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Planar Organic-inorganic Hybrid Perovskite Solar Cell by Electrospray

by

Wenjun Chen

A thesis submitted in partial satisfaction of the requirements for the degree of Master

in

Mechanical Engineering

Committee in charge:
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Spring 2015
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Dedicated to

My parents.
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For the past two years, I have received too many favors from a lot of people. When I first came to US from China, I was muddled in the total new environment. I am grateful that I met so many nice people, I appreciate the kindness from everyone that I knew in this two years.

Last but not least, I want to express my gratitude to my dear parents. They are the constant source of love and encouragement for me and they are the strongest backups for me. I am grateful for their love and supports, and I love them.
Curriculum Vita

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Perovskite Solar Cell Research Project
• Researched high scalability and high efficient perovskite solar cell.
• Investigated perovskite thin film deposition by electrospraying bi-solvent system precursor and post-annealing treatment for optimizing the film morphology.

Graduate Researcher, Vincent C. Tung Lab, University of California, Merced
Crumpled Graphene Research Project
• Studied graphene oxide (GO) & graphene nanoribbon (GNR) synthesis.
• Created GO crumples through electrospraying technique and GO surface modification for energy harvesting and energy storage applications.
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Bachelor’s Thesis Composition, Dalian University of Technology, China
High-entropy Alloy Thin Film Project
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National University Students Innovation Experimental Project
• Used the most common TIG method to weld aluminum alloy and stainless steel with an additional transition metal layer on the stainless steel, in order to avoid the nonhomogeneous stress distribution caused by different thermal expansion coefficient and low solid solubility.
PROFESSIONAL EXPERIENCE

University of California, Merced 2013 – Present
• Teaching Assistant
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Abstract

Planar Organic-inorganic Hybrid Perovskite Solar Cell by Electrospray
by
Wenjun Chen

Master
in
Mechanical Engineering
Professor Vincent C. Tung, Chair

Recently, the organic-inorganic perovskite solar cell has attracted great attention due to the easy processing and rapid developed power conversion efficiency. The tri-halide perovskite CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ possessing excellent optical and electronic properties, such as absorption hands span the visible region, long charge carrier diffusion lengths, and appropriate direct band gap, makes them ideal active layer material for photovoltaic devices. In this thesis, electrohydrodynamic spraying is used to deposit the perovskite precursor film, where this technique takes advantages of both the solution based process and vapor deposition to form the continuous flat thin film. As for the post heating treatment to convert the precursor to final perovskite crystals, heat gun annealing is utilized for faster anneal and better morphology compared with conventional annealing process. This heat gun annealing provides sufficient energy to let the solvent evaporate and precursor crystallize in a short time. Thus the final dense uniform perovskite film with large grain size is produced by our techniques, which is a good candidate as the active layer for the high-efficiency photovoltaic devices. The results further demonstrate that our techniques are reliable highly reproducible to prepare planar organic-inorganic perovskite photovoltaic devices with efficiencies up to 16%.
Chapter 1

Introduction

1.1 Background

Solar cells, or photovoltaic cells, convert sunlight directly to electricity are gaining an increasing interests due to the renewable energy demands. 85% of the solar cells are silicon based, mainly making from crystalline Si; with the rest being non-silicon based, which consists of polycrystalline thin film cells mostly made of cadmium telluride/cadmium sulfide\(^1\), and organic solar cells.

Over recent decades, the photovoltaics market has been dominated by product based on the use of silicon, annual production of Si-based photovoltaic (PV) in 2011 reached more than 15 gigawatts, which is an order of magnitude higher than other PV\(^2\). However silicon has withdraws that has made it difficult to displace as the favored photovoltaic material. The future promising generation of photovoltaic device should either get significantly higher energy conversion efficiencies or tremendously reduce the manufacture processing costs. The cell efficiency report from NREL (National Renewable Energy Laboratory) shows that the average power conversion efficiency of Si-based device is at 25% by the end of 2014, that is a relatively high efficiency. But when it comes to the fabrication processing, as the common method to produce the industry-dominant single-crystalline is using CVD (chemical vapor deposition) or PECVD (plasma-enhanced chemical vapor deposition)\(^3\), the stringent requirements for cleanliness and quality of control make it time consuming and costs considerably.

Another important branch of solar cells are made from organic photovoltaic material, it has developed during the past four decades, the perspective of cheap production and easy processing drives the development of organic photovoltaic devices\(^4\). The two competitive production techniques used today are either wet solution processing or dry thermal evaporation, which is easy to be scaled up and lower the cost. Since the development of semiconducting polymers, bringing these materials to incorporate into organic solar cells resulted in remarkable improvement within past years. However most of the organic semiconductors are hole conductors and have an optical band gap around 2 eV, which is considerably higher than that of silicon, thus limits the harvesting of the solar spectrum to a great extent. Due to the NREL cell efficiency report, the average power conversion efficiency of organic solar cells is around 11.1% by the end of 2014, which makes it hard to take place of the commercial Si-based solar cell in the industry. In addition to the high energy conversion efficiency and low fabrication cost, long-term operation without degradation of the active layer is an equally important factor. Neither the organic solar cell nor the new star dye-sensitized solar cell\(^5\) has a very good performance in the long-term operation without degradation, so it becomes another research challenge in the solar cell developing field.
With a recent forecast anticipating photovoltaics will contribute a third of new electricity generation capacity worldwide before 2030 [6]. As in order to assure the future large-scale use of photovoltaic, it requires the devices to have both lower cost and high energy conversion efficiency. A new generation of mixed organic-inorganic halide perovskite offers a combination of both strengths, promising to be an overwhelming mainstream in photovoltaic field [7-11].

1.2 Perovskite

Organic-inorganic perovskite solar cell as a new member of photovoltaic family has rapidly reached the power conversion efficiencies of more than 17% within past 5 years [12-19]. Not only because of the rapid developing of efficiencies, but also due to the easy fabrication processing, which all lead to make perovskite photovoltaic attractive to renewable energy researchers.

Perovskite, named after the Russian mineralogist Perovski, has a specific crystal structure with the ABX$_3$ formula as shown in Figure 1[20]. The cation B occupies in the center of a cubic-octahedral site with eight anion A sitting in the cubic site, and the octahedral site are shared with six anion X. In the perovskite photovoltaic case, cation B is usually Pb or Sn, A is the methylammonium ion and the X is the halide ion. The most studied was the oxide perovskite, halide perovskite started to attract attentions when it was reported to exhibit a semiconductor-to-metal transition with increasing dimensionality [21]. In addition to the changes in electrical properties, the band gap decreased with increasing the dimensionality from 2D to 3D [22], moreover the narrow band gap is beneficial for solar cell applications [23,24].
Other than the halide perovskite material has a narrow band gap, it has some intrinsic astounding properties. The organic inorganic trihalide perovskite material possesses the most important properties required being excellent absorbers: appropriate direct band gap \[25\], high absorption coefficient, excellent carrier transport, and apparent tolerance of defects \[26\].

As for the direct band gap, which means the momentum of the electrons and holes are the same in both conduction band and valence band, thus the electron doesn’t need to pass through an intermediate state nor transfer momentum to crystal lattice. In this case, a direct transition from the valence band to the conduction band of an electron does not require a photon of energy higher than that of the band gap, which is more favorable to construct a photovoltaic cell with high power conversion efficiencies. The second factor is the high absorption coefficient, it determines how far into a material light of a particular wavelength can penetrate before it is absorbed. Another photic property has to be mentioned is the wide absorption wavelength range, it can absorb the light wavelength from 300 nm to 770 nm, it can absorb all the visible light and a small part of the near-infrared light, which could contribute to efficient absorption of the solar light. From Figure 2 \[27\], it is easily to observe that both properties.

![Figure 2 Absorption coefficients common photovoltaic material](image)

The last thing concerned about perovskite is choosing the element composite, as mentioned before the trihalide perovskite has several advantages \[28\]. Most of the perovskite used in solar cell contains the Pb, Pb plays important role, first it has small effective masses and it can enhance both charges and lattice polarization, suppression of the formation of deep defect levels \[29-32\]. The most developed devices are using the iodide as the halogen, due to the recent research, the I and Cl mixed attracting more attentions. By adding the element Cl, it can reduce the lattice constant of iodide and significantly increase the formation energy of interstitial defects. Hence in this thesis I will mainly talk about the mixed trihalide perovskite \[CH_3NH_3PbI_{3-x}Cl_x\].
Chapter 2

Fundamental Theory

2.1 Electrohydrodynamic spraying

The mostly used methods to making the perovskite thin film are vapor deposition\textsuperscript{[33]} and solvent based fabrication, people use spin coating and spray coating for the easy solvent processing. By utilizing the vacuum thermal evaporation method, the thin film is very flat with good morphology, however it requires the special instrument and the grain size of perovskite is very small, leading to more grain boundaries that could affect the photovoltaic performance. As for the solvent processes, it is easier to be processed and suitable to be scaled up. But it wastes tremendous volume of precursor solution, for instance the spin coating method more than 70\% of solvent applied to the substrate will be wasted. Inspired by the crumple graphene oxide project in our research group, we considered using EHD spraying to form the perovskite thin film. Thus in this thesis, the method being used to form the CH$_3$NH$_3$PbI$_{(3-x)}$Cl$_x$ perovskite thin film is electrohydrodynamic (EHD) spraying.

EHD spraying is a method of liquid atomization by means of electrical forces, high electric potential applied to a capillary nozzle where the liquid flowing out from, the liquid would be dispersed into fine droplets forced by the high electric field \textsuperscript{[34]}. As shown in Figure 3 \textsuperscript{[34]}, the high voltage is applied to the capillary nozzle and the substrate is grounded, there would be a strong electric field building up at the capillary outlet. The capillary nozzle is usually made of fine, hypodermic needle, connected to a pumping tube filled with the liquid. The liquid flowed out from the nozzle outlet by the pressure of the pump, then elongated in the gravitational and electric field, finally disintegrated into droplets caused by the electrical forces. The charged droplets deposit onto the substrate due to the gravity and electrical field. The solvent in the droplets could evaporate during the flying time before or right upon the deposition onto the heated substrate, this can leave a layer of the solid particles on the substrate as Figure 3. (b) shown. On the other case, if the droplets were not dry upon the deposition they would coalesce and merge into the thin film.

Many modes of EHD spraying are distinguished in the literature based on the form of the meniscus, the motion of the jet, and a way it disintegrates into droplets \textsuperscript{[34]}. The different modes can be found in Figure 4. In this thesis, we are using the multi-jet mode to accomplish the EHD deposition. A few fine jets on the circumference of the capillary can be observed during the spraying, and the jet disintegrates into droplets due to the electrostatic forces. The multi-jet mode is beneficial to droplets merging to form a uniform thin film with good morphology.
Figure 3 The schematic figure of electrohydrodynamic deposition $^{[34]}$

Figure 4 Various modes of electrohydrodynamic spraying $^{[34]}$
One of the advantages of the EHD method is the size of the droplets can range from hundreds micrometers down to several tens of nanometers. Droplet generation and droplet size could be controlled by several parameters during the spraying, such as the applied voltage, the height of the nozzle from the substrate and the flow rate of the flowing liquid. Another advantage is that the charged droplets are self-dispersing in space to prevent the coagulation of the droplets. Also due to the opposite charge of the droplet and the substrate, the spray efficiency is much higher for the charged spray than for an uncharged spray. By taking advantage of this feature, EHD spraying is favorable to surface coating or thin film production.

2.2 Self-organization

We aimed to get the thin film of perovskite precursor on indium tin oxide (ITO) glass by using electrohydrodynamic spraying. There are some interesting stories about the droplets impacting on a solid surface. Impaction of a droplet on a dry solid surface could be different from that on a liquid surface or a wet surface. In the EHD spray, droplets may impact on a dry substrate or on a wet surface as a result of the impaction of the earlier droplets on the solid surface.

As for the formation of the thin film on a hot substrate, the films are usually metastable in the as-deposited state and might get dewetting or agglomeration to form the island due to the solvent evaporation. Several scenarios may occur upon droplet impact, depending on different surface temperatures and surface texture. At sufficient high temperature, the evaporation mode is the film boiling regime in which the droplet-solid contact is minimized by the rapid formation of vapor layer at the interface (Figure 5). As a result, the droplet will bounce off the solid surface upon impact. The lower temperature boundary of this regime is called the Leidenfrost point. If the surface temperature is lower than the Leidenfrost point, a transition boiling regime is encountered, where the droplet-solid contact is prolonged, the droplet dynamics changes and the heat transfer rate increases. At even lower surface temperature, the nucleate boiling regime prevails where complete wetting of the surface occurs and the heat transfer rate is the maximum. In the nucleate boiling regime, the boiling could cause the cavities, affecting the droplet deposition. A single-phase regime encountered when the temperature dropped down enough, where the heat transfer is dominated by single-phase convection. Figure 5 schematically shows the four different models. The first three scenarios involve liquid-gas-solid interfaces, which leads to damaged liquid thin film with bad morphology. Only in the single-phase regime, the film has a chance to maintain complete and continuous. While it is similar to the droplets impact on the cold solid surface, thus the following focus is the droplets impact on the cold solid surface.
Figure 5 Droplets impact behavior in droplet-heated surface interaction\textsuperscript{[9]}

Upon the droplet impact on the cold solid surface, it may conclude different processes such as spreading, receding, rebounding, splashing, coalescing, and drying. The initial impact and spreading characteristics form the foundation of a coating layer. However an air bubble could be trapped inside when the droplet hits on the solid surface, this is one reason of the bad integrity of the film, affecting the solar cell performance. The desired case for perovskite active layer formation is the deposition mode, which requires a low or moderate droplet impact velocity. In order to achieve this mode, we shortened the distance between the needle tip to the substrate, the flying time of the droplets is reduced correspondingly as well as the impact velocity.

Besides the EHD spraying factors, the properties of the droplet solution and the substrate are also crucial for the formation of the uniform thin film. The density, viscosity, surface tension of the droplet, the surface roughness, surface wettability of the substrate all affect the formation of the film and the quality of the film.

The perovskite precursor is the lead chloride ($\text{PbCl}_2$) and methylammonium iodide (MAI) mixed solution, dimethylformamide (DMF) is the most used solvent to dissolve the perovskite precursor. After annealing the mixed $\text{PbCl}_2$ and MAI solution become to 3D trihalide perovskite crystal. Due to this crystallize transition, each of the as-deposited droplets will form a ring made of the precipitation when the solvent evaporated, each ring works as a dewetting pattern, which cannot be rearranged by the following deposit droplets. In this case, the final perovskite film is not uniform with bad quality of crystal grain.

Figure 6 Deposition of perovskite precursor solution in DMF single solvent
Figure 6 shows the film formed by EHD deposition of mixed PbCl$_2$ and MAI solution in DMF single solvent. It is easy to observe the dewetting pattern of the thin film with bad morphology. It will lead to a lot pin holes and poor crystal grain quality in the final perovskite layer, resulting in low efficiency solar cell. Depositing perovskite precursor to form a thin film with good morphology is the crucial key for the high efficiency perovskite solar cell.

In order to achieve high quality of precursor as-deposit film, two-solvent system has been introduced into this project. The two-solvent system took the advantage of Marangoni effect, which helps the as-deposit film to do self-organization. The Marangoni effect is fluid phenomenon, as the tendency for heat and mass to travel to areas of higher surface tension within a liquid\cite{37}. Surface tension is a property of a liquid that causes the surface portion of liquid to be attracted to another surface. This is because a liquid with a high surface tension pulls more strongly on the surrounding liquid than one with a low surface tension, the presence of a gradient in surface tension will naturally cause the liquid to flow away from the regions of low surface tension. The surface tension gradient can be caused by concentration gradient or by a temperature gradient. So in this case, two different solvents with different boiling point and different vapor pressure are used to accomplish the Marangoni flow. In the end, after the Marangoni effect self-organization, the film should become flat and uniform.

The mostly used common solvent for PbCl$_2$ and MAI are all organic solvents, as shown in Table 1. They are dimethylformamide (DMF), n-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO) and gamma-butyrolactone (GBL).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling Point ($^\circ$C)</th>
<th>Surface Tension @20$^\circ$C (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>152</td>
<td>37.1</td>
</tr>
<tr>
<td>DMSO</td>
<td>189</td>
<td>43.54</td>
</tr>
<tr>
<td>NMP</td>
<td>202</td>
<td>40.79</td>
</tr>
<tr>
<td>GBL</td>
<td>204</td>
<td>35.4</td>
</tr>
</tbody>
</table>

DMF:NMP combination has been tried first, we put the ITO substrate in a covered petri dish after EHD deposition, so that the as-deposited film could accomplish the Marangoni flow to form a flat and uniform covered film as shown in Figure 7. Compare Figure 7 with Figure 6, the film morphology differences are obvious. Two-solvent system successfully accomplished self-organization, this uniform and flat film is the crucial basement for the further crystallization in the annealing process. Although our final bi-solvent system is DMSO:NMP system, this is due to the better grain connection after the annealing procedure described in details in the following section.
2.3 Annealing Process

As thin film photovoltaic, organic-inorganic hybrid perovskite solar cell’s performance is highly dependent on the film morphology, which in turn is dependent on the deposition techniques and subsequent treatments employed. As demonstrated by Burschka et al.\textsuperscript{[38]}, which includes the deposition technique and all the treatments and conditions the material is exposed to as part of the following conversion to final perovskite form. We also talked about the deposition method and the solvent engineering to help forming the good quality film, in this section we will mainly talk about the most important part, post-annealing treatment of perovskite thin film. The role of this post heating treatment is to convert the as-deposited solution into the perovskite material\textsuperscript{[39]}. It is found that the conversion requires sufficiently high temperature to ensure the vaporization of the solvent and the crystallization of the perovskite material.

The morphology, stoichiometry and crystallinity of the perovskite material greatly influence the overall photovoltaic device performance, which is highly depends on the annealing process. For most of the techniques where the perovskite material is deposited form solution, a subsequent heat treatment of the film is required. This has the dual purposes of removing any excess solvent remaining in the precursor film as well as facilitating the formation of the perovskite crystal structure. As we said before in this thesis, PbCl$_2$ is used as the precursor, the common anneal conversion time is 45 minutes at 100 °C like reported by Lee et al.\textsuperscript{[40]} Contrary to the case when PbI$_2$ is used as a precursor as reported by Kim et al.\textsuperscript{[41]} which only require 10 minutes of heating at 100 °C to complete the conversion. The conversion to the final perovskite was regarded as complete once the film showed a stable absorption profile resulting in a uniform black color as shown in Figure 8.
At low temperature, this conversion takes considerably long time, 3 h at 80 °C relative to 45 min at 100 °C. At 60 °C, even when left for more than 20 h the conversion was not complete as indicated by poorer film coloration [39]. In the case of high annealing temperature (>150 °C) the conversion is observed to occur almost instantaneously and in the case for temperature above 200 °C to quickly convert to yellow as shown in Figure 9. The yellow color of the film is supposed to be PbI$_2$ formation, which is also confirmed by the surface photovoltage spectroscopy measurements made by Supasai et al [42].
From the literature UV-vis absorption spectra results of perovskite films, the absorption onset of the perovskite remains constant for samples annealed between 60 and 175 °C, indicating that the optical bandgap of the perovskite in unaffected by the annealing temperature. It further confirms that the nature of the perovskite formed is unchanged by the annealing temperature. But the morphology of the final perovskite film is highly dependent on the annealing process. Figure 10 (a) is the film annealed by the most simple method, anneal on the hot plate at 100 °C for 45 min. From Figure 10 (c), the microscopy image shows the crystal structure of perovskite, a lot of uncovered spaces between each grain, which could have tremendous bad impacts on the photovoltaic performance due to the bad electronic transport between each grain. Because of our unique bi-solvent system, hot plate is no longer suitable for our case, two solvents with different boiling point and different surface tension will destroy the film morphology during the evaporation by the slow heating method.

Figure 10 Perovskite film annealed on hot plate vs. annealed by heat gun (a) Photograph of perovskite film on ITO glass annealed on hot plate at 100 °C for 45 min (b) Photograph of perovskite film on ITO glass annealed by heat gun at 105 °C for 4 min 30 s (c) Optical microscopy images of perovskite annealed on hot plate (d) Optical microscopy images of perovskite annealed by heat gun
As discussed before, our unique bi-solvent system solution process requires very high evaporation speed to make sure those two different solvents have the comparable evaporation rate during the annealing treatment. So the annealing method applied has to provide the sufficient heat at relatively low temperature (around 100 °C). One day when I was blow-drying my hair, it came to me an idea that why not applying the heat with the forced convection to make the evaporation faster but without increasing the temperature. Thus the heat gun was used in the annealing process, the heat gun anneal schematic set up is as the Figure 11 shown. The heat gun has the same working mechanism as the hair dryer, it blows out the hot wind from the outlet.

Figure 10 (b) and (d) confirmed the hypothesis made in the previous part, the rapid evaporation rate helps to form better film with good quality crystals. Compared Figure 10 (c) and (d), from the microscopy images it is very obvious that the grain size of the heat gun method is much bigger than that of the hot plate. At the same time, the gaps between the perovskite crystallites are much smaller, it forms a densely interconnected network of perovskite. In addition to the morphology, the total time of annealing is around 4 to 5 min, which is much shortened compared with the normal hot plate annealing (average at 45 min). Shorter process time makes it a better candidate for the scaled up mass production, and it is less energy consumption. Thus the heat gun annealing makes the organic inorganic perovskite solar cell more attractive and promising for utilization in industry.
Chapter 3

Experimental Section

3.1 Chemical Synthesis

Methylamine (2.0 M in methanol), hydriodic acid (47% in water) and lead(II) chloride (99.999% purity) were purchased from Sigma Aldrich. Synthesis of methylammonium iodide powder followed methods described in literature \cite{16,17}. 79 ml methylamine and 21 ml hydriodic acid were put in a flask, the mixed colorless semitransparent liquid was treated in ice bath for 2 h. Then put the mixed liquid in water bath at 50 °C under vacuum condition in order to let the solvent evaporate and crystallize to MAI. The mixed liquid turned into white crystal-like powder after over night heating. Wash the white powder by diethyl ether for 3 times, and put the as-washed MAI in the vacuum chamber over night to be dried. Figure 12 shows the MAI after vacuum dry, it is ready for further use.

![Figure 12 MAI powder after vacuum dried](image)

Perovskite precursor solution is made by methylammonium iodide (MAI) and lead chloride (PbCl$_2$) (3:1 molar ratio) dissolved in sequence into dimethylsulfoxide (DMSO) and n-methyl-2-pyrrolidone (NMP) (4:6 ratio) bi-solvent at the concentration of 2.64M and 0.88M. MAI is put into the bi-solvent first, followed by the magnate stir on the hot plate at 70 °C for 1 hour. Then put the PbCl$_2$ into the MAI solution, PbCl$_2$ is not easy to dissolve in the solvent so it requires heating at 70 °C with magnate stir over night to encourage dissolution. Then cooled down to room temperature, and filtered through a 0.45 µm PTFE filter before deposition.
3.2 Experimental Set-up

Figure 13 displays the set-up of electrohydrodynamic spraying we are using, it contains a pump to push the perovskite precursor at a constant flow rate. Under the yellow pump is the power supply, it provides the high electrical field to the needle and the substrate. A moving stage is utilized to make the substrate pass through the deposition area at a constant speed in order to get the uniform film. The annealing apparatus is also shown in the right side of Figure 13, the heat gun is pre-heated to 105 °C 5 min before annealing process. The total annealing time varies for different solution volume on the substrate, which also forms different thickness of the perovskite film. The average time is around 4 min 30 s.

Figure 13 Electrohydrodynamic spraying and heat gun annealing apparatus
3.3 Experiment Parameters

Table 2 Experimental parameters of the basic perovskite EHD spray

<table>
<thead>
<tr>
<th>Concentration MAI:PbCl₂ (M)</th>
<th>Solvent Ratio DMSO:NMP</th>
<th>Flow Rate (µl/min)</th>
<th>Voltage (kV)</th>
<th>Height (cm)</th>
<th>Moving Stage Speed (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.64:0.88</td>
<td>4:6</td>
<td>18</td>
<td>10.5</td>
<td>2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

All the parameters and conditions we need to tune can be found in Table 2, all the parameters are interdependent. The height from the needle tip to the substrate is 2 cm, helping to get the low velocity droplets when impact the substrate as we discussed in section 2.2. And 10.5 kV high voltage aimed to get multi-jet spray mode for bettering merging film as discussed in section 2.1. As for the flow rate and moving stage speed, they are supposed to change the volume of the precursor solution deposited on the substrate, correspondingly change the thickness of the perovskite film.

3.4 Perovskite Solar Cell Device Fabrication

A layer of poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was deposited on indium tin oxide (ITO) glass by spin coating, at the spin speed of 4000 rpm for 1 min, followed by annealing at 120 °C for 20 min. Then deposit the CH₃NH₃I₃-xClₓ perovskite film by electrohydrodynamic spraying and heat gun annealing. On the top of perovskite layer is phenyl-C₆₁-butyric acid methyl ester (PCBM) by spin coating at 1000 rpm for 1 min and annealed at 90 °C for 10 min. PCBM applied in 1,2-dichlorobenzene (ODCB). Those steps are all done in our lab on UCM campus, the next steps for completing the full solar cells are finished in Lawrence Berkeley National Laboratory (LBNL). We used Al as the electrodes, our photovoltaic cell has the same structure as Y.Yang’s [43].
Chapter 4

Results and Discussion

4.1 Characterization of perovskite film

X-ray diffraction (XRD) measurements were conducted to investigate the nature of the material formed following the heat gun annealing process. Figure 14 shows the XRD pattern of our perovskite film on ITO glass. The peak at 14.17, 28.49, and 43.27° are respectively assigned to the (110), (220), and (330) planes. The presence of these peaks indicates the conversion from precursor to perovskite materials appeared [44]. Compared with the results of M. Liu [33], the characteristic peaks are in identical positions as vapor deposited films and spin coating processed films. Thus this diffraction pattern indicated that our EHD spraying and heat gun annealing techniques have successfully produced the mixed halide perovskite with an orthorhombic crystal structure.

Figure 14 XRD pattern of heat gun annealing perovskite film
4.2 Solvent Combination

Figure 15 displays the perovskite film made by EHD spraying in different solvent combination, as discussed in section 2.2 bi-solvent system is taking advantages of Marangoni effect to form a uniform flat film. As shown in Table 1, both DMF:NMP and DMSO:NMP have different boiling point and surface energy, which makes the Marangoni flow happens during and after the liquid film deposited. We tried the simple ratio 4:6 for both systems, and it turns out that DMSO:NMP combination forms better film by optical photographs. The film of DMSO:NMP system is darker than it of DMF:NMP, indicating less empty gaps between crystal grains. This is also confirmed by the optical microscopy images in Figure 15, the crystal grains are more connected to each other leaving smaller empty spaces in film than DMF:NMP system. This is due to the big difference (50 °C) between the boiling point of DMF and NMP, two solvents are mixed in the liquid film before annealing. While during annealing, DMF evaporates faster than NMP, so the perovskite crystal formed in DMF-rich area can be damaged by the evaporation of NMP later. However the difference of boiling point between DMSO and NMP is only 10 °C, which leads to the comparative evaporating rate in the annealing process, leading to an undamaged dense film. Figure 16 is showing the perovskite ultraviolet-visible (UV-vis) absorption spectrum result of those two systems. Higher absorbance intensity of DMSO:NMP also proving that this combination creates dense film with better morphology, which is one of the important properties of the active layer for high-efficiency photovoltaic cells. The perovskite UV-vis absorption onset at 770 nm as reported \[13,45,46\]. Both absorption spectrums have the peak at around 770 nm, also confirming the result of XRD that our techniques produce perovskite.

Figure 15 Photographs and optical microscopy images of perovskite film by EHD spray in different solvent combination
In order to produce high quality perovskite film, we go a further step to study how the different ratio of DMSO to NMP affects the film morphology. From Figure 17 (a) the optical microscopy images show the difference of the film from different solvent ratio. DMSO:NMP=3:7 forms the worst film with a lot of empty spaces. This result is due to the high boiling point of dominant solvent (NMP) causing long time annealing and unbalanced evaporation within the film. DMSO:NMP=4:6 system creates the most connected crystal gains in the film. This is also confirmed by the scanning electron microscopy (SEM) images (Figure 17 b), homogeneous film was formed in DMSO:NMP=4:6 solvent system. It further confirmed bi-solvent system does work and form continuous perovskite film. However in other low coverage films, the crystal grains are separated by holes. In the low perovskite coverage film, light will pass through the empty space without absorption, decreasing the photocurrent. In addition the insufficient coverage results in a high frequency of shunt path. The morphology of perovskite film is significantly influenced by the ratio of two solvents, and the ratio of DMSO:NMP=4:6 could form the continuous perovskite film which has the potential to be the active layer of good photovoltaic performance.
Figure 17 Perovskite film from different ratio of DMSO to NMP

(a) Optical microscopy images (b) SEM images
4.3 Thickness Control

Recent work has shown that perovskite film thicknesses of 400-800 nm can be used to successfully prepare high-performance photovoltaic devices [46-48]. In order to get high efficiency photovoltaic devices, our techniques need the ability to control the film thickness. The easy way is to change the flow rate and/or the moving stage speed, so that the corresponding solution volume deposited on the substrate is changed, as well as the final perovskite film. This also takes the advantages of the spray coating [49]. Figure 18 shows the UV-vis absorbance of perovskite from different flow rate and higher flow rate results in higher absorbance of the film, indicating that increasing the flow rate could increase the thickness. It is also confirmed in Figure 19, the cross section SEM images of different flow rate, the images are corresponding to 16, 18, 26µL/min from top to bottom. The thicknesses are 240, 550, 1300 nm separately. Also from the cross section image, it is obvious that the perovskite film is dense and continuous. But for the 16 µL/min, the film is not flat or neat. This might due to the strong wind from the heat gun is uncontrollable and nondirectional, which will destroy the film during annealing especially when the film is thin. We need to study about the heat gun and make it controllable for further development.
Figure 19 Cross-section SEM images of perovskite film (a) at flow rate of 16 µL/min (b) at a flow rate of 18 16 µL/min (c) at a flow rate of 26 16 µL/min
4.4 Devices

The final photovoltaic devices are fabricated as described in section 3.4, and tested one set of the devices, the average efficiency is around 15%. As the first trial of final devices, it is an exciting and promising result. Due to the time limit of me, a lot of the improvement could be finished in order to improve the performance in the future.

Figure 20 Power conversion efficiency
Chapter 5

Conclusion

In summary, we have demonstrated that the electrohydrodynamic spraying of MAI and PbCl$_2$ precursor in the bi-solvent system, in combination with heat gun annealing process successfully formed dense uniform perovskite film. Our techniques are reliable highly reproducible to prepare planar organic-inorganic perovskite photovoltaic devices with efficiencies up to 16%. The electrohydrodynamic spraying takes the advantages both of the solution processing and vapor deposition method to produce continuous flat liquid film, while the unique bi-solvent system takes the advantage of Marangoni effect to let the as-deposited film accomplish self-organization. Those deposition techniques all lead to a film with good morphology, which is treated by the heat gun annealing. During the heat gun annealing process, the solvents evaporate and the crystallization happens faster compared with the conventional hot plate annealing. Which makes it competitive and promising for scale-up production in the industry.
Reference:


