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p-type Mesoscopic NiO as an Active Interfacial Layer for Carbon Counter Electrodes Based Perovskite Solar Cells

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Replacement of ZrO2 insulator layer in state-of-the-art TiO2/ZrO2/carbon structure by mesoscopic p-type NiO particles led to 39% increase of energy conversion efficiency of hole-conductor-free organometallic perovskite heterojunction solar cells with carbon counter electrodes. In these cells, the light absorber, CH3NH3PbI3, formed inside the pores of the entire TiO2/NiO/carbon layer upon sequential deposition of PbI2 and CH3NH3I. Photoluminescence, impedance spectroscopy and transient photovoltage decay measurements have revealed that introduction of NiO extended the electron lifetime and augmented the hole extraction to the counter electrode. As a result, the photocurrent and open-circuit voltage both increased, resulting in a cell with impressive energy conversion efficiency of 11.4% under AM1.5G condition.

Introduction

Organometal trihalide perovskite solar cells have shown promise as an efficient technology in utilization of solar energy. In the past three years, perovskite-based mesoscopic or thin-film heterojunction solar cells have achieved power conversion efficiencies (PCE) as high as 17.9%. However, stability, environmental friendliness as well fabrication cost, must be taken into account in order to make this type of device a viable solution for the conversion of solar energy to electricity. Theoretical studies show that the unique electronic structure and optical properties of perovskite materials contribute largely to their remarkable photovoltaic performance. Several exploratory investigation also indicates Sn may be an alternative to Pb, which is toxic and is the dominate source of perovskite salt. In the higher conduction band compared to CH3NH3PbI3 (-1.8 eV vs. -3.93 eV), Photo-induced absorption spectra and photoluminescence measurements also show that NiO can act as a hole collector. Nevertheless, these devices employ expensive PCBM as electron selective electrode, which could be problematic for practical application and need to be addressed.

Low-cost carbon black/graphite materials have been used as counter electrodes in dye-sensitized solar cells and showed good performance. Ku et al reported HTMs-free perovskite solar cells with a carbon black/graphite counter electrode, and PCE of 6.64% is achieved. The performance of HTMs-free solar cells is further improved when highly ordered mesoporous carbon or TiO2 nanosheets are employed. Recently, Han et al use 5-ammoniumvaleric acid iodide modified CH3NH3PbI3 perovskite as an absorber in HTMs-free solar cell. The resulting device shows PCE of 12.8% with promising stability. These results demonstrate that the potential of carbon materials as Earth-abundant materials for cost-effective perovskite heterojunction solar cells. In this HTM-free solar cell, the ZrO2 was used as a insulator to separate TiO2 layer and carbon layer. The perovskite CH3NH3PbI3 transports holes to the counter electrode. Since the diffusion length of CH3NH3PbI3 is ~100 nm, it is much smaller than the thickness of ZrO2 layer (1-2 µm). This will restrain the further improvement of devices performance of HTM-free
This study communicates a strategy to address aforementioned issues. We fabricated perovskite heterojunction solar cell using p-type mesoscopic NiO as an interfacial layer and carbon as counter electrode. In these cells, the mesoscopic pores are filled with CH$_3$NH$_3$PbI$_3$ by sequential deposition process. The mesoscopic NiO layer acted as a hole conductor or electron blocking layer to suppress charge recombination and facilitate the hole extraction. This type solar cell using inorganic materials (coded as TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon) can be fabricated in atmospheric environment, showing a promising PCE of 11.4% under standard test conditions. To our best knowledge, this is the first report on efficient perovskite heterojunction solar cells using all inorganic p-type and n-type mesoscopic materials fabricated with screen printing technology.

Results and Discussion

The devices were fabricated by screen-printing mesoscopic TiO$_2$ layer, NiO interfacial layer, carbon/graphite materials layer-by-layer on compact TiO$_2$ coated FTO glass, followed by sequential deposition of PbI$_2$ and CH$_3$NH$_3$I. A schematic representation of the cell structure is shown in Fig. 1. In this configuration, the cell has a compact TiO$_2$ layer as a hole blocking layer between the FTO and the mesoscopic TiO$_2$ layer, a carbon layer as the counter electrode on the top of NiO layer. Upon absorbing light, CH$_3$NH$_3$PbI$_3$ perovskite generates exciton, which efficiently separates into electrons and holes because of a low exciton binding energy (being ~0.5 eV). The photo-generated electron injects into the conduction band (CB, -4.0 eV) of the TiO$_2$ and hole injects into the valence band (VB, -5.2 eV) of the mesoscopic NiO layer. This will be different from reported TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device, replacement of ZrO$_2$ layer with no charge injection due to the mismatch of energy levels. The devices exhibited PCE of 11.4% with a $V_{OC}$ of 890 mV, and a FF of 0.71. As a comparison, a cell with TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon device was also fabricated and tested under same condition. Its photocurrent-voltage curve was also shown in Fig. 3a. The results showed a significant increase in $V_{OC}$, $J_{SC}$ and FF when ZrO$_2$ was replaced by NiO. Fig. 3b shows the incident photon to electron conversion efficiency (IPCE) spectrum of the two devices. Compared to TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon device, replacement of ZrO$_2$ by NiO resulted in a cell with higher IPCE values in the range from 400 to 800 nm. The calculated photocurrent from the IPCE spectrum gives a current density of 17.7 mA/cm$^2$ for a NiO device and 15.9 mA/cm$^2$ for a ZrO$_2$ device, respectively. These data are in agreement with the measured photocurrent densities. Since TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$) and TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$) films exhibited almost identical absorption spectra in the range of 400-800 nm as shown in Fig. S2, the TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device clearly posses higher charge separation or charge collection efficiency than the device with ZrO$_2$. The complete devices performance distribution of all devices is described in Fig. S3 and Fig. S4. The stability of TiO$_2$/NiO (CH$_3$NH$_3$PbI$_3$)/carbon devices was investigated in dark. Fig. S5 shows the evolution of device photovoltaic parameters, which were prolonged in dark at ambient temperature.
Fig. 3 a) Current-Voltage characteristics of TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device (black line) and TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon device (red line). b) IPCE spectra of TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device (line A) and TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon device (line B). Integrated current of TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device (line A’) and TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon device (line B’).

Table 1 Device performance of TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device and TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon device measured under simulated AM 1.5 (100 mW cm$^{-2}$) condition.

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (mV)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/NiO/C champion average $^a$</td>
<td>18.2</td>
<td>890</td>
<td>0.71</td>
<td>11.4</td>
</tr>
<tr>
<td>TiO$_2$/ZrO$_2$/C champion average $^b$</td>
<td>16.4</td>
<td>818</td>
<td>0.60</td>
<td>8.2</td>
</tr>
</tbody>
</table>

$^a$ Average device performance parameter were calculated with a standard deviation from 24 TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon devices; $^b$ Average device performance parameter were calculated with a standard deviation from 24 TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon devices. The complete devices performance distribution of all devices is described in Fig. S3 and Fig. S4.

As shown in Fig. 4, a fast photoluminescence (PL) quenching process was observed for the TiO$_2$(CH$_3$NH$_3$PbI$_3$) and NiO(CH$_3$NH$_3$PbI$_3$) films. The obtained lifetimes ($\tau_0$) of the photogenerated carriers (quoted as the time taken to reach 1/e of the initial intensity) were 5.3, and 2.3 ns for NiO(CH$_3$NH$_3$PbI$_3$), and TiO$_2$(CH$_3$NH$_3$PbI$_3$) films, respectively. Both were significantly lower than that of ZrO$_2$(CH$_3$NH$_3$PbI$_3$) film (24 ns). This result confirmed fast interfacial charge transfer processes occurred after the films were excited. $^{46, 54, 55}$ For TiO$_2$(CH$_3$NH$_3$PbI$_3$) film, this process involved the electron injection from the CB of CH$_3$NH$_3$PbI$_3$ to the CB of TiO$_2$. $^{26, 54, 55}$ because of its lower energy level. For NiO(CH$_3$NH$_3$PbI$_3$) film, situation may become complicated. This is because the CB of NiO is significant higher ($\sim$1.8 eV vs. -3.93 eV), but its VB energy level is quite close to that of CH$_3$NH$_3$PbI$_3$. Therefore NiO might mainly behave as a hole conductor. Therefore, the PL quenching may come from the hole injection from VB of CH$_3$NH$_3$PbI$_3$ to the VB of NiO. $^{26, 54, 55}$ Concurrently, the TiO$_2$ underneath the NiO blocks the flow of holes at the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface between two materials due to the large VB energy levels difference (-3.93 eV vs. -7.2 eV). This is consistent with Malinkiewicz’s report on organic charge-transport layer-based perovskite solar cells using polyTPD and PCBM as an electron and a hole blocking layer, respectively. $^{27}$

Measurements of photovoltage and short circuit current of devices under different light intensities indicated different interfacial charge recombination process. It was found the $J_{SC}$ exhibited a linear response to light intensities; whereas $V_{OC}$ displayed a linear response to the logarithm of incident photo flux as shown in Fig. S6. The slope of the photovoltage versus the logarithm of incident photo flux for a solar cell with an ideal photodiode behaviour is expected to be 59 mV/decade at 300K. $^{57}$ However, the slopes for TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device and TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon device were found to be -173 mV/decay and -240 mV/decay, respectively. This result indicates that the loss of photogenerated electron in TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon device is faster than that of TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device. This further indicates different interfacial charge recombination processes between these two devices, which are responsible for their photovoltage. $^{57}$

Electronic impedance measurement (IS) showed a large charge recombination resistance at photoactive layer interfaces in TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device. In dark IS measurement, with the applied bias from the working electrode of the IS system, the injected electrons from the FTO contact transport through mesoporousTiO$_2$, diffuse within the CH$_3$NH$_3$PbI$_3$, and eventually reach the carbon counter electrode. The Nyquist plots of TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device and TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon device showed two main features: (i) the arc at high frequency region assigned to charge transfer process at carbon counter electrode interface as this process is very fast; and (ii) the arc at low frequency region assigned to the charge recombination process at the photoactive interface as this process is slow. $^{36, 60}$ Fig. 5a presents the recombination resistance ($R_{rec}$) from impedance measurements in devices as a function of the bias. The Nyquist plots were shown in Fig. S7. The TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device displayed larger $R_{rec}$ than that of TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon device, indicating that charge recombination is slower in the former. Fig. 5b presents the resistance ($R_{CE}$) for the charge transfer process related to the counter electrode as a function of dark current. It was found that the TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device exhibited lower $R_{CE}$ than that of TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon device at a given current. This result indicates that charge transfer process at the counter electrode is much efficient when NiO was used. In the case of device with ZrO$_2$, CH$_3$NH$_3$PbI$_3$ acts as hole transporting material and participates in the hole extraction to the counter electrode. $^{50, 61, 62}$ However, in the case of device with NiO, the hole transporting property of NiO layer could benefit the hole extraction and collection efficiency. $^{56}$ Therefore, the TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device presented a higher fill factor.
Nevertheless, the CH$_3$NH$_2$PbI$_3$ photoluminescence emission for perovskite/TiO$_2$ photon into electricity. More studies are necessary to carry out in the near future for a more precise knowledge about the specific device.

The use of NiO increased the electron lifetime of the resulting devices. Fig. 6 presents the electron lifetime as a function of the incident light intensity from transient photovoltage decay measurements. It was observed that electron lifetime of TiO$_2$/NiO(CH$_3$NH$_2$PbI$_3$)/carbon device was longer than that of TiO$_2$/ZrO$_2$(CH$_3$NH$_2$PbI$_3$)/carbon device. This may be attributed to the dual function of NiO as a hole conductor and its electron blocking property. Therefore, the remarkable improvement of device performance for TiO$_2$/NiO(CH$_3$NH$_2$PbI$_3$)/carbon device can be attributed to the NiO layer. In TiO$_2$/ZrO$_2$(CH$_3$NH$_2$PbI$_3$)/carbon device, the photo-generated electron can be fast injected to the CB of TiO$_2$, as evidenced by a quick quenching of the photoluminescence emission for perovskite/TiO$_2$ in Fig. 4. The injected electron transports through the TiO$_2$ mesoporous network to the external circuit. Meanwhile, the photo-generated hole transports through the perovskite to the counter electrode due to the ambipolar charge transport properties of perovskite. However, in TiO$_2$/NiO(CH$_3$NH$_2$PbI$_3$)/carbon device the situation could be different. In accompany with electron injection and transporting in TiO$_2$, the photo-generated hole can be fast injected to the VB of NiO and diffuse in this layer (see Fig. 2), which directly connects to the counter electrode. Nevertheless, the CH$_3$NH$_2$PbI$_3$ heterojunction using mesoporous NiO interfacial layer was demonstrated to efficiently convert photon into electricity. More studies are necessary to carry out in the near future for a more precise knowledge about the specific device.

Conclusions

In summary, we have demonstrated an efficient perovskite heterojunction solar cell using p-type mesoscopic NiO as an interfacial layer. This type of solar cell using all inorganic p-type and n-type materials can be fabricated in atmospheric environment, presenting a promising power conversion efficiency of 11.4%. The open-circuit voltage, short-circuit current and fill factor of the TiO$_2$/NiO(CH$_3$NH$_2$PbI$_3$)/carbon device were significantly improved than the counterpart devices using mesoscopic ZrO$_2$ layer as separator, which was attributed to the enlarged electron lifetime and augmented interfacial charge transfer process on the carbon counter electrode because of the dual functions as an electron blocker and a hole conductor. This offers a viable pathway to develop efficient low-cost solar cells with attractive properties for scale up and practical applications.

Experimental Section

Device fabrication

Fabrication of TiO$_2$/NiO(CH$_3$NH$_2$PbI$_3$)/carbon device: FTO conducting glass were etched with sander to form two detached electrode patterns before being ultrasonically cleaned with detergent solution, deionized water and ethanol successively. A compact TiO$_2$ layer was deposited on the cleaned FTO glass by spray pyrolysis deposition with di-isopropoxytitanium bis(acetyl acetonate) solution at 450°C. The films were sintered at 500°C for 30 min and then cooled to room temperature. A 450 nm mesoporous TiO$_2$ (DSL. 18NR-T, 20 nm, Dyesol, Australia, diluted at 1/3.5 mass ratio of paste/terpineol) layer, a 1 µm NiO hole-conductor layer (NiO paste was used according to our recent report about p-type dye-sensitized solar cells) and a 8 µm carbon black/graphite layer (black/graphite mass ratio 1/4, prepared according literature) were subsequently prepared by screen printing onto FTO conducting glass layer by layer, which were sintered at 500°C, 500°C and 400°C for 30 min respectively. After that, the resulted films were infiltrated with PbI$_2$ by dropping a PbI$_2$ solution in DMF (462 mg ml$^{-1}$) that was kept at 70°C. After drying, the films were dipped into 2-propanol for 1-2
s before being dipped in a solution of CH$_3$NH$_3$I in 2-propanol (10 mg ml$^{-1}$) for 10 min and then rinsed with 2-propanol and the films changed colour from light yellow to black during the dipping process, indicating the formation of the perovskite CH$_3$NH$_3$PbI$_3$.

After drying, the fabrication of the device was finished.

**Fabrication of TiO$_2$/ZrO$_2$(CH$_3$NH$_3$PbI$_3$)/carbon device:** The device structure was prepared by substituting NiO hole-conductor layer with a 1 µm ZrO$_2$ spacer layer according to the procedure described above for the fabrication of TiO$_2$/NiO(CH$_3$NH$_3$PbI$_3$)/carbon device.

**Devices Characterization**

A xenon light source solar simulator (450W, Oriel, model 9119) with AM 1.5G filter (Oriel, model 91192) was used to give an irradiance of 100 mW cm$^{-2}$ at the surface of the solar cells. The current-voltage characteristics of the devices under these conditions were obtained by applying external potential bias to the devices and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). A similar data acquisition system was used to control the incident photon-to-current conversion efficiency (IPCE) measurement. A white light bias (1% sunlight intensity) was applied onto the devices during the IPCE measurements with AC model (10 Hz). The devices (-0.6 cm$^2$) were tested using a metal mask to prevent the scattering light.

**Time-Resolved Fluorescence Decay Measurements**

Time-resolved fluorescence decays measurements were recorded on a FLSP920 spectrometer (Edinburgh instruments, Inc.). A picosecond pulsed light-emitting diode centered (443 nm) with a frequency of 10 MHz was used. The NiO, TiO$_2$ and ZrO$_2$ nanoparticles were screen-printed on quartz substrates to form 0.8 µm thick films. After sintered at 500°C, 500°C, and 395°C for 60 s and then rinsed with 2-propanol. It is worth noting that the films changed colour from light yellow to black during the dipping process, indicating the formation of the perovskite CH$_3$NH$_3$PbI$_3$.

**Electrochemical Impedance Measurements and Transient Decay Measurements**

Electronic impedance spectroscopy (IS) was carried out on a ZAHNER ENNIUM Electrochemical Workstations in the frequency range 100 mHz to 2 M Hz with 10 mV AC amplitude in dark. The electron lifetime was determined by transient photocurrent decay measurements. For the photovoltage transient decay measurement, an array of diodes was used to produce a white light bias and blue-light diodes controlled by a fast solid-state switch was used to generate a pulse (0.05 s square pulse-width, 100 ns rise and fall time). The voltage dynamics were recorded on a PC-interfaced Keithley 2602A source meter with a 100 µs response time. The perturbation light source was set to a suitably low level for the voltage-decay kinetics to be monoexponential. By varying the intensity of white-light bias, the recombination rate constant and the electron diffusion rate constant could be estimated over a range of applied biases, which were used to evaluate the electron lifetime of the devices.

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**Notes and references**

Energy conversion efficiency = 11.4%

254x190mm (96 x 96 DPI)