td>0.68</td>
<td>7.8</td>
</tr>
<tr>
<td>b)$\text{NiO}_x$/CH$_3$NH$_3$PbI$_3$ (8000rpm)/PCBM</td>
<td>0.88</td>
<td>13.53</td>
<td>0.58</td>
<td>6.9</td>
</tr>
<tr>
<td>a)$\text{NiO}_x$/CH$_3$NH$_3$PbI$_3$ (8000rpm)/PCBM</td>
<td>0.72</td>
<td>10.71</td>
<td>0.59</td>
<td>4.6</td>
</tr>
<tr>
<td>c)$\text{NiO}_x$/CH$_3$NH$_3$PbI$_3$ (8000rpm)/PCBM</td>
<td>0.76</td>
<td>9.51</td>
<td>0.66</td>
<td>4.8</td>
</tr>
<tr>
<td>b)$\text{NiO}_x$/CH$_3$NH$_3$PbI$<em>3$ (9500rpm)/C$</em>{60}$</td>
<td>0.74</td>
<td>12.95</td>
<td>0.60</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Device configuration:
glass/ITO/NiO$_x$ or PEDOT:PSS/CH$_3$NH$_3$PbI$_3$ (8000 or 9500 rpm)/PCBM or C$_{60}$/BCP/Al

a) without UV-Ozone treatment of glass/ITO/NiO$_x$
b) 2 minutes of UV-Ozone treatment of glass/ITO/NiO$_x$
c) 4 minutes of UV-Ozone treatment of glass/ITO/NiO$_x$
References:

16. J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, S. I. Seok, Nano Lett. 2013, 13, 1764.


**Figure Captions**

FIG. 1. UV-Vis spectra and the corrected PL responses of CH$_3$NH$_3$PbI$_3$ perovskite film on the (●) (○) glass, (■) (□) glass/ITO/NiO$_x$, and (▲) (△) glass/ITO/PEDOT:PSS substrate by a spin coating process. The sample for the steady-state PL measurement was excited by the CW frequency-doubled DPSS laser beam (473 nm). The corrected PL responses of CH$_3$NH$_3$PbI$_3$ perovskite films are normalized to the LHE.

FIG. 2. HR-SEM images at the magnification of 10,000x for CH$_3$NH$_3$PbI$_3$ perovskite films on (a) the glass/ITO/PEDOT:PSS, (b) glass/ITO/NiO$_x$, and (c) glass/ITO/NiO$_x$ substrates at the spinning speed 8000 rpm, 8000 rpm, and 9500 rpm, respectively. (c), (d), and (e) HR-SEM images at the magnification of 50,000x for (a), (b), and (c), respectively. The ratio of surface coverage for images (a), (b), and (c) estimated by ImageJ software is approximately 85%, 89%, and 93%, respectively.

FIG. 3. UPS in the onset ($E_i$) and the cutoff ($E_{cut-off}$) energy regions of the surface measurement for the glass/ITO/PEDOT:PSS (blue curve) and 2-minute UV-Ozone treated glass/ITO/NiO$_x$ (red curve) substrates. Insets: Photographs of the water contact angle for the untreated and treated glass/ITO/NiO$_x$ substrate.

FIG. 4. (a) The configuration of the hybrid solar cell in this study of glass/ITO/NiO$_x/$CH$_3$NH$_3$PbI$_3$ perovskite/PCBM/BCP/Al. (b) Diagram the energy level of each layer.

FIG. 5. The $J-V$ curves of devices (●) glass/ITO/PEDOT:PSS/CH$_3$NH$_3$PbI$_3$ (9500 rpm)/PCBM/BCP/Al, (■) glass/ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$ (9500 rpm)/PCBM/BCP/Al,
(♦) glass/ITO/NiO_x/CH_3NH_3PbI_3 (8000 rpm)/PCBM/BCP/Al, (◇) glass/ITO/NiO_x/CH_3NH_3PbI_3 (9500 rpm)/C_60/BCP/Al under standard 1 sun AM 1.5G simulated solar irradiation.

FIG. 6. (■) The IPCE spectrum and (□) the integrated photocurrent calculated under AM 1.5G solar irradiation of the glass/ITO/NiO_x/CH_3NH_3PbI_3 (9500 rpm)/PCBM/BCP/Al device.
Figure 1. Jeng et al.
Figure 2. Jeng et al.
Figure 3. Jeng et al.
Figure 4. Jeng et al.
Figure 5. Jeng et al.
Figure 6. Jeng et al.