HIGH PERFORMANCE PEROVSKITE HYBRID SOLAR CELL
VIA INTERFACIAL ENGINEERING

A Thesis

Presented to

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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ABSTRACT

Perovskite (CH$_3$NH$_3$PbI$_3$ based materials) hybrid solar cell has been one of the most promising photovoltaic devices due to its lots of advantages such as low price of raw materials, easy fabricating procedure and relatively high power conversion efficiency (PCE) (compared to polymer solar cells) and so on. However, the still not very high efficiency of perovskite hybrid solar cells makes it at a disadvantageous position in the competition with traditional silicon solar cells. Thus, to make it more competitive, efficiency enhancement comes as a vital issue which need to be addressed.

There are three chapters in this thesis.

In chapter 1, a general introduction of perovskite hybrid solar cells including working mechanism and development is given out.

In chapter 2, we use the electrochemical material PSBEDOT to function as the hole transfer layer to observe the high performance of perovskite devices.

In chapter 3, to improve the efficiency of perovskite hybrid solar cells, we have blended commercially available Fe$_3$O$_4$ nanoparticles in to the active layer of perovskite hybrid solar cells to see any performance improvement. To further enhance the device performance, some magnetic treatments have been conducted in the perovskite layer of the device including the involvement of magnetic nanoparticles and external magnetic field. Finally, we have obtained a result with PCE reaching at 14.40% accompanied with a dramatically enhanced short current density.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>vii</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION TO PEROVSKITE SOLAR CELLS</td>
<td>1</td>
</tr>
<tr>
<td>1.1 World Energy Consumption and Energy Crisis</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Introduction to Solar Cell Devices</td>
<td>3</td>
</tr>
<tr>
<td>1.3 Perovskite Solar Cells</td>
<td>4</td>
</tr>
<tr>
<td>1.4 Device Fabricating Process</td>
<td>12</td>
</tr>
<tr>
<td>1.5 High Performance Perovskite Hybrid Solar Cells</td>
<td>14</td>
</tr>
<tr>
<td>II. HIGH PERFORMANCE PEROVSKITE DEVICE USING PSBEDOT AS HOLE TRANSFER LAYER (HTL) MATERIAL</td>
<td>17</td>
</tr>
<tr>
<td>2.1 Motivation of Research</td>
<td>17</td>
</tr>
<tr>
<td>2.2 Experimental Section</td>
<td>17</td>
</tr>
<tr>
<td>2.3 Results and Discussions</td>
<td>20</td>
</tr>
<tr>
<td>III. EFFICIENT CHARGE CARRIER TRANSFER IN HIGH QUALITY CH3NH3PBI3 FILM BASED PEROVSKITE HYBRID SOLAR CELLS VIA MAGNETIC TREATMENT</td>
<td>24</td>
</tr>
<tr>
<td>3.1 Motivation of Research</td>
<td>25</td>
</tr>
<tr>
<td>3.2 Magnetic Treatment by Using Water-soluble Magnetic Fe3O4 Nanoparticles</td>
<td>27</td>
</tr>
</tbody>
</table>
3.3 Magnetic Treatment by Using Ethanol-soluble Magnetic Fe$_3$O$_4$ Nanoparticles .................................................................................................................................29

3.4 Conclusion .................................................................................................................................56

REFERENCES ........................................................................................................................................57
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Device Performance of Each Experimental Group</td>
</tr>
<tr>
<td>2.2</td>
<td>Conductivity Independence vs. Film Thickness</td>
</tr>
<tr>
<td>3.1</td>
<td>PCE Characteristic Parameter With and Without Magnetic Field</td>
</tr>
<tr>
<td>3.2</td>
<td>Device Performance of Each Experimental Group</td>
</tr>
<tr>
<td>3.3</td>
<td>Comparison of Device Performance by Magnetic Treatment</td>
</tr>
<tr>
<td>3.4</td>
<td>Device performance of different blending concentrations</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>2</td>
</tr>
<tr>
<td>1.3</td>
<td>3</td>
</tr>
<tr>
<td>1.4</td>
<td>3</td>
</tr>
<tr>
<td>1.5</td>
<td>4</td>
</tr>
<tr>
<td>1.6</td>
<td>5</td>
</tr>
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<td>1.7</td>
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<td>1.8</td>
<td>6</td>
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<td>1.9</td>
<td>7</td>
</tr>
<tr>
<td>1.10</td>
<td>8</td>
</tr>
<tr>
<td>1.11</td>
<td>9</td>
</tr>
<tr>
<td>1.12</td>
<td>9</td>
</tr>
<tr>
<td>1.13</td>
<td>11</td>
</tr>
<tr>
<td>1.14</td>
<td>11</td>
</tr>
<tr>
<td>1.15</td>
<td>12</td>
</tr>
<tr>
<td>1.16</td>
<td>13</td>
</tr>
<tr>
<td>1.17</td>
<td>14</td>
</tr>
</tbody>
</table>
1.18 Cross section SEM images and band alignment of perovskite solar cell ..........15
1.19 J-V curve and efficiency of perovskite solar cell .................................................15
2.1 Chemical structure of PSBEDOT ........................................................................17
2.2 Device structure ..................................................................................................18
2.3 Synthesis schematic of PSBEDOT .......................................................................19
2.4 J-V curves of each experimental group ..................................................................20
2.5 Absorption curve ..................................................................................................21
2.6 J-V curves under dark condition ...........................................................................22
2.7 Impedance spectra ..............................................................................................23
3.1 Schematic procedure of fabricating magnetic treated CH₃NH₃PbI₃ film ..................33
3.2 Characterizations of magnetic Fe₃O₄ nanoparticles dissolved in ethanol ............34
3.3 Film morphology investigation images ..................................................................36
3.4 GIWAXS and XRD pattern of pristine CH₃NH₃PbI₃ film ......................................39
3.5 Mobility test ........................................................................................................42
3.6 Time resolved PL spectra of each experimental group .......................................43
3.7 Characterizations for pero-HSCs ..........................................................................44
3.8 Histograms of PCE distribution of each experimental group ..............................46
3.9 J-V curves under different scan rate and different scan direction of each experimental group ...........................................................................................................47
3.10 Stability figure of pero-HSCs ..............................................................................48
3.11 Schematic of synthesis procedure of Fe₃O₄ nanoparticle .................................49
3.12 Structure and morphology of Fe (acac)₃ and TREG ............................................49
3.13 Products morphology .........................................................................................50
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.14</td>
<td>FT-IR spectra of Fe$_3$O$_4$ nanoparticles dissolved in ethanol</td>
<td>51</td>
</tr>
<tr>
<td>3.15</td>
<td>TEM images of Fe$_3$O$_4$ nanoparticles dissolved in ethanol with different scale bar</td>
<td>52</td>
</tr>
<tr>
<td>3.16</td>
<td>Chemical structures of material used in perovskite hybrid solar cells</td>
<td>53</td>
</tr>
<tr>
<td>3.17</td>
<td>Device fabricating procedure</td>
<td>53</td>
</tr>
<tr>
<td>3.18</td>
<td>J-V curves of device under magnetic field</td>
<td>54</td>
</tr>
<tr>
<td>3.19</td>
<td>XRD pattern comparison of pristine perovskite device and the perovskite device under external magnetic field</td>
<td>55</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION TO PEROVSKITE SOLAR CELLS

1.1 World Energy Consumption and Energy Crisis

The following figure (Figure 1.1) briefly shows the statistical data of the percentage of each energy source in the global energy consumption in 2014. From the pie chart, the main energy source retains as three major fossil fuels-coal, oil and gas, which occupy 86% of the whole energy needs. By contrast, the solar energy (orange one in the pie chart) share nearly 0% in the total energy need. However, we all know that the fossil energy is limited and will be used up sooner or later. The following Figure 1.2 shows the estimated life time of each type fossil energy source. These two figures show that we human are suffering energy crisis nowadays and the following Figure 1.3 shows estimated energy transformation style in the past 200 years and the future 100 years, meanwhile, points the proper solution of the energy crisis-finding new clear energy source to replace the fossil energy. What we will talk in this paper-solar cells, is one of the most important energy sources in the new energy forms.
Figure 1.1. Statistical review of world energy 2015.


Figure 1.2. Fossil energy evolution and estimation.

http://prosandconsbiomassenergy.org/category/biomass-energy/
1.2 Introduction to Solar Cell Devices

Solar cell is a device which can transfer solar energy into electrical energy. The external structure of the solar cell device is shown in the Figure 1.4. The internal structure of the device is shown in the Figure 1.5, which introduce the working principles of the solar cell-light inducing into the active layer, holes and electrons.
generating and then transferring through the transporting layer and finally gathering at the electrode, forming the photo current.

Figure 1.5. Working principles of solar cell device.

http://home.howstuffworks.com/solar-light2.htm

1.3 Perovskite Solar Cells

Perovskite solar cells is a kind of solar cell device which use perovskite based material as the light absorbing layer.

1.3.1 Working mechanisms and development

Solar cells are usually composed of an N-type semiconductor and a P-type semiconductor. When the solar light is shining on the active layer in the solar cell, it can produce two excitons-electrons and holes. Then the electrons with negative charge transport through the N-type semiconductors (also called acceptor) finally gather around the cathode while the holes with positive charge transport through the P-type semiconductor (also called donor) finally gather around the anode. When you apply load in the external circuit, there will be current flows between the cathode and the anode. This is how photocurrent generates. Figure 1.6 is a rough description of the generation of photocurrent.
Figure 1.6. Basic working mechanisms of solar cell device.

Traditional silicon solar cell has limited development prospect due to its high cost in the silicon refining processing and pollution issue.\[1\] Meanwhile, polymer solar cells, which comes to another option for the solar cell device, does not have the very high device performance.\[2][3\] In recent years, the methyl ammonium lead halide perovskite (CH$_3$NH$_3$PbI$_3$) materials have emerged as promising candidates due to their excellent optical and electrical properties \[4-11\] such as the large light absorption coefficient ($5.7 \times 10^4$ cm$^{-1}$ at 600 nm)\[12\], high charge carrier mobility (hole mobility of 164 cm$^2$ V$^{-1}$ S$^{-1}$ and electron mobility of 24 cm$^2$V$^{-1}$S$^{-1}$ for CH$_3$NH$_3$PbI$_3$ single-crystal perovskite)\[13\], long charge diffusion length (~100nm)\[14,15\], easy fabricating procedure (solution-processing) etc. The following figures show the basic working mechanism of the perovskite layer and the development of perovskite solar cells compared to other type solar cells. The role that perovskite layer play in the total device structure is functioning as the active layer (also called light absorbing layer) (see Figure 1.7). Charge carriers then transport through hole transfer layer (HTL) and
electron transfer layer (ETL), gather at the corresponding electrode, form the photocurrent. That is how perovskite solar cells work. As for the device performance, from Figure 1.8 we can see, although perovskite solar cells have been researched for only a few tears, the efficiency has a huge improving which indicate that perovskite will be a very prospect material in photovoltaic field. [16]

Figure 1.7. Working mechanisms of perovskite layer.

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Figure 1.8. Device efficiency development.

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1.3.2 Component and properties of perovskite

Molecule structure. The perovskite chemical structure used in perovskite solar cells is CH$_3$NH$_3$PbX$_3$ (X=Cl, Br, I or their mixture). The name perovskite comes from CaTiO$_3$, a common mineral discovered by a Russian Mineralogist L. A. Perovski in 19$^{th}$ century. After the discovery, the definition of perovskite has changed into the materials that have ABO$_3$ structure. In 1991, German scientist David Mitzi firstly used perovskite materials in organic photovoltaics (OPV) field. $^{[17]}$ There are three major perovskite crystal structures-cubic, tetragonal and orthorhombic. The crystal structures are shown in the following figure.

![Perovskite crystal structures](image)

(a)Cubic structure   (b) Tetragonal structure (c) Orthorhombic structure

Figure 1.9. Perovskite crystal structures.

Properties of perovskite materials. Perovskite materials have unique optical and electrical properties, which make it as a promising photovoltaic material. The band gap of CH$_3$NH$_3$PbX$_3$ can be tuned by changing the mixture ratio of I and Br.$^{[18]}$ The band gap of MAPbI$_3$ and MAPbBr$_3$ are shown in the following Figure 1.10. The band gap of MAPbI$_3$ and MAPbBr$_3$ have an obvious difference due to the original difference of the crystal structure (Figure 1.11) between MAPbI$_3$ and MAPbBr$_3$. 

7
materials, which means, by using Br⁻ to replace I⁻ in MAPbI₃, we can get different band gap materials to facilitate the best device performance. Professor Jun Hong Noh investigate the energy band gap of the MAPb(I₁₋ₓBrₓ)₃ with different x, and finally get the conclusion \(E_g(x)=1.57+0.39x+0.33x^2\). [¹⁸] The following graph (Figure 1.12) illustrates the relationship obviously. The band gap tuning of the MAPb(I₁₋ₓBrₓ)₃ material shows great potential because it can match the energy gap of hole transport layer(HTL) and the electron(ETL) more easily, which make the choices of materials more variable.

![Figure 1.10. Band gap alignment of MAPbI₃ and MAPbBr₃.](image)

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Figure 1.1. Crystal structure of MAPbI$_3$ (distorted tetragonal perovskite) and MAPbBr$_3$ (cubic perovskite structure).

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Figure 1.12. The relationship of the bad gap of MAPb(I$_{1-x}$Br$_x$)$_3$ with the change of Br proportion(x).

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1.3.3 Device structures

Planar heterojunction (PHJ) structure. The planar heterojunction (PHJ) device structure was shown in Figure 1.13. There are usually two basic device structures—conventional structure and inverted structure. The total cell structure is consist of several layers which are packed on the ITO glass. For conventional structure, a high electrical conductivity conjugated polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) was functioned as the hole transfer layer (HTL) on the ITO substrate. Perovskite layer was functioned as the active layer to absorb the sunlight was spin-coated on the surface of PEDOT: PSS. On the top of perovskite active layer usually exists an electron transfer layer (ETL), whose function is transporting electrons to cathode. The last layer cathode is thermal deposited on the ETL layer. The \( \text{CH}_3\text{NH}_3\text{PbI}_3 / \) fullerene planar heterojunction structure was introduced by Jeng et al. \[^{[19]}\] As for the inverted structure, the differences are the electrons (holes) flow direction. Usually the ITO glass is used as the cathode while the topside layer was functioned as anode. Using low temperature solution processed \( \text{TiO}_x \) as electron extraction layer and fullerene derivate \( [6,6]\)-phenyl-C61-butyric acid methyl ester (PC\(_{61}\)BM) as ETL was first introduced by C, Liu. The PCE of this structure can reach 14.6\%. \[^{[20]}\]
Bulk heterojunction (BHJ) structure. A drawback of the perovskite structure is the diffusion length of electrons and holes are different ($L_{\text{eff, e}}/L_{\text{eff, h}} < 1$).\(^{[21]}\) To obtain the higher PCE of pero-HSCs (perovskite hybrid solar cells), Kai from our lab fabricated the bulk heterojunction perovskite hybrid solar cells (Figure 1.14), and got a 22% enhancement of Fill Factor (FF) in the device performance. The final PCE of the cell can reach nearly 14%.\(^{[22]}\)

Figure 1.14. The comparison of planar heterojunction structure (PHJ) and bulk heterojunction structure (BHJ).
Meso-superstructured (MS) structure. The reason why we use Meso-superstructured (MS) structure is that the MS structure is also a solution for the low FF caused by the different diffusion length of holes and electrons in pero-HSCs.\textsuperscript{[23]} In MS structure, a compact TiO$_2$ layer is deposited to enlarge the contact area of the active layer and the electron transfer layer (ETL), which gives a huge enhancement of FF.\textsuperscript{[24][25]} The device structure was firstly developed by Dr. M. M. Lee, he finally got a PCE value based on this device structure at 10.9\%.\textsuperscript{[23]} The device structure is shown in figure 1.15.

![Figure 1.15. The MS structure of perovskite hybrid solar cells.](image)

Copyright © 2012, American Association for the Advancement of Science\textsuperscript{[23]}

1.4 Device Fabricating Process

According to the difference of method fabricating active layer, there are usually two fabricating processes of active layer in perovskite hybrid solar cells- one step process and two-step process.
1.4.1 One step process fabricating perovskite layer

One step process of fabricating the active layer is extensively used in pero-HSCs. For one step process, the perovskite film is fabricated by the the mix solution of MAI and PbX2 (X=I, Br, I). The mole ration of each component is 1:1. The mix solution is usually dissolved in dimethylformamide (DMF) or dimethyl sulfide (DMSO) solvent, and then the solution is put under stirring for several hours. After these preparation procedures, the solution is drop casted or spin-coated on the substrate. After the spin-coating, usually a thermal annealing is conducted of the perovskite film to guarantee the sufficient reaction of the two components. The following Figure 1.16 shows the preparing process of perovskite film by one-step process. PbI2 is firstly spin-coated as the precursor and then MAI is spin-coated on the top of PbI2 layer. [26] [27] [28]

![Figure 1.16. Schematic illustration of one step process preparing perovskite film.](image)

Copyright © 2009, American Chemical Society [26]

1.4.2 Two-step process fabricating perovskite layer

Sequential deposition is widely used in the two-step process, [29] which divide the active perovskite layer into two parts-MAI and PbI2. The PbCl2 and PbBr2 cannot be
used because of the solubility issue.\textsuperscript{[30]} PbI\textsubscript{2} is dissolved in DMF or DMSO while and MAI is dissolved in ethanol or isopropanol. The PbI\textsubscript{2} solution is first spin-coated on the electrode buffer layer and then the MAI is spin-coated on the surface of PbI\textsubscript{2} solution. After the spin-coating, the perovskite film is annealed at 100°C for two hours. The total procedure is shown in the Figure 1.17.\textsuperscript{[31][32][33]}

Figure 1.17. Schematic illustration of two-step process perovskite film.

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1.5 High Performance Perovskite Hybrid Solar Cells

Obtaining perovskite devices of high performance is one of the most important goal we need to achieve in our future plan. Several methods are conducted including the interfacial engineering of perovskite layer, excitation transfer layer and so on. Yang Yang’s group has reported one method to fabricate perovskite device with power converted efficiency (PCE) approaching nearly 20%. Traditional perovskite device structure is active layer (perovskite layer) is sandwiched between hole transfer layer and electron transfer layer, where hole transfer layer is PEDOT: PSS or Spiro-OMeTAD usually and electron transfer layer is PCBM usually, respectively. In their experimental procedure, they use Yttrium-doped TiO\textsubscript{2} (Y-TiO\textsubscript{2}) to replace PCBM as electron transfer layer by fabricating inverted perovskite device structures.
From the cross section SEM image of perovskite solar cell, we can observe that the Y-TiO$_2$ layer is a very thin layer adhere on the ITO a layer. Meanwhile, the band alignment of the perovskite solar cell indicates that favorable alignment between the minimum conduction band of the Y-TiO2 and the HOMO of spiro-OMeTAD with the minimum conduction band and maximum valance band of the perovskite allows for the more efficient extraction process of photo generated carriers with less inducing excessive interface recombination, which is the original reason for the high...
performance of perovskite solar cells. The highest efficiency of perovskite solar cells
can reach 19.3% with a dramatically high $V_{OC} \ @ 1.13V$, which shows promising
future of the development of perovskite solar cells.
CHAPTER II

HIGH PERFORMANCE PEROVSKITE DEVICE USING PSBEDOT AS
HOLE TRANSFER LAYER (HTL) MATERIAL

2.1 Motivation of Research

Traditional hole transfer layer (HTL) material in perovskite hybrid devices is PEDOT: PSS. However, the water-soluble PEDOT: PSS usually gives acidity, which will prejudice the CH$_3$NH$_3$PbI$_3$ layer which is sensitive to the water. To solve this problem, a new HTL material- PSBEDOT is introduced to the perovskite device.

2.2 Experimental Section

In the experiment, we use the crosslinked PSBEDOT (a new conjugated polymer) to replace original PEDOT: PSS to function as the hole transfer layer. The chemical structure of the crosslinked PSBEDOT is shown as the Figure 2.1. And the total device structure is shown as the following Figure 2.2. The only difference between experimental group and pristine group is the hole transfer layer material.

Figure 2.1. Chemical structure of PSBEDOT.
As shown in Figure 2.3, the monomer of PSBEDOT-SBEDOT is synthesized by using three-step method as reported. In the first step, EDOT-Cl is firstly synthesized as the precursor and then an amidogen group is introduced into the reacting system and then the product is followed by the introducing of 1,3-propanesultone and then the final target product-SBEDOT is obtained. To get the conjugated polymer PSBEDOT, we use electro-polymerization method to prepare the surface of conjugated PSBEDOT which is attached on the surface of ITO glass. When the conjugated polymer PSBEDOT is compared with the pristine HTL material in perovskite solar cell device (PEDOT), advantages are shown obviously. For pristine PEDOT, we usually put it doped with strong acid to increase the conductivity of the material like PSS to form PEDOT: PSS, however, this may cause the degradation between the PEDOT layer and the active perovskite layer, which comes to an essential issue for the final device performance. Since the conjugated PSBEDOT is synthesized by using electrochemical method, no acidic dopants or leachable are added, the degradation issue does not need to be considered.
Figure 2.3. Synthesis schematic of PSBEDOT.

Thickness of HTL layer in solar cell device is a very important parameter in the device performance. When the thickness increase, the HTL layer can absorb more light and there will be more photons induced in the active layer which facilitate the photocurrent generation. When the thickness decrease, although the induced photon number may decrease, the charge transfer length in HTL will also be decreased, which may facilitate the charge transfer process in HTL layer in the total charge transfer process. In one word, thickness control of HTL material very important in the final device performance. For the pristine PEDOT: PSS, the thickness is usually controlled as around 40nm. However, for the conjugated PSBEDOT, we should investigate to find the best thickness of PSBEDOT film. The thickness of pristine PEDOT: PSS film can be controlled by using the different RPM speed in the spin procedure of fabricating PEDOT: PSS layer. For the conjugated PSBEDOT layer, the film thickness can be controlled by using different current and time in the electro-polymerization procedure.
2.3 Results and Discussions

To optimize the best experimental condition, device performance is firstly checked. The following figure (Figure 2.4) shows the J-V curves of each experimental PSBEDOT group (different thickness) compare pristine PEDOT: PSS group (thickness of 40nm). And the device performance comparison is shown the following Table 2.1. By the comparison, obvious difference can be seen between the experimental group and pristine group. (electrochemical PEDOT=PSBEDOT)

![J-V curves of each experimental group](image)

Figure 2.4. J-V curves of each experimental group.

<table>
<thead>
<tr>
<th>Active Layer</th>
<th>V&lt;sub&gt;OC&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine PEDOT:PSS</td>
<td>0.85</td>
<td>16.07</td>
<td>75.9</td>
<td>10.36</td>
</tr>
<tr>
<td>20nm electrochemical PEDOT</td>
<td>0.90</td>
<td>14.37</td>
<td>72.1</td>
<td>9.32</td>
</tr>
<tr>
<td>40nm electrochemical PEDOT</td>
<td>1.00</td>
<td>16.05</td>
<td>73.0</td>
<td>11.71</td>
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<tr>
<td>60nm electrochemical PEDOT</td>
<td>0.90</td>
<td>15.35</td>
<td>71.9</td>
<td>9.93</td>
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<tr>
<td>80nm electrochemical PEDOT</td>
<td>0.90</td>
<td>12.06</td>
<td>68.8</td>
<td>7.47</td>
</tr>
</tbody>
</table>

Table 2.1 Device Performance of Each Experimental Group

For the PSBEDOT group, we can see, the open circuit voltage (V<sub>OC</sub>) has an obvious increasing compared to the pristine PEDOT: PSS. And when the thickness of
PSBEDOT is controlled as 40nm, the device performance is best, which is corresponding to the thickness control balance mentioned before.

For the characterization, absorption spectra is firstly checked. From the absorption spectra (Figure 2.5), we can see, there is an increasing of absorbing light followed with the increasing thickness of PSBEDOT, however, all the absorbance curves of PSBEDOT under different conditions are locating on the top of pristine PEDOT absorption curve, which indicating there are fewer photons penetrating the PSBESOT layer than the PEDOT layer, which may come to another explanation for the decreasing photocurrent for the PSBEDOT based perovskite hybrid solar cells.

![Absorbance spectra(based on ITO glass)](image)

Figure 2.5. Absorption curve.

Meanwhile, the dark current of the perovskite devices are also checked to further investigate the influence to the perovskite device of different HTL materials. Figure 2.6 shows the J-V curves of different HTL materials under dark condition. Based on the model of J-V curves of perovskite hybrid solar cells, VOC can be approximately calculated by the following empirical formula: where $J_0$ is the reverse dark current.
density, $J_{ph}$ is the voltage-dependent photocurrent produced by the cells. The decreasing dark currents in the reverse bias region should be original reason for the increasing $V_{OC}$ value in the PEBEDOT group.

Figure 2.6. J-V curves under dark condition.

Impedance spectra (IS) is also conducted to investigate and characterize charge carrier transfer process. The major difference of charge carrier transfer process comes from the various value of $R_{CT}$. For the pristine PEDOT: PSS layer, the $R_{CT}$ value is the smallest at around $1050 \, \Omega$, meanwhile, for the PSBEDOT group, with the increasing value of the thickness of PSBEDOT, there shows an increasing trend of $R_{CT}$ value, which indicating an inefficient charge transfer process gradually. Therefore, the increasing $R_{CT}$ value should be the original source for the decreased short current density in the PSBEDOT group.

Table 2.2 shows the conductivity value variation with the PSBEDOT film thickness increasing, when the film thickness increasing from 20nm to 40nm, there is a huge decreasing conductivity value, however, when the thickness decrease from 40nm to
80nm, the decreasing value becomes small. The phenomenon indicates there existing an increasing of conductivity with the increasing of film thickness because of the stack effect, meanwhile, the little difference between film thickness of 40nm, 60nm and 80nm explain why the 40nm PSBEDOT film gives the best device performance.

By the replacement of PSBEDOT, we can see when the film thickness is 40nm, the device gives a best performance at 11.71% with the V_{OC} at 1.0V and J_{SC} at 16.05 mA/cm^{2}, which demonstrate that the PSBEDOT indeed is a good option for the hole transfer layer.

![Impedance spectra (IS).](image)

**Figure 2.7.** Impedance spectra (IS).

**Table 2.2 Conductivity Independence vs. Film Thickness**

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Conductivity(s/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20nm</td>
<td>472.6</td>
</tr>
<tr>
<td>40nm</td>
<td>398.6</td>
</tr>
<tr>
<td>60nm</td>
<td>391.3</td>
</tr>
<tr>
<td>80nm</td>
<td>389.4</td>
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23
CHAPTER III

EFFICIENT CHARGE CARRIER TRANSFER IN HIGH QUALITY CH$_3$NH$_3$PbI$_3$

FILM BASED PEROVSKITE HYBRID SOLAR CELLS VIA

MAGNETIC TREATMENT

The efficiency of the conventional low-temperature (100° C) solution-processed perovskite hybrid solar cells (pero-HSCs) fabricated by two-step method is closely related to the film morphology and polycrystalline patterns of the perovskite light harvester layer. In this study, we blended the Fe$_3$O$_4$ magnetic nanoparticles (MNPs) into the CH$_3$NH$_3$PbI$_3$ perovskite film and employed an external magnetic field (EMF) to tune the film morphology of the CH$_3$NH$_3$PbI$_3$: MNPs Nano-composites during the crystallization procedure. A high quality perovskite active layer was consequently achieved with dramatically reduced trap-density and significantly enhanced charge carrier mobility, which facilitates the charge carrier transfer process in the perovskite layer, thereby reducing the energy loss concomitantly. An enhanced photocurrent of 21.56 mA/cm$^2$ and a corresponding high efficiency of 14.40% has been realized with a dramatically reduced photocurrent hysteresis behavior and obvious enhanced device lifetime. Our method of using Fe$_3$O$_4$ MNPs and EMF treatment to enhance the device performance of pero-HSCs via manipulating the perovskite thin film quality offers an easy but effective way to efficient pero-HSCs.
3.1 Motivation of Research

Solar energy as a clean and renewable energy source has been proved to be a promising candidate for future energy. While currently employed photovoltaic devices are mainly based on the inorganic silicon materials, the relative high power conversion efficiency (PCE) of which is at the high expense of critical processing technics as well as sever environmental issues. Meanwhile the low dielectric constant induced strong exciton binding energy, as well as the uncertainty in the active layer morphology in organic semiconducting materials still limit PCEs of organic solar cells. In recent years, the methylammonium lead halide perovskite (CH$_3$NH$_3$PbI$_3$) materials have emerged as promising candidates due to their excellent optical and electrical properties such as the large light absorption coefficient (5.7 $\times$ 10$^4$ cm$^{-1}$ at 600 nm), high charge carrier mobility (hole mobility of 164 cm$^2$ V$^{-1}$ S$^{-1}$ and electron mobility of 24 cm$^2$ V$^{-1}$ S$^{-1}$ for CH$_3$NH$_3$PbI$_3$ single-crystal perovskite), long charge diffusion length (~100nm), easy fabricating procedure (solution-processing) etc. The PCE of CH$_3$NH$_3$PbI$_3$ based pero-HSCs has already surged to over 20% since it was firstly introduced in dye-sensitized solar cells (DSSC) by A. Kojima in 2009. Over the past six years, besides extending the materials of CH$_3$NH$_3$PbI$_3$ perovskite by congener substitution, the major efforts have been focused on the technics to improve the device performance via optimizing the thin film quality of perovskite, and optimizing the device structures. Although there have been fundamental studies including the photocurrent hysteresis, charge transport on the material science as well as pero-HSCs device physics, most of them are based
on the electrical field-induced behavior of perovskite materials or pero-HSCs devices. While the magnetic field-induced behavior has rarely addressed until recently Varden’s group did some fundamental research on the magnetic field effects in perovskite devices, measured the significant magneto-photocurrent, magneto-electroluminescence and magneto-photoluminescence responses in perovskite thin films and explained the high-efficiency charge separation in pero-HSCs devices.\textsuperscript{[56]} Nevertheless, the effect of magnetic field on the crystallization of perovskite thin film as well as the resulting film morphology are rarely addressed, knowing that the magnetic field can affect the packing of PbI\textsubscript{2} polycrystalline during filming process is very meaningful for our work. In addition, the magnetic field-induced morphological change can also be strengthened by introducing the magnetic nanoparticles (MNPs) such as Fe\textsubscript{3}O\textsubscript{4} MNPs.\textsuperscript{[16]}

In this scenario, we employed a tiny amount of Fe\textsubscript{3}O\textsubscript{4} MNPs into the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite light harvester and applied an external magnetic field (EMF) to tune the film morphology during the crystallization process. Consequently a high quality active layer was realized with dramatically reduced pin-holes and thus enhanced charge carrier mobility. The enhanced charge transfer properties of the active layer significantly boosted the photocurrent from 16.07 mA/cm\textsuperscript{2} of control device to 21.56 mA/cm\textsuperscript{2} of pero-HSCs with magnetic treatment.
3.2 Magnetic Treatment by Using Water-soluble Magnetic Fe₃O₄ Nanoparticles

Since perovskite structure is proved to have magnetism, we tried to add some magnetic nanoparticles to the active layer to facilitate the alignment of perovskite crystal structure.

3.2.1 Experimental section

Devices are fabricated on the clean ITO glass. First, put the clean ITO glass under the ultraviolet for 40 minutes. Then PEDOT: PSS is spin-coated on the substrate. After the spin-coating, the glass is annealing at 150°C for 10 minutes. The perovskite (CH₃NH₃PbI₃) film is fabricated by two step process. First, the PbI₂ dissolved in DMF is spin-coated on the PEDOT: PSS surface. After that, the glass is annealing at 70°C for 10 minutes. Then the glasses are divided into two parts. The MAI blended with magnetic Fe₃O₄ nanoparticles dissolved in ethanol is spin-coating on the surface of PbI₂ film. Another group is the control group, the pure MAI dissolved in ethanol is also spin-coated. After fabricating the perovskite film, the glass is heating at 100°C for two hours. During the heating process, the perovskite is crystallizing. We conduct an external a magnetostatic field during this process. Both the pure MAI and the MAI blended with magnetic Fe₃O₄ nanoparticles samples are under magnetostatic field. So the total samples are divided into four groups: pure MAI without magnetostatic field, pure MAI with magnetostatic field, MAI blended with magnetic Fe₃O₄ nanoparticles without magnetostatic field and MAI blended with magnetic Fe₃O₄ nanoparticles with magnetostatic field. Then PC₆₁BM film is spin-coated at the chilled glass. Then Al is evaporated in vacuum environment as the cathode.
In the experiment, several different blending concentrations were tried. The blending concentration cannot be too high because the magnetic Fe$_3$O$_4$ nanoparticles is dissolved in water while MAI may have some reactions with water. The blending concentration we have tried are 0.5% and 1.0%.

3.2.2 Results and discussions

The following table shows the efficiency value of each experimental group. From the comparison of the device performance we can see that by blending magnetic Fe$_3$O$_4$ nanoparticles into perovskite structure and conducting external magnetostatic field on the perovskite structure, the PCE has an obvious enhancement due to the great increasing of J_{sc}. By using magnetic as the only variable quantity, we can find that the J_{sc} has a great improvement, which proves that the external magnetostatic field is the main influence factor of the increasing J_{SC}.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAI</td>
<td>0.8499</td>
<td>16.0702</td>
<td>75.9%</td>
<td>10.3612%</td>
</tr>
<tr>
<td>MAI+0.5% Fe$_3$O$_4$ NPs</td>
<td>0.8500</td>
<td>17.2897</td>
<td>77.1%</td>
<td>11.3308%</td>
</tr>
<tr>
<td>MAI+1.0% Fe$_3$O$_4$ NPs</td>
<td>0.8500</td>
<td>16.3109</td>
<td>81.3%</td>
<td>11.2669%</td>
</tr>
</tbody>
</table>

Table 3.1 PCE Characteristic Parameter With and Without Magnetic Field

As we mentioned before, perovskite structure is proved to have magnetism. By blending magnetic Fe$_3$O$_4$ nanoparticles into perovskite structure during its crystal process, the conducting external magnetostatic field may help the total crystal process
more perfect like change the crystal orientation due to its effect on the extra magnetic Fe₃O₄ nanoparticles. It may become benefit to get a more structured perovskite film, which may enhance the charge carrier mobility and cause the increasing Jₑₑₑₑ.

From the comparison it can be seen that the Vₑₑₑₑ of the device have a little decrease by adding external magnetostatic field. That indicates the external magnetostatic field may have impact on the crystal process like reacting with some component. Nevertheless, by blending magnetic Fe₃O₄ nanoparticles into perovskite structure and conducting external magnetostatic field on the perovskite structure, the PCE of the device has a great enhancement. As we know, water is sensitive to MAI, to further increase the efficiency, the solvent dissolving Fe₃O₄ nanoparticles has been changed.

3.3 Magnetic Treatment by Using Ethanol-soluble Magnetic Fe₃O₄ Nanoparticles

Due to the solubility issue of water-soluble Fe₃O₄ nanoparticles, we have tried to put Fe₃O₄ nanoparticles dissolved in ethanol involving in the active layer of perovskite device.

3.3.1 Materials and experimental section

Materials: Poly (3, 4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS, Clevios™ HTL Solar) and phenyl-C₆₀-butyric acid methyl ester (PCBM, 99.5%) are purchased from Heraeus Precious and Solenne BV, respectively, and used as received. CH₃NH₃PbI₃ is prepared by two-step method, where the PbI₂ (99.999%, trace metals basis) precursor is purchased from Sigma-Aldrich and CH₃H₃I (MAI) is synthesized in our lab (supporting Information S1) according to previous literature. The Fe₃O₄ MNPs dissolved in ethanol is also synthesized in our lab according to the method
reported by Wei.  

Schematic synthesis procedure is shown in supporting information (Figure 3.11). The obtained Fe$_3$O$_4$ MNPs are well dispersed in ethanol solution.

Perovskite Precursor Preparation: PbI$_2$ solution (400 mg/mL in DMF) is prepared for overnight at 70°C under the magneton stirring. MAI is dissolved in ethanol and the solution concentration is 35mg/mL. The Fe$_3$O$_4$ MNPs (dissolved in ethanol) are mixed with MAI precursor at the blending concentration of 5%.

Pero-HSCs Fabrication: ITO glasses are cleaned by acetone, detergent, deionized water and isopropanol each for 45 minutes in sequence. Substrates then are dried in the vacuum drying chamber for over 12 hours. Cleaned ITO glass is processed under ultraviolet and O$_3$ for 40 minutes (each for 20 minutes) to make the surface activated also modify the work function of ITO. PEDOT: PSS is then spin coated on the surface of treated ITO substrate, followed with a thermal-annealing process at 150 °C for 10 min in the air and then transferred into the glovebox under nitrogen atmosphere. RPM is controlled at 4000r/s and the final thickness of the PEDOT: PSS layer comes to around 40nm. The perovskite film is prepared by using two-step process on the top of PEDOT: PSS layer, which will be introduced detailed in the following perovskite film preparation part. PCBM which functioned as the electron transport layer is dissolved in chlorobenzene (CB) with the concentration of 10mg/mL and is spin coated at RPM of 1000r/s for 45s on the surface of perovskite layer. An 80nm layer of Al is finally deposited as the cathode of the device in a high vacuum chamber by thermal evaporation method.
Perovskite Film Preparation: PbI\textsubscript{2} solution is firstly spin coated as the precursor on the surface of preheated PEDOT: PSS (70°C) substrate with a spin-rate of 3000r/s for 20s accompanied with an acceleration time of 3s. Substrate then is heated at 70°C for 10 minutes, a yellow homogenous film (PbI\textsubscript{2} film) is obtained. After cooling down to the room temperature and retaining at that temperature for 10 minutes, MAI (or MAI incorporation with Fe\textsubscript{3}O\textsubscript{4} MNPs) solution is spin coated with the same RPM and time as PbI\textsubscript{2} on the top of PbI\textsubscript{2} layer. The substrate is then transferred to the heating stage to anneal at 100°C for 2 hours. For the magnetic field treated group, an external vertical magnetic field is conducted on the top of the devices (the distance is controlled to ~10cm and the magnetic field intensity is controlled to 400~500 G) during the crystallization process. Before the experiments, some pre-experiments were carried out to find the best experimental conditions (see support information S4).

Perovskite Film Characterization: Ultraviolet–visible spectroscopy (UV-vis) absorption spectra is measured by using the HP 8453 spectrophotometer instrument. The instruments which used to get optical microscope image are U-LH100HGAPO model and Olympus MX51 Manual Microscope. For SEM measurement, we use FEI-Philips scanning transmission electron microscope and Model Tecnai T12T/STEM instruments. GIWAXS experiments are carried out in beamline 8-ID-E, Advanced Photon Source, Argonne National Lab. All the perovskite thin films (including pristine perovskite films and treated perovskite films) are prepared on the silicon surface. Charge carrier mobility is estimated by the space charge limited current (SCLC) method, via ITO/Al/Perovskite/MoO\textsubscript{3} (hole-only device) and,
ITO/AL/Perovskite/Al (electron-only device) respectively. Film thickness is measured by using Dektak 150 surface profilometer instrument.

Pero-HSCs Characterization: The J-V curves characteristic is measured by using the Keithley 2400 Source Measure Unit instrument. The solar cell devices are characterized by using a Newport Air Mass 1.5 Global (AM 1.5G) full spectrum solar simulator with irradiation intensity of 100 mW/cm$^2$. The light intensity is measured by a monosilicon detector (with KG-5 visible color filter) which is calibrated by National Renewable Energy Laboratory (NREL). The EQE spectra is obtained by using the QEX10 solar cell quantum efficiency measurement system with a 300w xenon lamp as the light source. Impedance spectra is measured by using the HP 4194A Impedance/gain-phase analyzer. All the pero-HSCs are measured under 100mW/cm$^2$ AM 1.5 G illumination, with frequency of 1HZ to 1MHz and oscillating voltage of 10 mV. All the devices are held at their respective open circuit voltages obtained from the J-V measurements, while the IS spectra are recorded. The active area of pero-HSCs is measured to be 0.045 cm$^2$

Fe$_3$O$_4$ magnetic nanoparticles Characterization: TEM measurements are recorded on a JEOL-1230 microscope with an accelerating voltage of 120 kV. The sample is prepared to dissolve in ethanol by using the copper wire mesh as the carrier. FT-IR is measured by using Nicolet 6700 FT-IR instrument. TGA measurement is conducted by using the Model Q50 Thermogravimetric Analysis Instrument.
3.3.2 Results and discussions

Figure 3.1 shows the schematic procedure of preparing the magnetic treated CH$_3$NH$_3$PbI$_3$ perovskite film. The static EMF (400~500 Gauss) is perpendicular to the surface of the CH$_3$NH$_3$PbI$_3$ perovskite film. The employment of the EMF is to affect the poly-crystallization process of the CH$_3$NH$_3$PbI$_3$ perovskite as well as to align the blended Fe$_3$O$_4$ MNPs in certain degree. The perpendicularly aligned Fe$_3$O$_4$ MNPs is reported to offer a vertical channel for charge carrier transport facilitation. To minimize the MNPs aggregation within the perovskite matrix, sufficient dispersion of the Fe$_3$O$_4$ MNPs is essential. Knowing that the commercial available Fe$_3$O$_4$ MNPs are coated with organo-ligand and dissolved in toluene or water, while the non-polar solvent toluene is difficult for blending the Fe$_3$O$_4$ MNPs with either PbI$_2$ or MAI precursor solutions and the water is proved to be detrimental to the CH$_3$NH$_3$PbI$_3$ film due to the large intermolecular interaction between MAI and H$_2$O. Therefore, the well dispersed Fe$_3$O$_4$ MNPs/ethanol solution is employed here to minimize the Fe$_3$O$_4$ MNPs aggregation and facilitate the EMF manipulation.

![Figure 3.1. Schematic procedure of fabricating magnetic treated CH$_3$NH$_3$PbI$_3$ film.](image)

33
Figure 3.2a shows the FT-IR analysis of Fe$_3$O$_4$ MNPs, which offers the compositional information of the products. The characteristic absorption peak of Fe$_3$O$_4$ is observed at 585 cm$^{-1}$ in the FT-IR spectra. TGA measurement can briefly give us the component and the purity information of the sample. The weight-loss versus temperature curve of the powder form product is shown in Figure 3.2b. From the TGA curve, a three-stage weight loss is observed. The weight loss of small amount at around 25-200°C in the first region is corresponding to the evaporation of adsorbed water and ethanol or ethyl acetate. The second part weight loss at around 200-350°C represents the evaporation of the TREG because the boiling point of TREG is around 280°C. The curve at 350-450°C is flat which indicates that Fe$_3$O$_4$ nanoparticles in stable at this temperature range. The third weight loss indicates that Fe$_3$O$_4$ MNPs may decompose at high temperature (>500°C)\[^{64}\]. The insert figure in Figure 2b shows the TEM image of the Fe$_3$O$_4$ MNPs/ethanol dispersion solution, where the average size is around 10 nm with a narrow particle size distribution. It should be noted that no

![Figure 3.2a](image1.png) ![Figure 3.2b](image2.png)

Figure 3.2. Characterizations of magnetic Fe$_3$O$_4$ nanoparticles dissolved in ethonal.

(a) FT-IR spectra and (b) TGA curve and TEM images.
detectable aggregation is observed, indicating that the Fe$_3$O$_4$ nanoparticles are well dispersed in ethanol.

The CH$_3$NH$_3$PbI$_3$ film morphology is firstly investigated by the optical microscopy (OM) measurement and scanning electron microscope (SEM) measurement. The results are shown in Figure 3.3a-c. From the OM images, the pristine CH$_3$NH$_3$PbI$_3$ film shows large pin-holes and the crystal domains are prone to aggregate, rendering a rough film. While after mixing the Fe$_3$O$_4$ MNPs into the CH$_3$NH$_3$PbI$_3$ film, the crystal domains are more uniform and the film is smoother with less uncovered area. Such uncovered area is dramatically reduced when the CH$_3$NH$_3$I$_3$/w Fe$_3$O$_4$ MNPs is further treated by the EMF. These observations are more clearly shown in the SEM images in Figure 3d-f. Figure 3.3d shows the SEM image of the pristine CH$_3$NH$_3$PbI$_3$ film, obvious pin-holes are observed between the crystal domains. When the CH$_3$NH$_3$PbI$_3$ film is incorporation with Fe$_3$O$_4$ MNPs (Figure 3.3e), both the size and the number of the pin-holes are reduced. For the further treated CH$_3$NH$_3$PbI$_3$ film (Figure 3.3f), more uniform and oriented film was obtained with a decreasing pin-hole area and increasing crystal domains. Figure 3.3g-i show the statistic pin-hole numbers of each experimental group (pinhole area as the horizontal ordinate and log pinhole number as the vertical coordinate). For the all the CH$_3$NH$_3$PbI$_3$ films, the sizes of the majority of the pin-holes are less than 0.1mm$^2$ (area) while the pristine CH$_3$NH$_3$PbI$_3$ gives a huge amount of pin-holes in this region. When the pristine CH$_3$NH$_3$PbI$_3$ film is incorporation with Fe$_3$O$_4$ MNPs, fewer large-size pin-holes are observed. For the further treated CH$_3$NH$_3$PbI$_3$ film, both the number and the size of the pin-holes are
dramatically reduced, heralds a more uniform CH$_3$NH$_3$PbI$_3$ film, which is corresponding to the SEM image what we have observed visually.

Figure 3.3. Film morphology investigation images. (a) OM image of pristine CH$_3$NH$_3$PbI$_3$ film; (b) OM image of CH$_3$NH$_3$PbI$_3$ film incorporation with Fe$_3$O$_4$ MNPs; (c) OM image of CH$_3$NH$_3$PbI$_3$ film incorporation with Fe$_3$O$_4$ MNPs under external magnetic field; (d) SEM image of pristine CH$_3$NH$_3$PbI$_3$ film; (e) SEM image of CH$_3$NH$_3$PbI$_3$ film incorporation with Fe$_3$O$_4$ MNPs; (f) SEM image of CH$_3$NH$_3$PbI$_3$ film incorporation with Fe$_3$O$_4$ MNPs under external magnetic field; (g) Statistic pin-hole numbers of pristine CH$_3$NH$_3$PbI$_3$ film; (h) Statistic pin-hole numbers of CH$_3$NH$_3$PbI$_3$ film incorporation with Fe$_3$O$_4$ MNPs; and (i) Statistic pin-hole numbers of CH$_3$NH$_3$PbI$_3$ film incorporation with Fe$_3$O$_4$ MNPs under external magnetic field.
To further understand the magnetic effect on the film morphology, the x-ray scattering measurements are carried out. Figure 3.4a-c shows the GIWAXS profiles of pristine CH$_3$NH$_3$PbI$_3$ film and the treated CH$_3$NH$_3$PbI$_3$ film. The GIWAXS measurements are employed here to investigate both the crystal structure and the orientations of the crystallization in CH$_3$NH$_3$PbI$_3$ film since 1D XRD pattern can only provide the information of perovskite crystal structure. The observation of strongly scattering rings in pristine CH$_3$NH$_3$PbI$_3$ film (Figure 3.4a) indicates that the main existence form of the crystal domains is polycrystalline. When the CH$_3$NH$_3$PbI$_3$ film is incorporation with Fe$_3$O$_4$ MNPs (Figure 3.4b), the emerging more rings identify the existence of Fe$_3$O$_4$ MNPs while highly oriented crystal domains are observed in the in-plane direction which indicate the more aligned perovskite crystal patterns. When the CH$_3$NH$_3$PbI$_3$ incorporation with Fe$_3$O$_4$ MNPs film is further treated by the external magnetic field (Figure 3.4c), the orientation in in-plane direction becomes stronger, indicating a more oriented and less amorphous perovskite crystal structure. In other words, the treatment facilities the perovskite crystallization process, leading to a highly ordered perovskite crystal structure.\textsuperscript{[65-69]}

Figure 3.4d compares the XRD pattern of each experimental group, the three major peaks shown in the pristine perovskite group, at 1.0, 2.0 and 2.3 Å$^{-1}$ corresponding to the (110), (220), and (310) lattice planes, are in the identical positions of the CH$_3$NH$_3$PbI$_3$ films, which indicates the existing of tetragonal perovskite crystal structure.\textsuperscript{[70]} A new peak (q=0.75 Å$^{-1}$) is observed in both CH$_3$NH$_3$PbI$_3$ incorporation with Fe$_3$O$_4$ MNPs and CH$_3$NH$_3$PbI$_3$ incorporation with Fe$_3$O$_4$ MNPs under external
magnetic field films, which is due to the existence of Fe$_3$O$_4$ MNPs. Meantime, the existence of Fe$_3$O$_4$ MNPs suggests that the nanoparticles are physically doped within the CH$_3$NH$_3$PbI$_3$ matrix and there are no obvious chemical reactions between the Fe$_3$O$_4$ and CH$_3$NH$_3$PbI$_3$. In addition, the new peaks at q=0.9 Å$^{-1}$ and q=1.4 Å$^{-1}$ are observed in both CH$_3$NH$_3$PbI$_3$ incorporation with Fe$_3$O$_4$ MNPs and CH$_3$NH$_3$PbI$_3$ incorporation with Fe$_3$O$_4$ MNPs under external magnetic field films, which correspond to the (020) peak in orthorhombic crystal structure and the (110) peak in cubic crystal structure, respectively. It should be noted that the CH$_3$NH$_3$PbI$_3$ incorporation with Fe$_3$O$_4$ MNPs under external magnetic field film shows sharper perovskite peaks, which suggests that film possess high crystallinity, indicating the more perfect perovskite crystal structure. Furthermore, the obtained highly ordered crystal domains in CH$_3$NH$_3$PbI$_3$ film represent the increasing grain boundaries, leading to the decreasing pin-hole area and trap density, which may facilitate the charge carrier transport process.
Figure 3.4. GIWAXS and XRD pattern of pristine CH$_3$NH$_3$PbI$_3$ film. (a) GIWAXS pattern of pristine CH$_3$NH$_3$PbI$_3$ film; (b) GIWAXS pattern of CH$_3$NH$_3$PbI$_3$ film incorporation with Fe$_3$O$_4$ MNPs; (c) GIWAXS pattern of CH$_3$NH$_3$PbI$_3$ film incorporation with Fe$_3$O$_4$ MNPs under external magnetic field; and (d) XRD pattern comparison of each experimental group.

To verify the optimized crystal patterns induced improved charge carrier transport properties of the CH$_3$NH$_3$PbI$_3$ films, we applied the space charge limited current (SCLC) measurement to estimate the charge carrier mobility (both holes and electrons). For mobility test, hole-only device (also called hole-only diode) and electron-only device (also called electron-only diode) are fabricated to measure the
dark current of the device under different applied voltage region. In the hole-only device, MoO$_3$ layer (100nm) and Al layer (20nm) were fabricated as the electrode of the device, and in the electron-only device, the top Al layer (100nm) and the bottom Al (20nm) layer were fabricated as the electrode of the device respectively. Figure 3.5a and b shows the current and voltage dependency curve under dark condition and the devices structures of the hole-only device and electron-only devices are shown in the insert picture in the Figure 3.5a and b. For the original J-V curves (Figure 3.5a and b), SCLC region need to be ferret out firstly. At low applied voltage (also called Ohmic region), the slope of the J-V curve is approximately equal to 1, and the curve is fitted as the equation: \( J = N_0 \varepsilon \mu V / L \), where \( J \) is the dark current, \( N_0 \) is thermal carrier concentration, \( \varepsilon \) is the elementary charge, \( \mu \) is the charge carrier mobility, \( V \) is the bias voltage and \( L \) is the film thickness. The charge carrier mobility is related with the thermal carrier concentration and cannot be calculated by this equation. However, at higher voltage (also called space charge limited current region), the slope of the J-V curve is approximately equal to 2 and is well fitted as this equation: \( J_D = 9 \varepsilon \varepsilon_0 \mu V^2 / 8L^3 \) (\( J_D \) is the dark current of the device, \( \varepsilon \) is the permittivity of the CH$_3$NH$_3$PbI$_3$ film, \( \varepsilon_0 \) is permittivity of vacuum, \( V \) is the applied voltage and \( L \) is the CH$_3$NH$_3$PbI$_3$ film thickness, respectively). Between the low voltage region and the high voltage region, there is a trap filled process with the increasing voltage, the voltage at a critical point that all the traps are filled out is called trap filled voltage (\( V_T \)). In SCLC region, the current is dominated by charge carriers injected from the contacts and the current-voltage characteristics becomes quadratic (\( J \sim V^2 \)) relationship. The current is
then only dependent on the mobility and no more on the charge carrier density, hence, the mobility can be estimated from the simple current-voltage measurement. Figure 3.5c and d show the extracted curve of $J^{1/2}$ and $V$ (linear relationship) of hole-only device and electron-only device respectively, the large slope of the device indicates the high charge carrier mobility. The calculated hole mobility of the pristine perovskite film is $4.4 \times 10^{-3} \text{cm}^2\text{V}^{-1}\text{S}^{-1}$, and the value of treated group increased to $12.3 \times 10^{-3} \text{cm}^2\text{V}^{-1}\text{S}^{-1}$, three times larger than the pristine one. The mobility of the electron has also increased from $8.5 \times 10^{-3} \text{cm}^2\text{V}^{-1}\text{S}^{-1}$ to $33 \times 10^{-3} \text{cm}^2\text{V}^{-1}\text{S}^{-1}$. The increasing of both hole mobility and electron mobility were helpful to explain the increasing short current density of the device. The measured dark current curve cannot only characterize the charge carrier mobility, but it also can supply the information to approximately calculate the trap density of the CH$_3$NH$_3$PbI$_3$ film by using the following equation: $V_T = e n_t L^2 / 2 \varepsilon \varepsilon_0$ ($V_T$ is the trap-filled voltage (see support information), $e$ is the elementary charge and $n_t$ is the trap density). The calculated trap density is $7.1 \times 10^{18} \text{cm}^{-3}$ (pristine CH$_3$NH$_3$PbI$_3$ film), $1.2 \times 10^{18} \text{cm}^{-3}$ (CH$_3$NH$_3$PbI$_3$ film incorporation with Fe$_3$O$_4$ MNPs), and $8.9 \times 10^{16} \text{cm}^{-3}$ (CH$_3$NH$_3$PbI$_3$ film incorporation with Fe$_3$O$_4$ MNPs under external magnetic field). The decreasing trap density in CH$_3$NH$_3$PbI$_3$ film is corresponding to the film quality enhancement after the treatment which we observed from SEM image.
Figure 3.5. Mobility test. (a) Hole only device structure and original J-V curves; (b) Electron only device structure and original J-V curves; (c) Extracted J$_{1/2}$-V curve of the hole-only device; and (d) Extracted J$_{1/2}$-V curve of the electron-only device.

To further verify the enhancement in charge carrier mobility in CH$_3$NH$_3$PbI$_3$ film, time-resolved photoluminescence (PL) measurement is conducted on the CH$_3$NH$_3$PbI$_3$ film, as shown in Figure 3.6. The lifetime of charge carriers in these three thin films can be obtained by fitting the data with two exponential decay curves. Under the treatment of the incorporation with Fe$_3$O$_4$ MNPs and an external magnetic field, the lifetime of the charge carriers in CH$_3$NH$_3$PbI$_3$ film has an obvious increment. According to the following equation: $L_D = (K_B T \mu t/e)^{1/2}$ ($K_B$ is Boltzmann constant, $T$ is absolute temperature, $\mu$ is the carrier mobility of the device, $t$ is the life time of the charge carriers and $e$ is the elementary charge, respectively), the charge carrier diffusion length ($L_D$) has a linear relationship with the charge carrier lifetime.
(t), which is to say the treated film does give us a long charge carrier diffusion length, heralding the more efficiency charge carrier transfer process.\cite{76-78}

Figure 3.6. Time resolved PL spectra of each experimental group.

To study the photovoltaic performance of the CH$_3$NH$_3$PbI$_3$ films. The low-temperature solution-processed planar heterojunction (PHJ) device structure of ITO/PEDOT: PSS/Perovskite/PCBM/Al has been employed here. Figure 3.7a shows the J-V curves at illumination (AM 1.5, light intensity of 100 mW/cm$^2$). From the figure we can see that an obvious device performance improving is observed by the incorporation of Fe$_3$O$_4$ MNPs and external magnetic field treatment including the dramatic enhanced short current density ($J_{SC}$). The highest PCE value obtained can reach 14.40%, nearly 40% higher than the pristine device, with a large $J_{SC}$ reaching 21.56 mA/cm$^2$ simultaneously (Table 3.2). The value of $R_S$ (series resistance) and $R_{Sh}$ (shunt resistance) can be extracted from the J-V curves, which are shown in Table 3.2. The J-V characteristic curves of a single heterojunction solar cell is described as the following equation.\cite{79} The decreasing $R_S$ is necessary for the solar cell device with a high fill factor according to that equation.\cite{80}
Table 3.2 Device Performance of Each Experimental Group

<table>
<thead>
<tr>
<th>Active Layer</th>
<th>$V_{oc}$(V)</th>
<th>$J_{sc}$(MA/cm²)</th>
<th>FF(%)</th>
<th>PCE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/O NPs; W/O MF</td>
<td>0.85</td>
<td>16.07</td>
<td>75.9</td>
<td>10.36</td>
</tr>
<tr>
<td>W/NPs; W/O MF</td>
<td>0.85</td>
<td>17.29</td>
<td>77.1</td>
<td>11.33</td>
</tr>
<tr>
<td>W/NPs; W/O MF</td>
<td>0.85</td>
<td>21.56</td>
<td>78.6</td>
<td>14.40</td>
</tr>
</tbody>
</table>

Figure 3.7. Characterizations for pero-HSCs. (a) J-V curves at illumination (AM 1.5, light intensity of 100 mW/cm²); (b) EQE spectra; (c) J-V curves under dark condition; and (d) Impedance spectra.

EQE (external quantum efficiency) spectra is used to characterize the charge carriers collected by the electrode. EQE is defined as the ratio that charge carriers collected by the electrode to the incident photons. The value is related to the absorption light and the collection of charges. The nearly same absorption spectra (Support Information)
indicates that the cause of increasing $J_{SC}$ is not because of the absorbing photon number. Meanwhile, the absorption edge obtained in EQE spectra is around 800nm, which is almost the same as we observed in the absorption spectra. Hence, the better ability to get charge carrier transferring comes to the best explanation of the huge increment of $J_{SC}$. Figure 3.7b gives the EQE spectra of each experimental group, the integrated $J_{SC}$ of the treated group (incorporation of Fe$_3$O$_4$ MNPs and external magnetic field) is 21.01mA/cm$^2$, which is approximately corresponding to the $J_{SC}$ what we have got from the J-V measurement. The high EQE value of the treated group also indicates a facilitated charge carrier transfer process in the CH$_3$NH$_3$PbI$_3$ films. [81]

Dark current is also measured to estimate the trap effects in experimental group. Figure 3.7c shows the J-V curves under dark conditions. For the CH$_3$NH$_3$PbI$_3$ film incorporation with Fe$_3$O$_4$ MNPs and external magnetic field, the decreased $J_D$ in the reverse region indicates the leakage currents are suppressed, which is originated from the reduced defects in the CH$_3$NH$_3$PbI$_3$ thin film, [82] corresponding to the restrained charge carrier recombination process and facilitated charge carrier transfer process.

Impedance spectra (IS) is carried out to characterize the resistance in the charge carrier transfer process. Perovskite hybrid solar cells can be described as p-i-n junction structure, where $R_S$ is the series resistance, $R_{CT}$ is charge carrier transfer resistance and $C$ is the capacitance. Impedance measurement is carried out in the dark environment under an applied voltage closed to the open circuit voltage. Under this condition, the charge carrier recombination resistance ($R_{rec}$, $R_{rec}<<R_{CT}$) from hole
transfer layer (HTL) to electron transfer layer (ETL) becomes the lowest value. Therefore we can use the circuit model as showed in the inset of Figure 3.7d. Figure 3.7d shows the comparison of Nyquist plots of device impedance among each experimental group. In our experiment, since the device structures of each group are all the same, the value of $R_S$ can be assumed as the same. The major difference comes from the various value of $R_{CT}$. From the result, decreasing $R_{CT}$ value of each group are observed-1150Ω (pristine perovskite), 850Ω (perovskite incorporation with Fe$_3$O$_4$ MNPs) and 625Ω (perovskite incorporation with Fe$_3$O$_4$ MNPs under external magnetic field). The reduced charge carrier resistance presages the better charge carrier transfer process.

![Figure 3.8](image)

Figure 3.8. Histograms of PCE distribution of each experimental group. (a) Pristine CH$_3$NH$_3$PbI$_3$; (b) CH$_3$NH$_3$PbI$_3$ incorporation with Fe$_3$O$_4$ MNPs under external magnetic field; and (c) CH$_3$NH$_3$PbI$_3$ incorporation with Fe$_3$O$_4$ MNPs under external magnetic field.

Reproducibility of the device performance is one of the significant issues needed to be considered in perovskite hybrid solar cells. To demonstrate the treatment optimizing good device performance more powerfully, over than 100 pieces of device were
fabricated. Figure 3.8 shows the histograms of the PCE distribution of each experimental group under different treatments. When the CH$_3$NH$_3$PbI$_3$ is treated by the incorporation of Fe$_3$O$_4$ MNPs and external magnetic field, the PCE value of the device is more concentrated than the pristine perovskite device. Figure 3.9 shows the J-V curves of each experimental group under different scan rate and different scan direction. For the magnetic treated perovskite device, more stable J-V curve is observed regardless of scan rate and scan direction which indicating the minimized photocurrent hysteresis behavior due to the dramatically reduced defects in CH$_3$NH$_3$PbI$_3$ film.

![Figure 3.9](image)

Figure 3.9. J-V curves under different scan rate and different scan direction of each experimental group. (a) Pristine CH$_3$NH$_3$PbI$_3$; (b) CH$_3$NH$_3$PbI$_3$ incorporation with Fe$_3$O$_4$ MNPs under external magnetic field; and (c) CH$_3$NH$_3$PbI$_3$ incorporation with Fe$_3$O$_4$ MNPs under external magnetic field.

Stability of the perovskite hybrid solar cells is another issue which cannot be ignored. Efficiency value decay is one of the infusive parameters to evaluate the stability properties of the device. Figure 3.10, the PCE value decay of experimental group decay is obtained under vacuum atmosphere. From the line chart we can see, when the CH$_3$NH$_3$PbI$_3$ film is treated by the incorporation of Fe$_3$O$_4$ MNPs and external
magnetic field, the PCE decay is a little bit lower than the pristine CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} film. The insert equation modifies the decay curve as a linear relationship, from the simulation equation, the approximately calculated t\textsubscript{1/2} (time of PCE decay to the half) value of each experimental group is 485 (pristine CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} film), 399 (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} film incorporation with Fe\textsubscript{3}O\textsubscript{4} MNPs) and 364 hours (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} film incorporation with Fe\textsubscript{3}O\textsubscript{4} MNPs under external magnetic field), respectively. Obvious enhanced life time means the better stability of pero-HSCs.

![Figure 3.10.](image)

Figure 3.10. Stability figure of pero-HSCs.

3.3.3 Supporting information

S1 Synthesis and Characterization of Fe\textsubscript{3}O\textsubscript{4} magnetic nanoparticles

S1.1 Synthesis of Fe\textsubscript{3}O\textsubscript{4} magnetic nanoparticles

The synthesis process is shown in the following schematic (Figure 3.11), all the experiment procedure is operated under N\textsubscript{2} protection. Fe (acac)\textsubscript{3} (99%) was purchased from Acros and triethylene glycol (TREG) (99%) was bought from Aldrich. The structures and morphology of the two reactants are shown in the Figure 3.12. The
final products Fe₃O₄ magnetic nanoparticles can be easily dissolved in ethanol, Figure 3.13 shows the solution form of Fe₃O₄ nanoparticles dissolved in ethanol.

Figure 3.11. Schematic of synthesis procedure of Fe₃O₄ nanoparticle.

Figure 3.12 Structure and morphology of Fe (acac)₃ and TREG.
The color of synthesized Fe₃O₄/ethanol solution is nigger-brown due to the existence of Fe²⁺ and Fe³⁺ (Figure 3.13).

![Image](image.png)

**Figure 3.13. Products morphology.**

### S1.2 Characterization of Fe₃O₄ magnetic nanoparticles

FT-IR The strong peak at 585cm⁻¹ in the spectra corresponding to the Fe-O bond, the rest peaks are corresponding to the bond in the solvent due to the sample was measured dissolved in ethanol (Figure 3.13, C-O stretch at about 1800cm⁻¹, C-H stretch at about 2600cm⁻¹ and O-H stretch at about 3100cm⁻¹).
Figure 3.14. FT-IR spectra of Fe$_3$O$_4$ nanoparticles dissolved in ethanol.

TEM. The sample is prepared to dissolve in ethanol by using the copper wire mesh as the carrier. TEM images shows the morphology and distribution of the Fe$_3$O$_4$ nanoparticles clearly. Figure 3.15 shows TEM image of Fe$_3$O$_4$ nanoparticles under different amplification factor.
Figure 3.15. TEM images of Fe$_3$O$_4$ nanoparticles dissolved in ethanol with different scale bar.

S2 Materials and fabrication of perovskite hybrid solar cells

MAI, which forms the second layer of the perovskite was synthesized in our lab by according the following chemical reaction:
$\text{CH}_3\text{NH}_2 + \text{HI} = \text{CH}_3\text{NH}_3\text{I}$

(a) PEDOT: PSS  
(b) PC$_{60}$BM

Figure 3.16. Chemical structures of material used in perovskite hybrid solar cells.

S3 Device fabricating procedure

Figure 3.17. Device fabricating procedure.

S4 Pre-experiments

The pre-experiments include two parts: (a) Investigation of the role of external magnetic field playing in the device performance. (b) Different trials to optimize the best blending concentrations.

S4.1 Investigation of the role of external magnetic field playing in the device performance
To understand the magnetic effects on the performance of perovskite hybrid solar cells, the experiment is designed as followed: ITO/PEDOT: PSS/Perovskite/PCBM/Al as the pristine group; ITO/PEDOT: PSS/Perovskite (under magnetic field) /PCBM/Al as the experimental group. The comparisons of device performance are shown in the following Table 3.3 and Figure 3.18.

Table 3.3 Comparison of Device Performance by Magnetic Treatment

<table>
<thead>
<tr>
<th>Active Layer</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>0.85</td>
<td>16.07</td>
<td>75.9</td>
<td>10.36</td>
</tr>
<tr>
<td>Under magnetic field</td>
<td>0.85</td>
<td>17.50</td>
<td>75.3</td>
<td>11.20</td>
</tr>
</tbody>
</table>

Figure 3.18. J-V curves of device under magnetic field.

The J-V curves characteristic is measured by using the Keithley 2400 Source Measure Unit instrument. The solar cell devices are characterized using a Newport Air Mass 1.5 Global (AM 1.5G) full spectrum solar simulator with irradiation intensity of 100 mW/cm$^2$. The light intensity is measured by a monosilicon detector (with KG-5
visible color filter) which is calibrated by National Renewable Energy Laboratory (NREL).

The increasing $J_{SC}$ can be explained by the XRD pattern. The following figure gives the comparison of the pristine perovskite device and the device of perovskite under magnetic field. The sharper perovskite peak ((220) and (310)) in latter one (under magnetic field) presents the well-organized crystal structure, as mentioned in the main text, explains the current increment after the magnetic treatment.

![Figure 3.19. XRD pattern comparison of pristine perovskite device and the perovskite device under external magnetic field.](image)

(a) Pristine perovskite film  
(b) Perovskite film under magnetic field

S4.2 Different trials to optimize the best blending concentration

To find the best blending concentrations of the Fe$_3$O$_4$ nanoparticles inside the perovskite layer, several trials have been applied. Table 3.4 shows the device performances of the different blending concentrations, which optimize the best experimental condition comes to the 5% (blending concentration). The experiments are all conducted under an external magnetic field. With the increasing blending concentration higher than 5%, the film quality becomes worse, so it gives the inferior device performance.
Table 3.4 Device Performance of Different Blending Concentrations

<table>
<thead>
<tr>
<th>Blending concentration</th>
<th>$V_{OC}$(V)</th>
<th>$J_{SC}$(mA/cm²)</th>
<th>FF(%)</th>
<th>PCE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0.85</td>
<td>17.50</td>
<td>75.3</td>
<td>11.20</td>
</tr>
<tr>
<td>1%</td>
<td>0.85</td>
<td>18.01</td>
<td>78.4</td>
<td>12.00</td>
</tr>
<tr>
<td>5%</td>
<td>0.85</td>
<td>21.56</td>
<td>78.6</td>
<td>14.40</td>
</tr>
<tr>
<td>10%</td>
<td>0.85</td>
<td>14.69</td>
<td>73.0</td>
<td>9.12</td>
</tr>
</tbody>
</table>

3.4 Conclusion

By using neutral PSBEDOT to replace the pristine acidic PEDOT: PSS as the hole extraction layer, we can obtain perovskite hybrid solar cell devices with high open circuit voltage and comparable short-circuit current density. The magnetic nanoparticles and an external magnetic field can increase the charge transferring efficiency, tune the film morphology of the perovskite hybrid active layer, resulting in 40% enhancement in efficiency.
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