P-contact metal oxide in efficient $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite/PCBM planar-heterjunction hybrid solar cells

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About Taiwan and Tainan (台南)

The oldest city in Taiwan
Population: 760,000
National Cheng Kung University (NCKU)

NCKU established in 1931
9 colleges,
78 departments and institutes,
54 doctoral programs
more than 1,400 faculty members
more than 23,000 students at NCKU
Dutch Colony & Zheng’s Regime

Anping Fort

Chikan Tower
Outlines

I. Development of perovskite-based solar cells

II. Perovskite/fullerene PHJ hybrid solar cells

III. NiO$_x$ electrode interlayer in perovskite-based solar cells

IV. Conclusions
Perovskite type crystal

Ball and stick model of the basic perovskite structure

Extended network structure connected by the corner-shared octahedron.

The basic structure of perovskite is AMX$_3$, where the M atom is typically a metal cation and X is an anion (O$_2^-$, Cl, Br, I, etc.) A is another cation that fills the hole among the octahedral and balances the charge of the whole network.

Organometal halide perovskite-based mesoscopic solar cells

Valence band level

\[
\begin{align*}
\text{CH}_3\text{NH}_3\text{PbBr}_3 & \rightarrow 5.38 \text{ eV} \\
\text{CH}_3\text{NH}_3\text{PbCl}_3 & \rightarrow 5.44 \text{ eV}
\end{align*}
\]

<table>
<thead>
<tr>
<th>perovskite sensitizer on TiO₂</th>
<th>( J_{sc} ) (mA/cm²)</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{NH}_3\text{PbBr}_3 )</td>
<td>5.57</td>
<td>0.96</td>
<td>0.59</td>
<td>3.13</td>
</tr>
<tr>
<td>( \text{CH}_3\text{NH}_3\text{PbI}_3 )</td>
<td>11.0</td>
<td>0.61</td>
<td>0.57</td>
<td>3.81</td>
</tr>
</tbody>
</table>

Hybrid perovskite-based solar cells

*Solid state perovskite-based* mesoscopic solar cells

Methylammonium lead iodide chloride (CH$_3$NH$_3$PbI$_2$Cl)

Faster electron diffusion through the **perovskite** phase than through the n-type TiO$_2$.

<table>
<thead>
<tr>
<th></th>
<th>$V_{OC}$</th>
<th>$J_{SC}$</th>
<th>PCE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.80</td>
<td>17.8</td>
<td>7.6</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.98</td>
<td>17.8</td>
<td>10.9</td>
</tr>
</tbody>
</table>


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Hole conductor free perovskite-based mesoscopic solar cells

Application of \((\text{CH}_3\text{NH}_3\text{PbI}_3)\) perovskite/TiO\(_2\) nanosheets instead of TiO\(_2\) nanoporous structure.

CH\(_3\)NH\(_3\)PbI\(_3\) nanocrystals act as an efficient light harvester and as a hole transporter in solar cells.

Donor-acceptor heterojunction solar cells

Our work: Donor-Acceptor planar heterojunction

Light

Donor

Acceptor

\( V_{oc} \)

CH\(_3\)NH\(_3\)PbI\(_3\)

TiO\(_2\)

Lee, Burschka, Etgar….work

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Perovskite/fullerene PHJ hybrid solar cells

World first proposed **perovskite/fullerene** hybrid solar cell

![Diagram of a planar heterojunction solar cell](image)

- **Negative electrode**: ITO
- **Active layer**: CH$_3$NH$_3$PbI$_3$ (Donor)
- **Exciton- or hole-blocking layer**: C$_{60}$ (Acceptor)
- **Positive electrode**: Al

**Planar Heterojunction**

*Jeng et al., Adv. Mater. 25, 3727 (2013).*
Excitons are separated at donor-acceptor interface, and transported by CH$_3$NH$_3$PbI$_3$ perovskite and C$_{60}$, respectively, to yield the photovoltaic effect.
Application of acceptors with higher LUMO levels

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perovskite/C$_{60}$</td>
<td>0.55</td>
<td>5.21</td>
<td>0.57</td>
<td>1.6</td>
</tr>
<tr>
<td>Perovskite/PCBM</td>
<td>0.65</td>
<td>5.89</td>
<td>0.63</td>
<td>2.4</td>
</tr>
<tr>
<td>Perovskite/ICBA</td>
<td>0.75</td>
<td>5.44</td>
<td>0.51</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Methylammonium lead iodide perovskite/fullerene-based hybrid solar cells

Jun-Yuan Jeng, Yi-Fang Chiang, Mu-Huan Lee, Shin-Rung Peng, Tzung-Fang Guo, Peter Chen, and Ten-Chin Wen

A novel design simplifies fabrication of all-solid-state, ultrathin organic/inorganic photovoltaics with respectable efficiency.

Turning solar energy into a clean, practical alternative power source will require new types of devices that generate electrical power directly from solar irradiation with high efficiency and at low cost. Recent studies report solar cells based on materials known as organometal halide perovskites that have promising photovoltaic efficiencies.

1–5 These devices employ a submicron, crystalline, and well-oriented thin film of organolead iodide perovskite as the light absorber (or as both light absorber and carrier conductor) deposited on the surface of meso (i.e., 1–1000nm)-structured titanium dioxide (TiO$\textsubscript{2}$) or aluminum oxide layers through a simple spin-coating process.

1, 4 The function of methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) perovskite is akin to that of the 'electron donor' material in donor-acceptor polymer/organic planar- and bulk-heterojunction solar cells (i.e., PHJs and BHJs, two typical configurations of these types of cells). Accordingly, we propose depositing or growing a thin layer of acceptor material on CH$_3$NH$_3$PbI$_3$ perovskite film to create a donor-acceptor contact interface for charge separation, in which the hybrid CH$_3$NH$_3$PbI$_3$/acceptor PHJ yields the photovoltaic effect under irradiation.

Several studies have reported that a thin layer of crystalline CH$_3$NH$_3$PbI$_3$ perovskite is easily prepared by spin-casting a solution of equimolar CH$_3$NH$_3$I and PbI$_2$ (precursor solution) on the substrate.

4–6 However, the process of crystal growth can coarsen the film and markedly degrade device performance or result in device failure. To ensure rapid solvent evaporation and, therefore, inhibit crystal coarsening, we preheated the substrate at an elevated temperature of 60$\textdegree$C for 5min and cast the precursor solution at a high spinning speed of 6000rpm.

Figure 1. (a) Methylammonium lead iodide (CH$_3$NH$_3$I) and PbI$_2$ (precursor solution) dissolves in $\text{-}$butyrolactone solution. (b) Spin-coating process of CH$_3$NH$_3$PbI$_3$ perovskite solution on indium tin oxide (ITO)/glass substrate.

Figure 2. (a) UV-visible spectra of films prepared from $\text{-}$butyrolactone and dimethylformamide (DMF) solutions. (b) The photograph indicates a smooth and uniform topography of perovskite film on the substrate as seen by the naked eye.

Figure 1 shows the CH$_3$NH$_3$PbI$_3$ perovskite solution and spin-coating process we use to prepare the film on an indium tin oxide (ITO)/glass substrate. The film is post-annealed at 100$\textdegree$C for 15min to a thickness of approximately 20–30nm. Figure 2 shows the UV-visible spectrum and a photograph of the film. Its absorption covers a wide range of light from the visible to the infrared region.

Flexible perovskite/PCBM PHJ solar cell

\[ V_{OC} = 0.92 \, V \]
\[ J_{SC} = 7.93 \, mA/cm^2 \]
\[ FF = 0.62 \]
\[ PCE = 4.6 \% \]

UPS (He I) measurement of glass/ITO (ITO-1) and PET/ITO (ITO-2)

\[ \phi = 21.21 - (E_{\text{cut-off}} - E_i) \]

\[ \phi_{\text{ITO-1}} = 4.8 \text{ eV} \]

\[ \phi_{\text{ITO-2}} = 5.2 \text{ eV} \]
Electrode Interfaces to perovskite/fullerene hybrid solar cells

Tuning $V_{oc}$ by the work function of ITO electrode

$\text{CH}_3\text{NH}_3\text{PbI}_3$

PET-ITO 5.2 eV

Glass-ITO 4.8 eV

PEDOT:PSS -5.1~-5.2 -5.4

$\text{C}_6\text{O}$ -4.5

PCBM -3.9

BCP -3.5

Al -4.2

-5.9

-6.2

-7.0

Increase $V_{oc}$
### Perovskite OPVs made by different ITO electrodes

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>perovskite/C₆₀(30nm) (ITO 1)</td>
<td>0.50</td>
<td>5.90</td>
<td>0.64</td>
<td>1.87</td>
</tr>
<tr>
<td>perovskite/C₆₀(30nm) (ITO 2)</td>
<td>0.84</td>
<td>8.18</td>
<td>0.53</td>
<td>3.62</td>
</tr>
<tr>
<td>perovskite/PCBM(20nm) (ITO 1)</td>
<td>0.68</td>
<td>6.57</td>
<td>0.69</td>
<td>3.10</td>
</tr>
<tr>
<td>perovskite/PCBM(30nm) (ITO 2)</td>
<td><strong>1.06</strong></td>
<td>6.20</td>
<td>0.47</td>
<td><strong>3.13</strong></td>
</tr>
<tr>
<td>perovskite/PCBM(20nm) (ITO 2)</td>
<td><strong>0.92</strong></td>
<td><strong>7.93</strong></td>
<td><strong>0.62</strong></td>
<td><strong>4.54</strong></td>
</tr>
</tbody>
</table>

p-NiO interlayer polymer BHJ solar cells

Table 1. Response parameters for the glass/ITO/interlayer/P3HT:PCBM/LiF/Al BHJ photovoltaic devices in Fig. 4

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{oc}$, V</th>
<th>$J_{sc}$, mA/cm²</th>
<th>FF, %</th>
<th>Efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>40-nm PEDOT:PSS</td>
<td>0.624</td>
<td>9.54</td>
<td>40.4</td>
<td>2.40</td>
</tr>
<tr>
<td>Control</td>
<td>0.515</td>
<td>10.7</td>
<td>50.7</td>
<td>2.87</td>
</tr>
<tr>
<td>5-nm NiO</td>
<td>0.634</td>
<td>11.5</td>
<td>63.3</td>
<td>4.75</td>
</tr>
<tr>
<td>10-nm NiO</td>
<td>0.638</td>
<td>11.3</td>
<td>69.3</td>
<td>5.16</td>
</tr>
<tr>
<td>20-nm NiO</td>
<td>0.591</td>
<td>8.83</td>
<td>55.2</td>
<td>2.96</td>
</tr>
<tr>
<td>43-nm NiO</td>
<td>0.586</td>
<td>8.09</td>
<td>52.4</td>
<td>2.55</td>
</tr>
<tr>
<td>77-nm NiO</td>
<td>0.581</td>
<td>7.49</td>
<td>49.8</td>
<td>2.23</td>
</tr>
</tbody>
</table>

The control has the structure: glass/ITO/P3HT:PCBM/LiF/Al. Interlayers in the device column are deposited directly onto ITO.

Irwin et al., PNAS 105, 2783 (2008).
**Solution-processed NiO\(_x\) in polymer BHJ PVs I.**

![Diagram of solar cell structure](image)

<table>
<thead>
<tr>
<th>HTL</th>
<th>(V_{oc}) (mV)</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>(FF)</th>
<th>(PCE) (%)</th>
<th>(\phi_w) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO(_x)</td>
<td>879 ± 7</td>
<td>−11.5 ± 0.4</td>
<td>0.65 ± 0.01</td>
<td>6.7 ± 0.1</td>
<td>−5.3</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>845 ± 8</td>
<td>−11.1 ± 0.1</td>
<td>0.60 ± 0.01</td>
<td>5.7 ± 0.1</td>
<td>−5.1</td>
</tr>
</tbody>
</table>


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Solution-processed NiO\textsubscript{x} in polymer BHJ PVs II.

Table with three different NiO precursor processing temperatures:

<table>
<thead>
<tr>
<th>HTL</th>
<th>$V_{oc}$</th>
<th>$J_{sc}$</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[V]</td>
<td>[mA cm$^{-2}$]</td>
<td>[%]</td>
<td>[%]</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>0.83 (0.005)</td>
<td>12.7 (0.2)</td>
<td>64.2 (0.3)</td>
<td>6.8 (0.1)</td>
</tr>
<tr>
<td>5 nm NiO</td>
<td>0.82 (0.006)</td>
<td>13.9 (0.3)</td>
<td>68.4 (0.4)</td>
<td>7.8 (0.2)</td>
</tr>
</tbody>
</table>

Nickel oxide electrode interlayer in perovskite-based solar cells

Reasons for applying NiO$_x$ as the electrode interlayer

I. NiO$_x$ electrode interlayer is a p-type semiconductor of high work function of 5.4 eV. The alignment of energy level minimizes the interfacial energy losses for the hole transfer and optimizes the photovoltage output of device.

II. The conformal coverage of the perovskite film on NiO$_x$ enhances the light harvesting, reduces the leakage current, increases short-circuit current ($J_{SC}$), and elevates the power conversion efficiency (PCE) of the devices.

III. NiO$_x$ is an inorganic metal oxide in nature.

Photo physical properties of nickel oxide/perovskite

Table 1 | Steady-state photoluminescence quenching efficiency.

<table>
<thead>
<tr>
<th>p-type layers</th>
<th>n-type layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>95</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>99.8</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>99.8</td>
</tr>
<tr>
<td>Spiro-OMeTAD</td>
<td>99.1</td>
</tr>
</tbody>
</table>

The photoluminescence quenching from the perovskite was quantified for both p- and n-type charge collection layers contacting the perovskite absorber. The quenching efficiency was calculated by integrating the photoluminescence spectra over wavelength and comparing with the neat perovskite layer. We note that this is not measured in an integrating sphere, so only represents an estimation of the quenching efficiency.

Perovskite on PEDOT:PSS and NiO$_x$

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Corrected PL Intensity (a.u.)

PEDOT/perovskite
8000 rpm

NiO$_x$/perovskite
8000 rpm

NiO$_x$/perovskite
9500 rpm
UPS (He I) measurement of glass/ITO/PEDOT:PSS and glass/ITO/NiO$_x$

$\phi_{\text{PEDOT:PSS}} = 5.1 \text{ eV}$

$\phi_{\text{NiO}_x} = 5.4 \text{ eV}$
Configurations of NiO$_x$ electrode interlayer perovskite solar cells
NiO$_x$ electrode interlayer perovskite solar cells

Efficient NiO$_x$/perovskite hybrid solar cell, $PCE = 8.0\%$, $V_{OC} = 0.92V$, FF = 0.68

PEDOT/perovskite (8000 rpm)

NiO$_x$/perovskite (8000 rpm)

NiO$_x$/perovskite (9500 rpm)

Photovoltaic parameters of NiO$_x$/perovskite 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$_3$ (9500 rpm)/PCBM</td>
<td>0.62</td>
<td>9.39</td>
<td>0.66</td>
<td>3.9</td>
</tr>
<tr>
<td>b)$^{a}$ NiO$_x$/CH$_3$NH$_3$PbI$_3$ (9500 rpm)/PCBM</td>
<td>0.92</td>
<td>12.43</td>
<td>0.68</td>
<td>7.8</td>
</tr>
<tr>
<td>b)$^{a}$ NiO$_x$/CH$_3$NH$_3$PbI$_3$ (8000 rpm)/PCBM</td>
<td>0.88</td>
<td>13.53</td>
<td>0.58</td>
<td>6.9</td>
</tr>
<tr>
<td>a)$^{b}$ NiO$_x$/CH$_3$NH$_3$PbI$_3$ (8000 rpm)/PCBM</td>
<td>0.72</td>
<td>10.71</td>
<td>0.59</td>
<td>4.6</td>
</tr>
<tr>
<td>c)$^{b}$ NiO$_x$/CH$_3$NH$_3$PbI$_3$ (8000 rpm)/PCBM</td>
<td>0.76</td>
<td>9.51</td>
<td>0.66</td>
<td>4.8</td>
</tr>
<tr>
<td>b)$^{b}$ NiO$_x$/CH$_3$NH$_3$PbI$<em>3$ (9500 rpm)/C$</em>{60}$</td>
<td>0.74</td>
<td>12.95</td>
<td>0.60</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Photovoltaic parameters of p-type mesoscopic perovskite solar cells

Photovoltaic parameters of p-type mesoscopic perovskite solar cells

Table 1 | The photovoltaic parameters of mesoscopic and planar heterojunction NiO/perovskite solar cells. Their IV characteristic curves and IPCE responses are illustrated in Figure 3 (a) and (b) respectively

<table>
<thead>
<tr>
<th>Device</th>
<th>Voltage (mV)</th>
<th>Current Density (mA/cm²)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoscopic NiO&lt;sub&gt;nc&lt;/sub&gt;/Perovskite/PC&lt;sub&gt;71&lt;/sub&gt;BM</td>
<td>1000</td>
<td>14.65</td>
<td>0.64</td>
<td>9.44</td>
</tr>
<tr>
<td>Mesoscopic NiO&lt;sub&gt;nc&lt;/sub&gt;/Perovskite/PC&lt;sub&gt;61&lt;/sub&gt;BM</td>
<td>1040</td>
<td>13.24</td>
<td>0.69</td>
<td>9.51</td>
</tr>
<tr>
<td>Planar NiOx/Perovskite/PC&lt;sub&gt;61&lt;/sub&gt;BM</td>
<td>920</td>
<td>11.77</td>
<td>0.68</td>
<td>7.40</td>
</tr>
</tbody>
</table>

Low temperature sputtered nickel oxide compact layer for mesoscopic NiO/perovskite cells

Photovoltaic parameters of NiO\textsubscript{x} compact layer under different oxygen flow rate

![Image](http://example.com/image.png)

<table>
<thead>
<tr>
<th></th>
<th>A-0-150</th>
<th>B-5-150</th>
<th>B-10-150</th>
<th>B-15-150</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_{OC}) (V)</td>
<td>1.00</td>
<td>1.00</td>
<td>0.96</td>
<td>0.94</td>
</tr>
<tr>
<td>(J_{SC}) (mA/cm(^2))</td>
<td>17.4</td>
<td>18.2</td>
<td>19.8</td>
<td>14.4</td>
</tr>
<tr>
<td>FF</td>
<td>0.61</td>
<td>0.59</td>
<td>0.61</td>
<td>0.60</td>
</tr>
<tr>
<td>PCE (%)</td>
<td>10.7</td>
<td>10.8</td>
<td>11.6</td>
<td>8.1</td>
</tr>
<tr>
<td>integrated IPCE current (mA/cm(^2))</td>
<td>14.06</td>
<td>15.15</td>
<td>15.63</td>
<td>12.99</td>
</tr>
</tbody>
</table>
Photoinduced transient absorption measurement of NiO$_x$/perovskite junction

Long-lived charge-separation species: NiO$^+$

Femtosecond excitonic relaxation dynamics of perovskite on mesoporous films of Al₂O₃ and NiO nanoparticles

Conclusions

• NiOₓ or NiO is an ideal, p-type electrode interlayer for fabricating efficient perovskite-based solar cell.

• Quality of the perovskite films determines the efficiency.

• PHJ perovskite-based solar cell of ~8 % PCE applying NiOₓ electrode interlayer.

• p-type mesoscopic NiO/perovskite-based solar cells of 12 % PCE.

• Fundamental physics, interfaces, operation lifetime……
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