Hybrid organic solar cell with perovskite structure as absorption material and manufacturing method thereof

Introduction
Concern about the increasing energy demands, the harmful ecological impact and global warming drive the development of clean, inexpensive and renewable energy sources. Since the sun is our only external energy source, harvesting its energy, which is clean, non-hazardous and infinite, satisfies the main objectives of all alternative energy strategies. With attractive features, such as good photovoltaic performance, low-cost material, simple processibility, tunable energy gap, application on flexible substrate, hybrid organic solar cell (HOSC) provides promising methods for future large-scale mass production.

Invention
A primary object of the present invention is to provide a HOSC employing perovskite as absorption material and manufacturing method thereof. The embodiment of HOSC is provided in Fig. 1. The HOSC architecture is composed of a conductive substrate (consisting of transparent conductive film covered on glass or flexible substrate), a hole transport layer (PEDOT:PSS, TFB, or PTPD), an active layer, a hole blocking layer (BCP, Bphen, TPyPb, or DPPS) and a negative electrode (Al, Ag, or Au), in which the active layer has a light absorption layer (LAL) and an electron acceptor layer (EAL). The LAL made of perovskite material is represented by the following formula: $C_nH_{2n+1}XY_3$, where $n$ is positive integer from 1 to 9, $X$ is Pb, Sn or Ge, and $Y$ is I, Br or Cl. The EAL is made of fullerene or its derivatives. A planar heterojunction (PHJ) is formed between the LAL and the EAL. The perovskite as a LAL has simple structure and facile fabricating process with relatively low cost, so that it has benefit to carry out the mass production of HOSCs of flexible solid-state form.
A secondary object of the present invention is to provide manufacturing method of the HOSC along with the fabrication of perovskite absorber. HOSC by using C60 or derivatives with different lowest unoccupied molecular orbitals (LUMO) as an EAL, controlling a surface morphology of perovskite material in virtue of casting the precursor at various spinning speed (6000-8000 rpm) and changing the organic solvent (γ-butyrolactone or DMF) of the precursor, or utilizing a conductive substrate with different transparent conductive films, resulting in a power conversion efficiency above 3%.

**Principle**

Figure 2 displays the energy band diagram of HOSC employing fullerene derivatives of C60 and PCBM as electron acceptor. Under irradiation, excitons are generated by the absorption of light in the perovskite absorber. The oppositely charged holes and electrons in excitons are then separated at the donor–acceptor interface, as depicted in Figure 2, and are transported by CH₃NH₃PbI₃ perovskite and electron acceptor (C₆₀ or PCBM), respectively, resulting in the photovoltaic effect.
Experimental data
The current density-voltage (J-V) curve of the HOSC with a power conversion efficiency above 3% is provided in Fig. 3, in which the active layer is made of perovskite(DMF)/C_{60} or perovskite(DMF)/fullerene derivatives. Table 1 provides the photovoltaic characteristics of HOSC employing fullerene or derivatives and perovskite materials dissolved in different solvent.
### Table 1. Comparison of photovoltaic characteristics of different active layers within the hybrid organic solar cell

<table>
<thead>
<tr>
<th>HOSC</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Rs (ohm cm²)</th>
<th>Rx (M ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perovskite(y-butyrolactone)/ C60 (30 nm)</td>
<td>0.55</td>
<td>5.21</td>
<td>0.57</td>
<td>1.6</td>
<td>4.49</td>
<td>2.01</td>
</tr>
<tr>
<td>Perovskite(y-butyrolactone)/ PCBM (25 nm)</td>
<td>0.65</td>
<td>5.89</td>
<td>0.63</td>
<td>2.4</td>
<td>4.50</td>
<td>19.39</td>
</tr>
<tr>
<td>Perovskite(y-butyrolactone)/ ICBA (30 nm)</td>
<td>0.75</td>
<td>5.44</td>
<td>0.51</td>
<td>2.1</td>
<td>8.31</td>
<td>17.21</td>
</tr>
<tr>
<td>Perovskite(DMF)/ C60 (30 nm)</td>
<td>0.55</td>
<td>9.02</td>
<td>0.61</td>
<td>3.0</td>
<td>1.75</td>
<td>0.44</td>
</tr>
<tr>
<td>Perovskite(DMF)/ PCBM (25 nm)</td>
<td>0.60</td>
<td>10.32</td>
<td>0.63</td>
<td>3.9</td>
<td>1.82</td>
<td>3.93</td>
</tr>
<tr>
<td>Perovskite(DMF)/ ICBA (30 nm)</td>
<td>0.58</td>
<td>10.03</td>
<td>0.58</td>
<td>3.4</td>
<td>2.42</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Recent achievements

We provide a solution-processed NiOx thin film as a hole transport layer on the ITO substrate to replace organic PEDOT:PSS and realize CH₃NH₃PbI₃/PCBM PHJ hybrid organic solar cells. A UV-ozone (UVO) treatment of the ITO/NiOx substrate is performed to improve surface wetting capability and resulted in an improvement of the perovskite coverage. The work function of NiOx thin film is further modified to be 5.4 eV for better matching with the valence band (VB) edge of CH₃NH₃PbI₃ perovskite. The hybrid cell composed of ITO/spin-coated NiOₓ/CH₃NH₃PbI₃ (DMF)/PCBM/BCP/Al was provided to deliver an efficiency of 7.8 %. [1] To improve the performance of HOSC, we incorporate a mesoporous NiO as a host to adsorb more amount of perovskite for the improvement of light harvesting. A similar device structure is constructed as ITO/compact NiO/mesoporous NiO/sequentially deposited CH₃NH₃PbI₃/PCBM/BCP/Al. The arrangement of energy level, in which the VB position of NiO is close to that of perovskite and LUMO of PCBM is nearly identical with the CB edge of perovskite, is suitable for receiving high output voltage and minimizing energy loss for charge separation process between the absorber and selective contacts. The champion cell delivers a Voc of 1.04 V, a Jsc of 13.24 mA/cm², and a FF of 69 %, leading to an overall efficiency of 9.51 %. [2] Furthermore, we introduce a low-temperature sputtered NiOx film to serve as a pinho-less compact layer for optimizing charge collection losses in the NiO/perovskite interface. High quality of NiOx compact layer formed by sputter deposition has benefits to the charge collection, leading to a remarkable improvement in device performance and reproducibility as compared to the PSCs employing solution-processed NiOx. [1] A full device of ITO/sputtered-compact NiO/mesoporous NiO/sequentially deposited CH₃NH₃PbI₃/PCBM/BCP/Al is demonstrated, in which the compact NiOx layer is deposited by RF magnetron sputtering system in pure Ar gas or reactive sputter method under a mixture of Ar and O₂ gas. By optimizing the oxygen doping ration of
10% and the thickness of mesoporous NiO layer, a decent PCE of 11.6% is obtained.

[3] We further propose Ni/Au bilayer to simultaneously function as HTM and conductive electrode by oxidizing this e-beam-sputtered film in O₂ atmosphere with annealing process. The bi-functional p-type electrode composed of proper thickness of Ni (10 nm) and Au (7 nm) under an annealing temperature of 500°C shows decent optical transparent (transmission > 60% in the visible spectrum), good electrical conductivity and favorable work function matching the VB of perovskite. A transparent conductive film-free HOSC is fabricated with a device configuration of glass/Au: NiOₓ/gas-assisted deposition CH₃NH₃PbI₃/C₆₀/BCP/Al, delivering a JSC of 13.04 mA/cm², a VOC of 1.02 V, a FF of 0.77 and a decent PCE of 10.24%. [4]

References