

Solar Photovoltaics: Fundamental Technology and Applications
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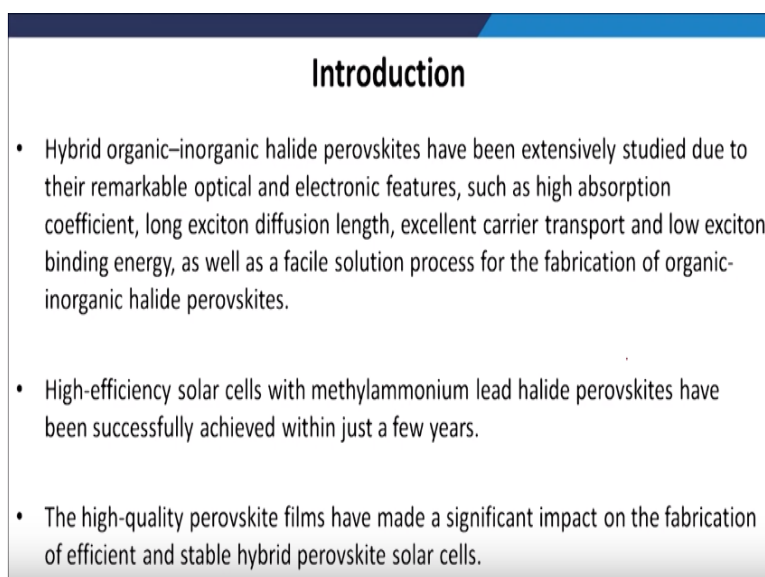
Lecture – 29
Morphology Optimization of Perovskite Solar Cells

Welcome to our solar photovoltaic course. Now today we will discuss about the perovskite and morphology optimization. Now we have seen that one of the important parameter for tuning the high efficiency in a perovskite solar cell is not only the charge carrier generation but how the charge carrier transport or how they diffuse along the active layer.

Now very often this property how the charge carrier transport to the diffusion layer or to the active layer that depends upon the morphology of the devices. So that is why the change in morphology changes the grain size changes the charge transport properties and the photo physics significantly.

So today we will discuss about the different technology for the morphology optimization in the perovskite solar cell and how they can lead to the different kinds of photo physics in these devices.

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Introduction

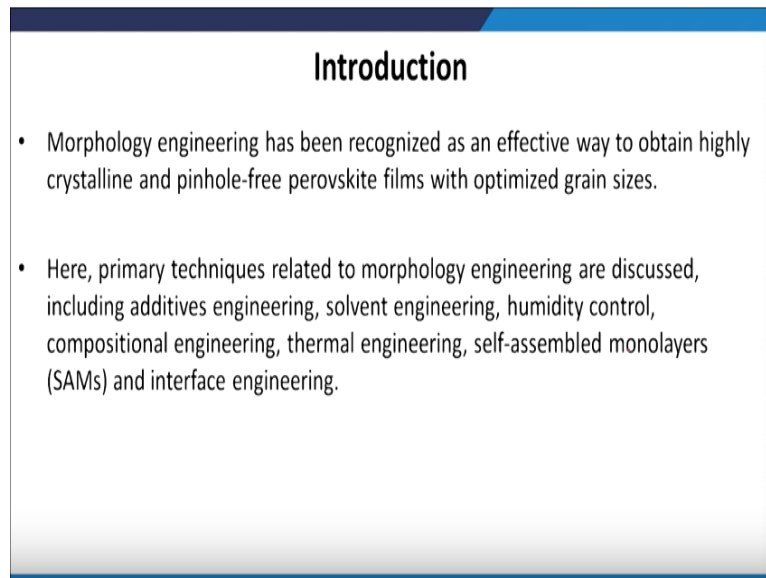
- Hybrid organic–inorganic halide perovskites have been extensively studied due to their remarkable optical and electronic features, such as high absorption coefficient, long exciton diffusion length, excellent carrier transport and low exciton binding energy, as well as a facile solution process for the fabrication of organic–inorganic halide perovskites.
- High-efficiency solar cells with methylammonium lead halide perovskites have been successfully achieved within just a few years.
- The high-quality perovskite films have made a significant impact on the fabrication of efficient and stable hybrid perovskite solar cells.

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diffusion length, excellent carrier transport and low exciton binding energy as well as a facile solution process for the fabrication of organic-inorganic halide perovskite.

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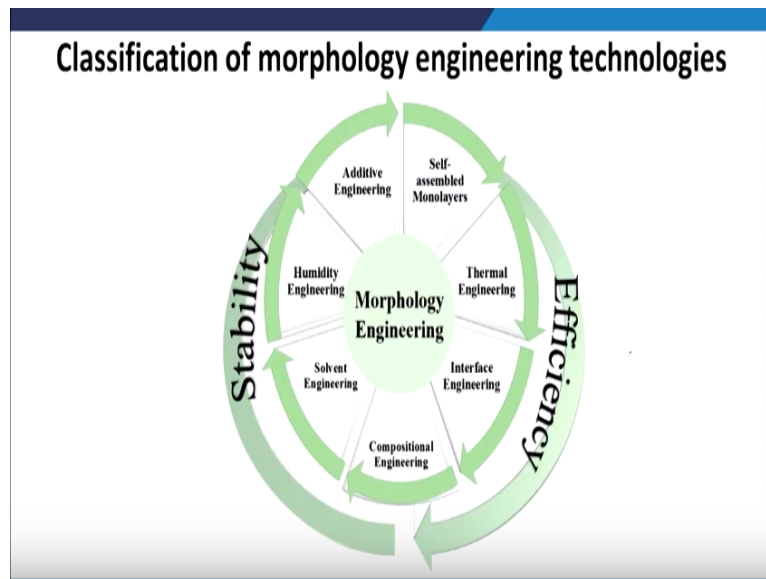


Introduction

- Morphology engineering has been recognized as an effective way to obtain highly crystalline and pinhole-free perovskite films with optimized grain sizes.
- Here, primary techniques related to morphology engineering are discussed, including additives engineering, solvent engineering, humidity control, compositional engineering, thermal engineering, self-assembled monolayers (SAMs) and interface engineering.

Now morphology engineering has been recognized as an effective way to obtain highly crystalline and pinhole-free perovskite film with optimum grain size. Here primary techniques related to morphology engineering are discussed introducing additive engineering, solvent engineering, humidity control, compositional engineering, thermal engineering, self-assembled monolayer and interface engineering.

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Let us look at this chart, so the classification of the morphology engineering can be many pools. It can be additive engineering, that means while fabricating the active layer we can put an external additive as a solvent. We can use humidity engineering that means if we control the humidity or if we change the humidity that affects the morphology significantly.

Then we can do solvent engineering that means if we change the solvent, so like for example if we change from DMF to DMSO or to NMP for toluene. So basically what we have changing is the dielectric constant. If the dielectric constant is different than the polarity is also different. If the polarity is different the way, the perovskite crystallize that also different. So the morphology also becomes different.

That is called solvent engineering. Then the compositional mapping or compositional engineering, so in the perovskite we know there is a cationic group and there is an anionic group. Now we can change a single cation to 2 or 3 cation and instead of a single anion we can use 2 or 3 anions and when we make a combination of all of these cation and anion that is called combinational approach or combinational engineering.

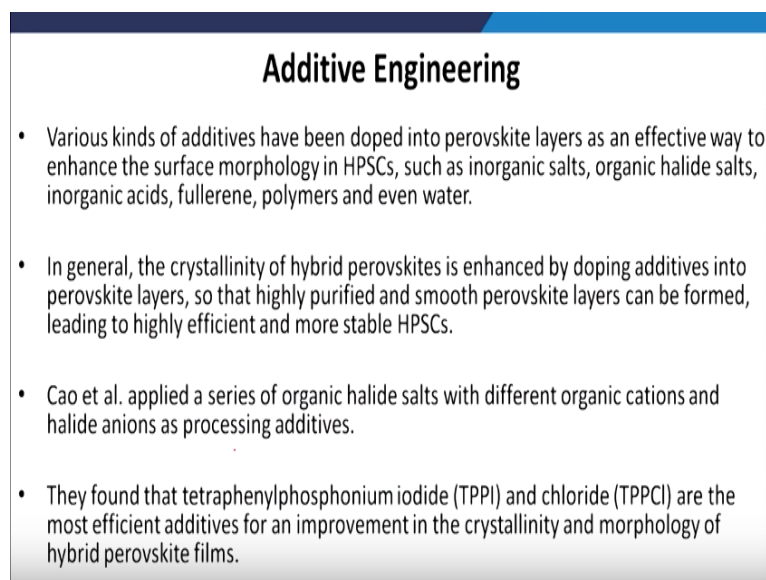
Then there are interface engineering, so perovskite forms a very important layer at its interface or charge transport interface. For example, if I take a CH₃ NH₃ lead iodide, now for a p-i-n geometry we use PEDOT PSS as a hole transport layer and PCBM as an electron transport layer. Now the perovskite PEDOT PSS interface and perovskite PCBM interface is very very important while designing an efficient solar cell.

Instead of PCBM, if we use some other electron acceptor layer or instead of PCB, let us say in addition to PCMB we use BCP as a small molecule or if we evaporate the C60 then the morphology will be completely different. Then thermal engineering, so what temperature we anneal the perovskite like after making perovskite film with this precursor solution then usually we anneal the film.

So, annealing mean heating the film at particular temperature. Now usually we heat it at 120 degrees Celsius, now if we heat at 150 degree Celsius or if we heat at 100 degrees Celsius or if we heat at 90 degrees Celsius, the resultant crystallinity packing and morphology will be way different. That is called morphological optimization and then the self-assembled monolayers. So how do we make the films? We can make the films by one step approach.

We can make the films by two step approach. We can do a self-assembly. So these also change the packing or crystallinity of the film. So, that also changes the morphology of the perovskite film. So these are all different technology for the morphology optimization and what it changes. It changes the efficiency as well as the stability the two important parameter in a perovskite solar cell.

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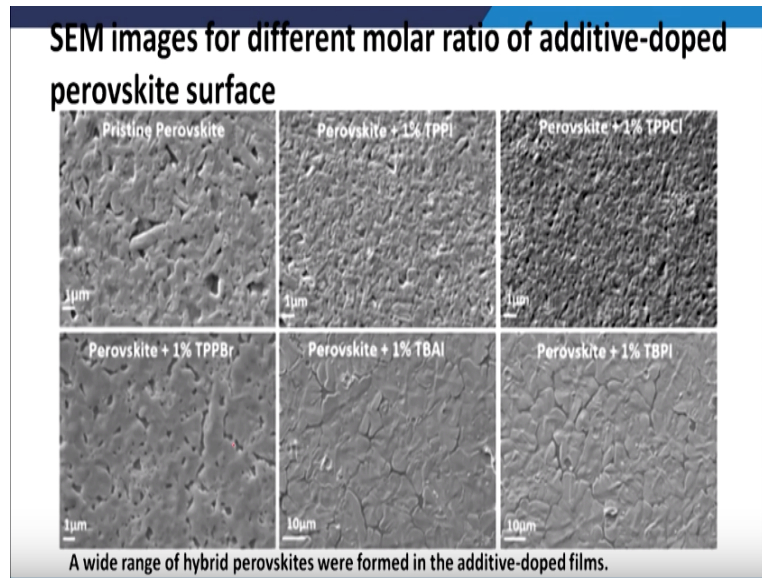
Additive Engineering

- Various kinds of additives have been doped into perovskite layers as an effective way to enhance the surface morphology in HPSCs, such as inorganic salts, organic halide salts, inorganic acids, fullerene, polymers and even water.
- In general, the crystallinity of hybrid perovskites is enhanced by doping additives into perovskite layers, so that highly purified and smooth perovskite layers can be formed, leading to highly efficient and more stable HPSCs.
- Cao et al. applied a series of organic halide salts with different organic cations and halide anions as processing additives.
- They found that tetraphenylphosphonium iodide (TPPI) and chloride (TPPCI) are the most efficient additives for an improvement in the crystallinity and morphology of hybrid perovskite films.

Now let us look one by one factor. First is the additive engineering, various kind of additives have been doped into the perovskite layer as an effective way to enhance the surface morphology in a hybrid perovskite solar cell. For example, in organic salts, organic halide salts inorganic acids, fullerenes, polymers and even water. In general, the crystallinity of hybrid perovskites is enhanced by doping additives into the perovskite layers.

So that highly purified and smooth perovskite layers can be formed leading to highly efficient and more stable hybrid perovskite solar cells. Cao et al. applied series of organic halide salts with different organic cations and halide anions as processing additives. They found that TPPI tetraphenylphosphonium iodide and chloride are the most efficient additives for an improvement in the crystallinity and morphology of the hybrid perovskite film.

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For example, if we use a different, different additives like with the perovskite only perovskite, this is the SEM image if we use 1% TPPI, so the morphology improves. If we use 1% TPPCL, the morphology further changes. So what we mean by changing the morphology is the smoothness, uniformity, crystallinity, and the packing and these all affects the charge transport properties.

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Additive Engineering

- Liu et al. have shown that the perovskite film quality could be ameliorated by adding methylamine solution-based additives, considerably reducing intrinsic defect density in thick polycrystalline layers. The shallow electronic disorder was then diminished, resulting in a sufficient carrier lifetime.
- As a result of extended carrier diffusion length, heterojunction planar perovskite solar cells could be fabricated with a 650 nm-thick absorber layer, attaining a power conversion efficiency of 20.02% (average 18.44%), with a highly stable output efficiency of 19.01% under simulated AM 1.5 solar illumination of one sun (100 mWcm⁻²).

So there are different approach by this for example, Liu et al. have sown that perovskite film quality can be improved by adding methylamine solution-based additive considering reducing intrinsic defect density in a thick polycrystalline layer. As a result, the extended carrier diffusion length and heterojunction planar solar cells are fabricated with a 650 nanometre thickness layer and that can give an efficiency of 20.02%.

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Additive engineering

- By using hydrogen iodide (HI) as an additive, smoother perovskite layers can be fabricated through an intramolecular exchange process, resulting in a decrease in deep-level defects, and the defect-engineered thin perovskite layers enable the fabrication of PSCs with a higher PCE. HI was also applied to an HC(NH₂)₂PbI₃ perovskite solar cell with a PCE of 16%.
- Furthermore, acids and some metal ions can also be used as dopants into the perovskite layer.

By using hydrogen iodide HI as an additive, smoother perovskite layer can be fabricated through an intermolecular exchange process resulting in a decrease in the deep-level defects and the defect-engineered thin perovskite layers enable the fabrication of perovskite solar cells with a higher PC efficiency.

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Self-assembled monolayers (SAMs)

- Self-assembled monolayers (SAMs) were firstly applied to the field of synthetic sophistication.
- Self-assembly, leading to a super-molecular organic silane layer, can improve the surface morphology of hybrid perovskites.
- Hierarchical organization of interlocking components provides very complex systems. The ability to combine the head and tail groups of constituent molecules makes SAMs an effective method for surface modification.
- Although the exact mechanisms of SAMs have remained ambiguous until now, it is still an attractive approach in the field of HPSCs.

Similarly, the self-assembled monolayers, self-assembled monolayers are firstly applied to the field of synthetic sophistication. Self-assembly leading to a super-molecular organic silane layer can improve the surface morphology of hybrid perovskite. Hierarchical organizations of interlocking components provide very complex systems.

The ability to combine the head and tail group of constituent molecules makes self-assembled monolayers as effective method for surface modification. Well for self-assembled monolayers, we do a silent chemistry, so you use silent molecule. Now these are like an anti-polar, so it has an hydrophobic group. It is an hydrophilic group.

So now the way the hydrophobic or hydrophilic group, they assemble on the perovskite layer that change the way of the packing or the crystallinity. Although the exact mechanisms of the SAMs have remained ambiguous until now, it is still an attractive approach in the field of perovskite solar cell.

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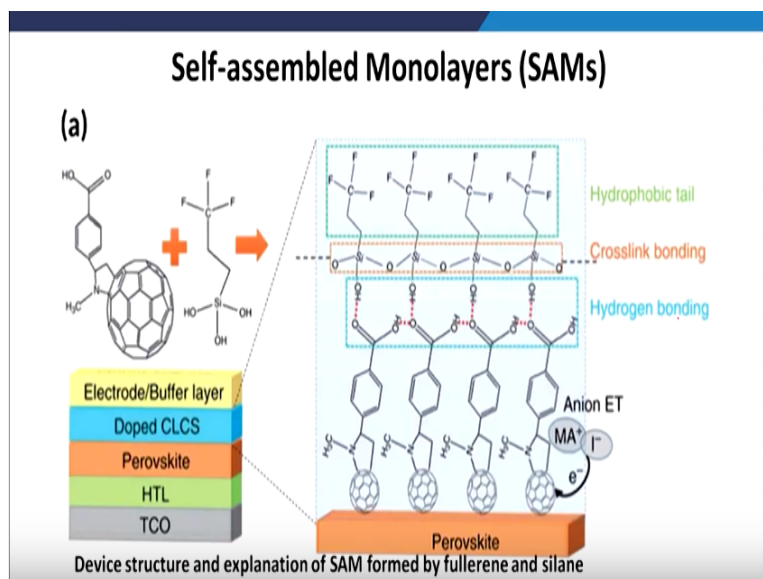
Self-assembled Monolayers (SAMs)

- The power efficiency of HPSCs can also be enhanced by introducing silanes as SAMs between titanium oxide and the perovskite layer. The results of SEM and FTIR measurements showed that an organic silane layer can improve the surface morphology of hybrid perovskites by incorporating SAMs between TiO_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$, and printable HPSCs have reached an efficiency of 12.7% in large-area devices.
- Huang and his co-workers reported that the stable perovskite solar devices delivered an efficiency of 19.5% with a high fill factor of 80.6% by the introduction of crosslinkable silane molecules with hydrophobic functionalization and doped fullerene as electron transport layers, as shown in Figure.

The power efficiency of the hybrid perovskite solar cell can also be enhanced by introducing silanes as self-assembled monolayers between titanium oxide and the perovskite layer. The resultant SEM and FTIR measurements showed that an organic silane layer can improve the surface morphology of the hybrid perovskite by incorporating SAMs between TiO_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ lead iodide and printable HPSCs have reached an efficiency of 12.7% in the large-area devices.

Huang and his co-worker reported that the stable perovskite solar cell device can offer an efficiency of 19.5% with a fill factor of 80.6% by the introduction of crosslinkable silane molecule with hydrophobic functionalization and doped fullerene as an electron transport layer as shown in that next figure.

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So you see here, like between the transparent conductive oxide, we put a hole transport layer and then there is a perovskite and then there is a doped CLCS layer and then we put the electrode layer. So here we are showing an example of a silane like you know, if we put a crosslinkable silane bonding, which has a hydrophobic tail which is protruding towards outside so that it makes a hydrogen bond with the transport layer and that increased the stability and the efficiency of the perovskite solar cell.

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Thermal Engineering

- Hybrid perovskite films are generally formed by heat treatments to get rid of residual solvents in the solution-based process, produce the perovskite from its precursors, improve crystallization and enhance grain growth.
- For hybrid organic-inorganic perovskite itself, it typically takes a sufficient annealing time to achieve full conversion. During the annealing process, the quality of the hybrid perovskite films depends on several significant factors, such as the film thickness, the heating duration, the temperature, and film composition.

Another important technique in the morphology optimization is the thermal engineering. Hybrid perovskite films can generally be formed by heat treatments to get rid of residual solvents in the solution-based process, produce the perovskite films from precursors and improve crystallization and enhance the grain growth. For hybrid inorganic-organic perovskite, it typically takes a sufficient annealing time to achieve full conversion.

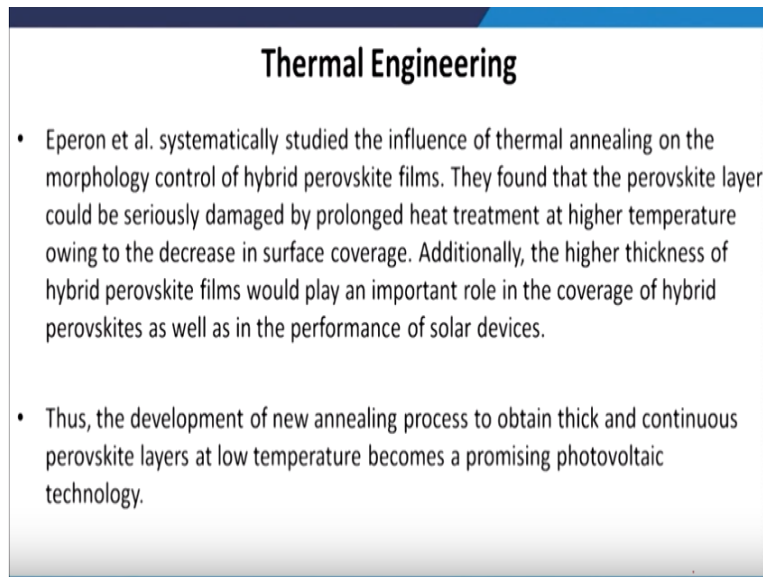
During the annealing process, the quality of the hybrid perovskite film depends on several significant factors such as the film thickness, the heating duration, the temperature, and the film composition. So for example, if I take 2 perovskite precursors, CH₃NH₃ iodide and lead iodide and if we mix them to get a CH₃NH₃ iodide and lead iodide okay. So it depends upon at what temperature, we have centered this film.

And I said that if the temperature changes from 100 to 120 degree centigrade or 150 degrees Celsius, the resultant morphology of this film will be completely different. Similarly, how long we have heated the film, have we heated the film for 10 minutes or 5 minutes? That will also change the morphology. And also what is the ratio whether you have used the less lead

iodide or where you have used a further less iodide or whether you have used an excess lead iodide.

That also changes the morphology. So, all these parameters affect the morphology of the perovskite film. Now there are several groups which are working on the thermal engineering.

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Thermal Engineering

- Eperon et al. systematically studied the influence of thermal annealing on the morphology control of hybrid perovskite films. They found that the perovskite layer could be seriously damaged by prolonged heat treatment at higher temperature owing to the decrease in surface coverage. Additionally, the higher thickness of hybrid perovskite films would play an important role in the coverage of hybrid perovskites as well as in the performance of solar devices.
- Thus, the development of new annealing process to obtain thick and continuous perovskite layers at low temperature becomes a promising photovoltaic technology.

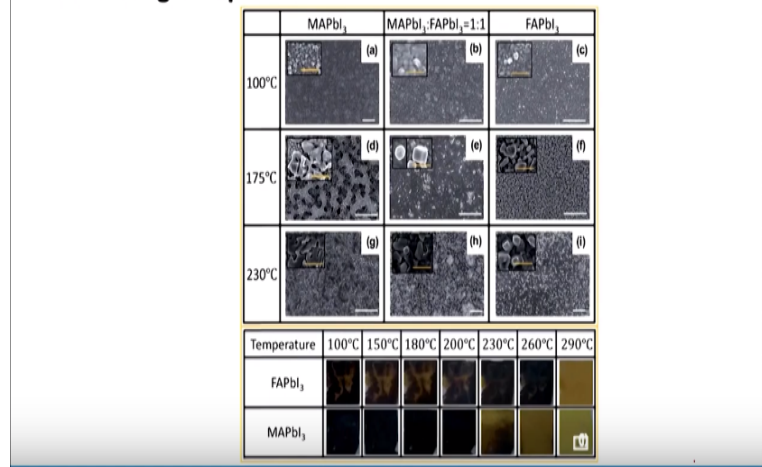
For example, this Eperon groups, they have systematically studied the influence of thermal annealing on the morphology control of the hybrid perovskite film. They found that perovskite layer could be seriously damaged by prolonged heat treatment at high temperature owing to the decrease in surface coverage. So for example, if you expose the perovskite film at a very high temperature for quite a long time, the film will damage.

Additionally, the higher thickness of the hybrid perovskite film would play an important role in the coverage of hybrid perovskite as well as in the performance of that solar cell device. Thus the development of new annealing process to obtain thick and continuous perovskite layer at low temperature become a promising photovoltaic technology. If we wanted to make perovskite solar cell on a roll to roll transparent substrate.

Then we have to make it at a low temperature because we cannot process the perovskite at high temperature in a transparent substrate.

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SEM images of perovskite compositions at various annealing temperatures



Here we are showing that three different perovskite comparison. For example, MAPbI₃ and MAPbI₃:FAPbI₃=1:1 ratio and for FAPbI₃ one is the methyl ammonium and other is the formamidinium and in both case we are using iodine. So if we change the temperature from 100 degree to 175 degree to 230 degrees Celsius, what will happen to the film morphology?

You can see that when we go from the 100 to 175 degree, the grains become larger but at the same time the continuity becomes the films gets apart. Similarly, when we go to the 230 degrees Celsius, the film started degrading. Now instead of the only MAPbI₃, if we use a composition of the MA and FA group then the morphology is much better. You can see a well-defined grain with a distinct grain boundary.

If we change the temperature, this grain become larger which is the require thing which we need. But if we change to further temperature then irregularity comes or the surface roughness will increase. In the last figure we are showing the FAPbI₃, the formamidinium based only lead iodide things. Here the morphology is not as good as the MAPbI₃ or not as good as the compositional mapping.

But still we get a larger grain size as we increase the temperature. In the lower graph, we are showing that systematically if we change the temperature from a 100 degree to 290 degrees Celsius, how the grains will be different for MAPbI₃ as well as for FAPbI₃.

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Thermal Engineering

- The temperature dependence of formamidinium lead iodide (FAPbI₃), methylammonium lead iodide (MAPbI₃) and their mixture (FAPbI₃ : MAPbI₃) has been investigated.
- Figure shows the SEM images of hybrid perovskite compositions at various annealing temperatures. The best coverage of MAPbI₃ films was achieved at 100°C (Fig. a), while the coverage at 175°C was not as good as that at 100°C (Fig. d), and the MAPbI₃ at 230°C decomposes to PbI₂ (Fig. g). The mixture at all annealing temperatures shows good coverage (Fig. b, e and h). The crystals of FAPbI₃ perovskite films are hardly observable at 100°C while the FAPbI₃ crystals at 175°C and 230°C can undoubtedly be recognized (Fig. c, f and i).

So the temperature dependence of the formamidinium lead iodide, methylammonium lead iodide and their mixture has been investigated in details and the last figures that show that SEM image of the hybrid perovskite compositions at various annealing temperature. The best coverage of the lead perovskite example, for example MAPbI₃ films were achieved at 100 degree Celsius while the coverage at 175 degree was not good like for 100 degree Celsius and the MAPbI₃ at 230 degree Celsius decompose to lead iodide.

The mixture at all annealing temperatures shows good coverage. The crystal of lead iodide along with the FA pattern, so that is FAPbI₃ perovskite films are hardly observable at 100 degree Celsius while the FAPbI₃ crystallize at 175 degree Celsius and 230 degree Celsius can undoubtedly be recognized. So once we go to MA to FA, the change of the temperature effect is very visible.

For the MAPbI₃, 100 degree Celsius we get a continuous film. Once we go to the 150 degree Celsius or 175 degree Celsius, the grains become larger but it also started degrading. If we go to high temperature like 230 degrees Celsius, it degrade to lead iodide. But for the case of the FAPs perovskite FAPbI₃, we get a better uniformity, coverage, and the grain size in the case of 175 degree Celsius and if we go to 230 degrees centigrade the change is also very obvious.

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Thermal Engineering

- As illustrated in Fig. j, the MAPbI₃ perovskite showed a dark color up to 200°C, and at 230°C the perovskites started to decompose. Furthermore, the FAPbI₃ perovskites had a dark color up to 260°C, and then began to decompose. As a result, the optimized annealing temperature for a mixture of FAPbI₃ and MAPbI₃ is about 175 °C.

So as shown in the figure, the MAPbI₃ perovskite showed a dark color at 200 degree centigrade and at 230 degree centigrade the perovskite started decomposing. Furthermore, the FAPbI₃ perovskite had a dark color up to 260 degree Celsius and there after that they started decomposition. So basically the FAPbI₃ perovskite has a better thermal stability than the MAPbI₃ perovskite.

So as a result, optimized annealing temperature for a mixture of the FA and MAPbI₃ perovskite is at 175 degree centigrade where you get a uniform coating and also a very uniform grain size. Now what about the interface engineering?

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Interface Engineering

- The interface plays a crucial role in photovoltaic devices. The high performance of solar cells can be pursued by controlling the carrier behavior across relevant interfaces.
- The long-term stability of solar devices can also be achieved by retarding interface aging. As a result, rapid progress related to interface engineering has been made by managing the carrier dynamics at the interfaces; and designing a rational structure to improve the performance and stability of the devices.
- The stability of photovoltaic devices has been widely addressed by interface engineering. Planar heterojunction (PHJ) HPSCs are mostly degraded due to the interface decay of perovskite/cathode. When PHJ-HPSCs were exposed to air, numerous bubbles were produced instantly at the interface and then grew. After one hour's exposure to air, the efficiency of the solar devices was completely lost, owing to the peeling of the cathode electrode from the device.

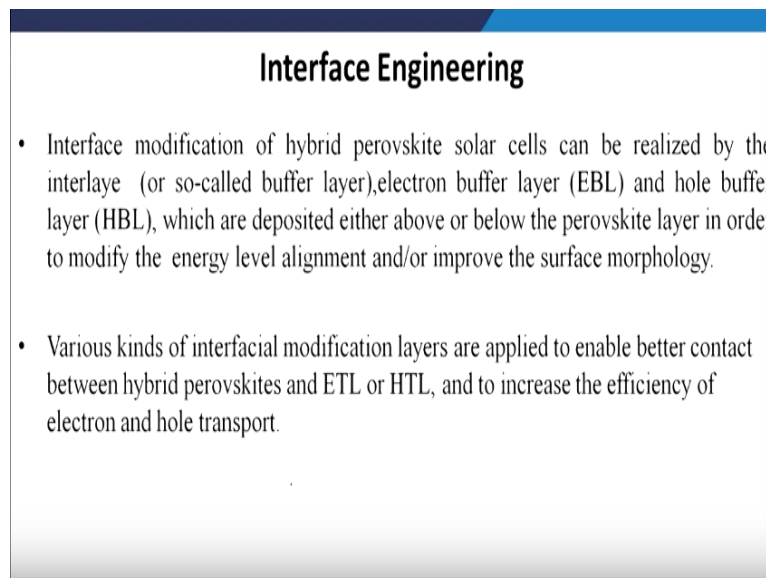
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performance of solar cells can be pursued by controlling the carrier behaviour across the relative interface. The long-term stability of solar device can also be achieved by retarding interface aging.

As a result, rapid progress related to the interface engineering has been made by managing the carrier dynamics at the interface and designing a rational structure to improve the performance and stability of the devices. The stability of photovoltaic devices has been widely addressed by interface engineering. Planar hetero junction hybrid perovskite solar cells are mostly degraded due to the interface decay of perovskite cathode.

When PHJ-HPSC were exposed to air, numerous bubbles were produced instantly at the interface and then those bubbles grew. After one's hour exposure to the air, the efficiency of the solar cell device was completely lost, owing to the peeling of the cathode electrode from the device. So if we expose it to the more and more humidity or more and more water vapour, so the cathode layer will started peeling up from the interfacial layer.

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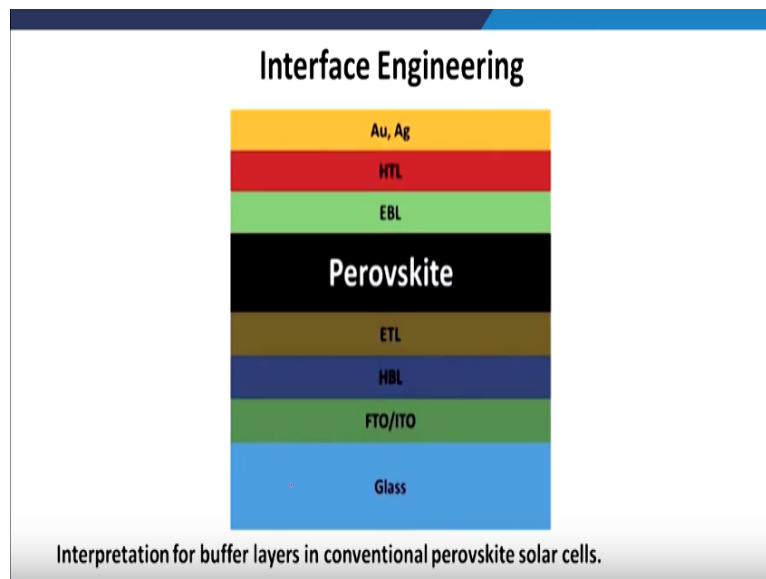


Interface Engineering

- Interface modification of hybrid perovskite solar cells can be realized by the interlayer (or so-called buffer layer), electron buffer layer (EBL) and hole buffer layer (HBL), which are deposited either above or below the perovskite layer in order to modify the energy level alignment and/or improve the surface morphology.
- Various kinds of interfacial modification layers are applied to enable better contact between hybrid perovskites and ETL or HTL, and to increase the efficiency of electron and hole transport.

Interface modification of the hybrid perovskite solar cell can be realized by the interlayer or the so-called buffer layer, electron buffer layer EBL and the hole buffer layer HBL, which are deposited either above or below the perovskite layer in order to modify the energy level alignment and to improve the surface morphology. Various kinds of interface modification layers are applied to enable better contact between hybrid perovskite and ETL or HTL, and to increase the efficiency of the electron and hole transport.

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For example, here we are showing the interface engineering. You can see that on the ITO substrate we put a hole blocking layer and an electron transport layer. And then we put a perovskite layer and in the top we have an electron blocking layer and then the hole transport layer.

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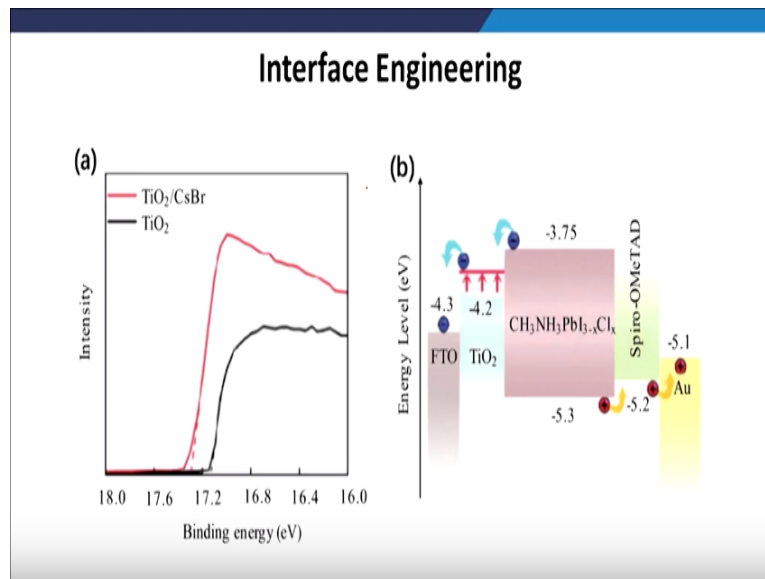
Interface Engineering

- Cesium bromide (CsBr) was also used as an efficient interfacial modification layer between the electron collection layer and the $\text{CH}_3\text{NH}_3\text{PbI}_3\text{-xCl}_x$ absorber layer to enhance the performance of planar heterojunction perovskite solar cells, because the decline in the work function of the c-TiO₂ layer results in an increase in the open-circuit voltage (Figure a and b).
- In addition, the solar devices with CsBr interface modification showed improved stability under ultraviolet illumination due to the decreased chemical activity and reduced defect density at the c-TiO₂/perovskite interface.

Cesium bromide was also used as an efficient interfacial modification layer between the electron collection layer and the CH_3NH_3 lead iodide chlorine absorber layer to enhance the performance of the planar hetero junction perovskite solar cell. In addition to the solar cell device, the CsBr interface modification showed improved stability under the UV light and due to the decreased chemical activity and reduced defect density at the c-TiO₂ perovskite interface.

So if you use cesium bromide as an interfacial layer so not only the efficiency increase, but the stability also increase now because the UV degradation now got reduced.

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For example, here we are showing the only TiO₂ layer and the TiO₂ layer in the presence of the cesium bromide. So, this y axis is the intensity and the x axis is the binding energy and also it has been shown that why we use the TiO₂ and this kind of solar cell. So the CsBr will be energetically favourable or the energetics will match in this kind of devices.

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Compositional Engineering

- The general formulas of three-dimensional (3D) organic-inorganic halide perovskites is ABX_3 , where A is a monovalent cation such as methylammonium (MA), formamidinium (FA), or cesium (Cs), B is a divalent metal cation such as Pb^{2+} , Cd^{2+} , Sn^{2+} , Pd^{2+} , Mn^{2+} and X is a halide anion. An important aspect that makes hybrid perovskites successful is the adaptability of this structure type towards A, B or X site substitution, which allows for tailoring of properties to meet particular requirements.
- A central principle in the development of hybrid organic-inorganic perovskites is Goldschmidt's tolerance factor (TF), which can evaluate ionic size mismatches which the perovskite structure will tolerate until a different structure type is formed.

Now another important approach is the compositional engineering. The general formulas of the three-dimensional organic-inorganic halide perovskite is ABX_3 , where A is the monovalent cation such as methylammonium, formamidinium, or cesium, B is a divalent metal cation such as lead, cadmium, tin, palladium or manganese and X is a halide anion.

An important aspect that makes halide perovskite successful is the adaptability of the structure type towards A, B, and X size distribution, which allows for tailoring of the properties to meet particular requirements. A central principle in the development of hybrid organic-inorganic perovskite is the Goldschmidt's tolerance factor, which can evaluate the ionic size mismatch which the perovskite structure will tolerate until a different structure type is formed.

So in the ABX₃ crystal structure, we can change either the A site, we can change the B site, we can change the X site. If we change either of them or is any one of these three so not only the band gap changes, but the morphology also changes.

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Compositional Engineering

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

0.9 < t < 1	Cubic Structure
0.7 < t < 0.9	Tetragonal/orthorhombic
t < 0.7 and t > 1	Non-perovskite structure
t > 1	2D layer structure

But one has to make sure that the tolerance factor, the value of t, which is basically the radius of the r_A + the radius of the X divided by square root of r_B + r_X that value we need to calculate once we make these changes and if the tolerance factor value is between 0.9 to 1 then it is a cubic structure. If it is between 0.7 to 0.9 then it is a tetragonal or orthorhombic structure. If it is less than 0.7 or greater than 1 then it is a non-perovskite structure.

So to have a perovskite structure we have to have the tolerance factor of value between 0.7 and less than 1. So it should be between 0.7 and 1, if it is 0.7 to 0.9 then it is an orthorhombic or tetragonal, if it is 0.9 to 1 then it is a cubic structure. And t > 1 is a 2D layer perovskite structure.

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Compositional Engineering

- Compositional engineering is one of the most effective ways to modify the surface morphology of hybrid perovskite films for the fabrication of highly efficient and stable HPSCs.
- For instance, Jeon et al. found that $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ possessed the best photoelectron properties among similar kinds of hybrid perovskites with the general form $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$, delivering HPSCs with an efficiency greater than 18%. They demonstrated that the incorporation of MAPbBr₃ into FAPbI₃ can stabilize the perovskite phase of FAPbI₃ perovskites.

Compositional engineering is one of the most effective ways to modify the surface morphology of the hybrid perovskite for the fabrication of highly efficient and stable solar cell. For instance, like one of the research group, Jeon et al. they found that if we use a compositional mapping of FA and Pb group.

So they possessed the best photoelectron properties among similar kinds of hybrid perovskite with the general form of FAPbI₃ 1-x, MAPbBr₃x, delivering HPSC with an efficiency greater than 18%. They demonstrated that the incorporation of the MAPbBr₃ into the FAPbI₃ can stabilize the perovskite phase of FAPbI₃ perovskite.

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Compositional Engineering

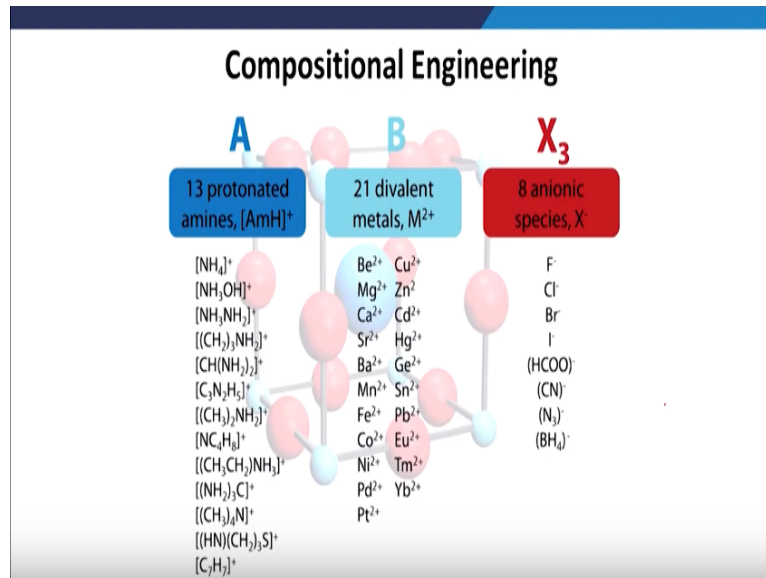
- The A-site cations (typically methylammonium $\text{MA}^+ = \text{CH}_3\text{NH}_3^+$) of 3D hybrid perovskites have recently concentrated on hybrid perovskites formamidinium (FA or $\text{NH}_2\text{CH}=\text{NH}_2^+$), cesium (Cs) and rubidium (Rb) cations. The ionic radius of the FA cations is larger than that of the MA cations, leading to a reduced band gap (1.48 eV) of FAPbI₃ compared to that of MAPbI₃ (1.57 eV).
- In addition, compared to MA-based HPSC, FA based HPSCs have shown improved long-term stability, making them more suitable for application in a single-junction solar cell.

The A-site cations typically methylammonium of 3D hybrid perovskite have recently concentrated on hybrid perovskite formamidinium, cesium, and rubidium cations. The ionic

radius of the FA cations is larger than that of MA cations leading to a reduced band gap of FAPbI₃ compared to that of MAPbI₃.

In addition, compared to MA-based HPSC, FA based HPSCs have shown improved long-term stability, making them more suitable for application in a single-junction solar cell. So not only the efficiency but stability also increases in this kind of compositional mapping.

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Now compositional mapping can be several pool, but here like A which is can be possible of 13 protonated amines. For example, it can be NH₄⁺, NH₃OH⁺, NH₃NH₂⁺ or all of these things. As a B, we can use these 21 divalent metals, M²⁺, as an X, we can use any of this. So if we use any of the combination with the any of the other combination.

We can get a compositional mapping and all of this structural combination will give us the perovskite structure. So this chart we can use as a master chart while publicating the perovskite but we have to also calculate the tolerance factor to make sure that the value of t is between 0.7 and 1. So that it is a 3D perovskite, if it is t > 1 then it will be a 2D perovskite.

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Compositional Engineering

- Mixed-cation perovskites have become more attractive because pure perovskite materials, such as MAPbI₃, FAPbI₃ and CsPbI₃, come with various drawbacks.
- Furthermore, the combination of different cations can merge the merits of the constituents while avoiding their disadvantages in the perovskite layer. It has been shown that the enhanced photovoltaic efficiency and long-term stability of HPSCs could be achieved by introducing different cations into the crystal structure of the perovskite.
- For example, Saliba et al. used a mixture of a triple Cs/MA/FA cation to fabricate HPSCs, reaching a stabilized power output of 21.1% and 18% after 250 hours under operational conditions, because highly monolithic grains of purer perovskite were obtained by adding small amounts of inorganic cesium in a “triple cation” (Cs/MA/FA) configuration.

Mixed-cation perovskite have become more attractive because pure perovskite material such as MAPbI₃, FAPbI₃, and CsPbI₃ come with various drawbacks. Furthermore, the combination of different cations can merge the merits of the, constitutes while avoiding their disadvantage in the perovskite layer.

So while we do the compositional mapping, we not only get the advantage of the single perovskite layers, but also solve the disadvantage we can eliminate. It has been shown that the enhanced photovoltaic efficiency and long-term stability of the hybrid perovskite solar cell could be achieved by introducing different cations into the crystal structure of the perovskite.

For examples, Saliba et al. used a mixture of triple caesium, MA, FA cation to fabricate hybrid perovskite solar cell reaching a stabilized power output of 21.1% and 18% after 250 hours under operational condition.

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Compositional Engineering

- Over 80% of the initial efficiency for the optimized HPSCs can be retained in dark conditions for 200 h.
- Tai et al. reported that a lead(II) thiocyanate ($\text{Pb}(\text{SCN})_2$) precursor was used to fabricate HPSCs in ambient air. The pinhole-free morphology of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}(\text{SCN})_x$ perovskite film can be prepared under high humidity to avoid direct carrier recombination at the HTM/ TiO_2 interface. $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}(\text{SCN})_x$ based HPSCs showed excellent moisture stability because of a strong ionic interactions between SCN^- and adjacent Pb atoms, and the formation of hydrogen bonds between SCN^- and CH_3NH_3^+ .

Now over 80% of the initial efficiency of the optimized hybrid perovskite solar can be retained in the dark condition for 200 hours. So basically the Tai et al. they have reported that a lead thiocyanate precursor was used to fabricate the solar cell in ambient air. The pinhole-free morphology of the, this lead thiocyanate based perovskite solar cell can be prepared under high humidity to avoid direct carrier recombination at the HTM TiO_2 interface.

And not only the stability increase in this thiocyanate base devices but also the efficiency can also be tuned.

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Solvent Engineering

- The control of the crystallization and hence the kinetics of film formation during deposition and annealing are the way to the improvement of device performance. Optimal film morphology can only be accomplished by effectively controlling the nucleation and growth of the perovskite, for that solvent-engineering is a very viable strategy.
- To improve the morphology of hybrid perovskites, various methods of solvent engineering and solvent annealing have been developed.
- The solvent engineering approach is an attractive way to conquer the limitations of the one-step spin-coating process, and tends to make smoother perovskite film with reduced defect states. On the other hand, solvent annealing can reduce residual PbX_2 in the two-step process; thus perovskite with improved crystallinity would be formed.

Now another important tuning parameter is the solvent engineering, the control of the crystallization and hence the kinetics of the film growth that can be controlled by changing the solvent. To improve the morphology of the hybrid perovskite, various methods of solvent

engineering and solvent annealing have been developed. The solvent engineering approach is an attractive way to conquer the limitation of the one-step spin-coating process and tends to make smoother perovskite film with reduced defect density.

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Solvent Engineering

- Solvent engineering is a class of fabrication techniques that introduce a solvent to coordinate with the precursor solution, in order to form precursor PbI_2 -solvent complexes to prevent other chemical reactions in solution. A film of this precursor-solvent complex is then cast and subsequently converted to the hybrid perovskite.
- Spiccia et al. reported that uniform hybrid perovskites could be deposited by a solvent-induced and fast crystallization method consisting of spin-coating a $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solution, followed immediately by exposure of the wet film to chlorobenzene to induce crystallization. The chlorobenzene was dropped on top of the wet perovskite film during the spin coating process, resulting in the fast crystallization of hybrid perovskites with the formation of homogeneous grains.

Solvent engineering is a class of fabrication technique that introduces a solvent to coordinate with the precursor solution, in order to form precursor lead iodide solvent complex for preventing other chemical reaction in solution. A film of this precursor-solvent complex is then cast and subsequently converted to the hybrid perovskite.

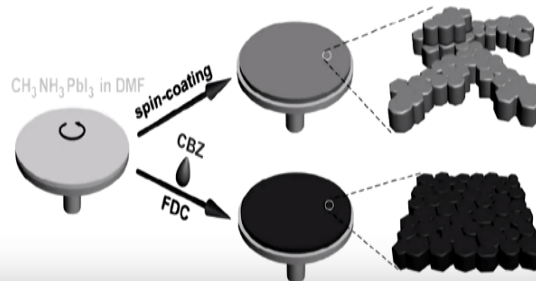
Spiccia et al. reported that uniform hybrid perovskite could be deposited by a solvent-induced and fast crystallization method consisting of spin-coating. A CH_3NH_3 lead iodide precursor solution followed immediately by exposure of the wet film to chlorobenzene to induce crystallization.

The chlorobenzene was dropped on top of the wet perovskite film during the spin coating process resulting in the fast crystallization of hybrid perovskite with the formation of homogeneous grains.

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Solvent Engineering

- From the TEM image, a perovskite film with large crystalline grains showed freedom from grain boundaries parallel to the plane of the electrodes. By using this thin-film processing technology, the HPSCs reached an average PCE of 13.9% with stabilized power output under working conditions.



Now you see in this figure, here we have this CH_3NH_3 lead iodide in DMF solvent which we can spin coat. Now if we spin coat in the presence of that chlorobenzene, so then what will happen. We have in the both the case if we compare the morphology, we get a larger crystallizations, if we use the chlorobenzene as another solvent additive and the efficiency also increase in this case.

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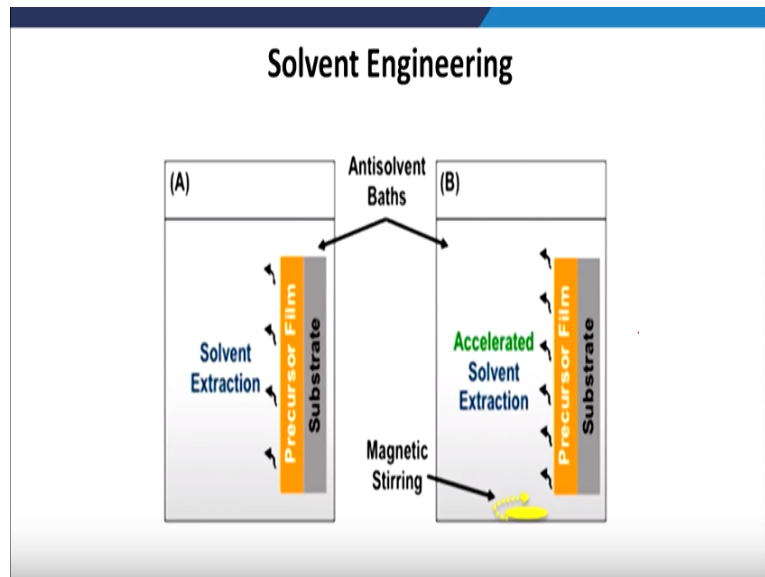
Solvent Engineering

- Y. Zhou *et al.* employed an antisolvent-solvent extraction process for crystallization behavior of mix halide perovskites at room temperature (Figure a).
- In this strategy, a little amount of solvent diffuses within the large amount of antisolvent. For the crystallization procedure super-saturation state and nucleation are accomplished by this antisolvent-solvent extraction method and nucleation rate may be improved by magnetic stirring of antisolvent.

Now this Y. Zhou et al. they have employed an anti-solvent extraction method for the crystallization of the mixed halide. So, basically while loading the perovskite in a solvent, if we add an anti-solvent, so anti-solvent means a solvent that does not mix to this precursor solvent very well. So because of the difference in the polarity, the anti-solvent will not able to mix with the solvent.

So then they will slow down the crystallization process. As a result, you will get a larger grain size. In this strategy, a little amount of solvent diffused with the larger amount of antisolvent. For the crystallization procedure a super saturation state and nucleation are accomplished by the antisolvent-solvent extraction method and the nucleation rate may be improved by magnetic stirring of antisolvent.

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So you can see here the solvent extraction which is happening precursor film in the substrate and yet accelerated solvent extraction is happening due to the magnetic stirring.

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Humidity control

- Hybrid perovskites are extremely moisture sensitive; thus the photovoltaic performance of HPSCs rapidly degrades in moist atmosphere due to the hygroscopic nature of methylammonium (MA^+ , CH_3NH_3^+) cations in hybrid perovskite materials. When exposed to air, the decomposition of hybrid perovskites would occur in the presence of water and light.
- The degradation mechanism of hybrid perovskites could be described by equations.

$$\text{CH}_3\text{NH}_3\text{PbI}_2 (\text{s}) \leftrightarrow \text{CH}_3\text{NH}_3 (\text{aq}) + \text{PbI}_2 (\text{s})$$

$$\text{CH}_3\text{NH}_3 (\text{aq}) \leftrightarrow \text{CH}_3\text{NH}_2 (\text{aq}) + \text{HI} (\text{aq})$$

$$4\text{HI} (\text{aq}) + \text{O}_2 \leftrightarrow 2\text{I}_2 (\text{s}) + \text{H}_2\text{O}$$

$$2\text{HI} (\text{aq}) \leftrightarrow \text{H}_2\uparrow + \text{I}_2 (\text{s})$$

Another very important parameter for making solar cell is the humidity control. Hybrid perovskites are extremely sensitive towards the humidity and they are moisture sensitive thus the photovoltaic performance of the solar cell rapidly degrades in moist environment due to

the hygroscopic nature of methylammonium cations in hybrid perovskite materials. There are a series of reactions happens when you expose the CH₃NH₃ lead iodide to the moisture.

For example, it degrades to CH₃NH₃ and lead iodide. Now this aqua CH₃NH₃ they can further degrade to CH₃NH₂ and HI hydroiodic acid, which is an aqua solution. Now this 4HI and oxygen can react to make iodine and this 2HI also can further disintegrates to hydrogen and iodine. It is individual components. So if we keep the perovskite material under the normal humidity condition very soon it will degrade to its constituents.

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Humidity Control

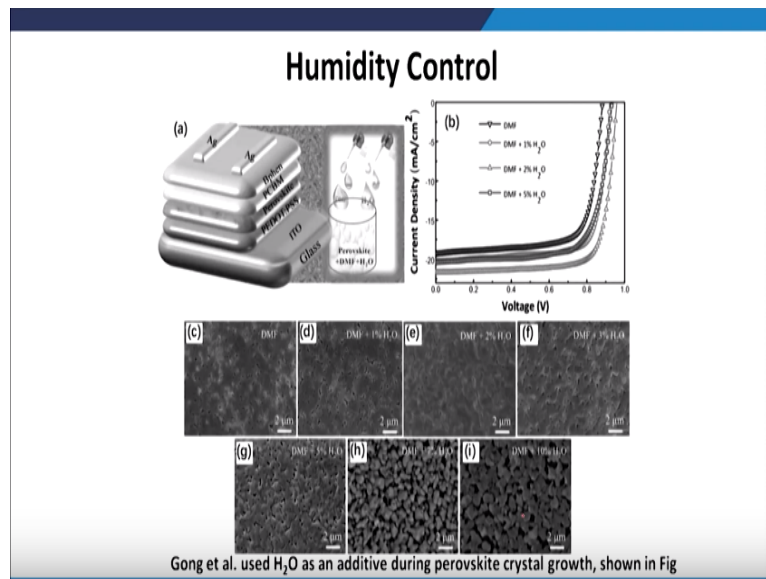
- In this process, CH₃NH₃PbI₃ could react with the water and then decompose to CH₃NH₃I and PbI₂. The electron injection rate could be reduced in the presence of more PbI₂ byproducts, but carrier recombination lifetimes could be extended upon passivation.
- It has been doubted that the existence of water vapor during the film deposition process has a positive influence on film formation because both perovskite precursor materials and lead halide perovskites exhibit some degree of solubility in water.
- In comparison to a film grown in dry conditions, Zhou et al. found that CH₃NH₃PbI_{3-x}Cl_x film grown under controlled humidity conditions (30 ± 5% relative humidity) exhibited improved optoelectronic properties. This is likely due to the fact that moisture could induce the reconstruction process during film formation by partial dissolution of the reactant species and an acceleration of the mass transport within the film.

In this process, CH₃NH₃ lead iodide could react with the water and decompose to its constituents per CH₃NH₃ I and lead iodide. The electron injection rate could be reduced in the presence of more lead iodide byproducts, but carrier recombination lifetime could be extended upon passivation. It has been doubted that the existence of the water vapor during the film deposition process has a positive influence on film formation.

Because both perovskite precursor materials and lead halide perovskite exhibits some degree of solubility in water. In comparison to a film grown in dry condition, Zhou et al found that CH₃NH₃ lead iodine and chlorine mixture that film growth under controlled humidity condition 30 + minus 5% relative humidity exhibit improved optoelectronic properties.

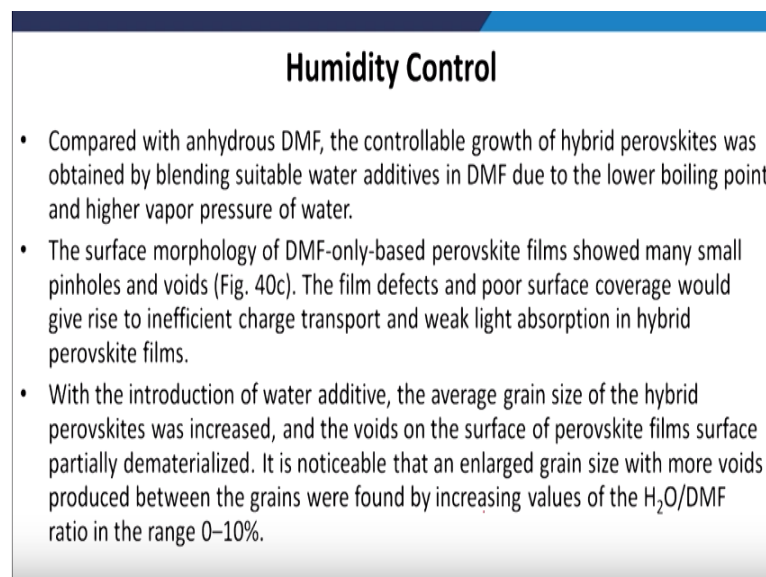
This is likely due to the fact that moisture could induce the reconstruction process during film formation by partial dissolution of the reactant species and an acceleration of the mass transport within the film.

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For example, here, you see that on the ITO put PEDOT PSS, perovskite, PCBM, and then BCP and then the silver electrode we have deposited and if we put perovskite and the DMF, the H₂O. So as we increase the percentage of the water to 1% to 2% to 5% if we look at I-V curve, the I-V curves falls down. So the efficiency drops down and even if you look at the morphology, if we exposed to different, different water vapor, so the crystal started disintegrating.

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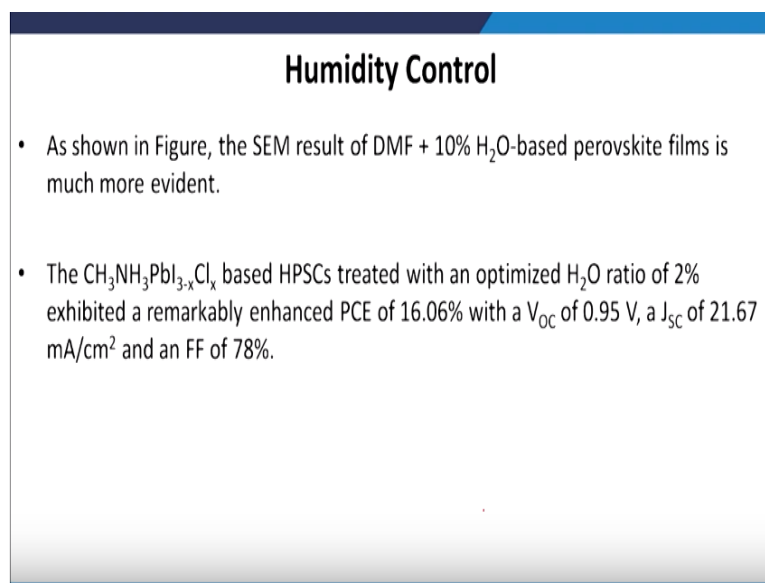


So we here into the humidity control, compared with anhydrous DMF, the controllable growth of hybrid perovskite was obtained by blending suitable water additives in DMF due to the lower boiling point and higher vapor pressure of water. The surface morphology of the DMF-only-based perovskite films showed many small pinholes and voids.

The film defects and poor surface coverage would give rise to inefficient charge transport and weak light absorption in hybrid perovskite film. If we have a lot of defects in the system then the absorptions will get affected. With the introduction of the water additives, the average grain size of the hybrid perovskite was increased and the voids on the surface of perovskite film surface partially dematerialized.

It is noticeable that enlarged grain sizes with more voids produced between the grains were found by increasing the value of the H₂O, DMF ratio in the range 0-10%.

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Humidity Control

- As shown in Figure, the SEM result of DMF + 10% H₂O-based perovskite films is much more evident.
- The CH₃NH₃PbI_{3-x}Cl_x based HPSCs treated with an optimized H₂O ratio of 2% exhibited a remarkably enhanced PCE of 16.06% with a V_{OC} of 0.95 V, a J_{SC} of 21.67 mA/cm² and an FF of 78%.

As shown in the figure, the SEM result of the DMF+10%H₂O vapor based perovskite is much more evident. The CH₃NH₃ lead iodine chlorine based devices they treated with an optimum water vapor ratio of 2% exhibit a remarkable enhancement of the PSE with 16.06% with a Voc value of 0.9 volt and the Jsc value of 21.61 or 67 million vapor centimetre square and a fill factor value of 78%.

So, a very optimized exposure to the water with the DMF solvent sometimes helps to improve the current and the fill factor.

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Conclusions

- Despite the rapid progress in the performance of hybrid perovskite solar cells, there are still many more opportunities for further improvement.
- Morphology engineering has the great potential to considerably enhance the efficiency and stability of hybrid perovskite solar cells.
- However, the interaction mechanism between the hybrid perovskite and other interface layers still remains unclear and needs to be further explored to facilitate the application of morphology engineering. Most of the techniques of morphology engineering have been limited to specific conditions during the fabrication of hybrid perovskite films.

So in conclusion, we have despite the rapid progress in the performance of the hybrid perovskite solar cell, there are still more opportunities for the further improvement of the device. Morphology engineering has the great potential to considerably enhance the efficiency and stability of the hybrid perovskite solar cell.

However, the interaction mechanism between the hybrid perovskite and other interfacial layers still remains unclear and needs to be further explored to facilitate the application of the morphology engineering. Most of the techniques of the morphology engineering have been limited to specific condition during the fabrication of hybrid perovskite films.

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Conclusions

- With regard to the next direction in morphology engineering, film quality could be improved by either integrating these existing techniques with different functions or by exploring new technologies to reach distinctive and goal-oriented morphology control.
- In addition to experimental approaches, theoretical calculations still cannot be performed regularly in the area of morphology control, but can definitely make a significant contribution to further advances in the design of morphological techniques.

So with regard to the next direction in the morphology engineering, film quality could be improved by either integrating these existing techniques with different function by exploring

new technologies to reach distinctive and goal oriented morphology control. In addition to the experimental approach, theoretical calculations still cannot be performed regularly in the area of morphology control.

But can definitely make a significant contribute to further enhancement in the design of morphological techniques. So there are so many morphological optimization and techniques are there like solvent engineering, like thermal engineering, compositional mapping, then self-assembled monolayers etc, etc. All of these things change the grain size, all of these things change the efficiency as well as the stability.

But we cannot try all sorts of combinations to see what is the maximum morphology optimization we get. So in this regards, probably some theoretical calculus and a theoretical modelling help us along with the experiment to achieve a most optimized morphology and most optimized photophysics, which can lead to that higher efficiency as well as higher stability in a perovskite solar cell. Thank you so much.