



Research Progress of Solar Cells Based on Organic–Inorganic Hybrid Perovskites Methylamine Lead Halide

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ABSTRACT

Methylamine lead halide is a kind of perovskite structural crystalline materials compounded by organic methylamine and inorganic lead halide, which has attracted great attention in photovoltaic research. Solution processed photovoltaics incorporating methylamine lead halide perovskite absorbers have achieved efficiencies of nearly 16% in solid-state device configurations, superseding traditional dye sensitized solar cells, evaporated and tandem organic solar cells, as well as various thin film photovoltaic. Now, interest has been soaring in this research domain, resulting in more and more controversies that related to the promotion and development of resulting photovoltaic devices. Therefore it is urgent and important to clarify the operating mechanism of such perovskite-based solar cells for their further development. In this Progress Report, we introduced the structure and preparation of organic–inorganic hybrid perovskite methylamine lead halide, and reviewed its latest investigation in solar cell application. Meanwhile, comparative analysis of some different views and key issues such as materials selection, device architecture etc. have been done.

KEYWORDS: Inorganic–Organic Hybrid, Perovskite, Solar Cells, Methylamine Lead Halide.

1. INTRODUCTION

Photovoltaic is a promising green energy technology that converts sunlight to electricity, with broad potential to contribute significantly to solving the future energy problem. Although highly efficient solar cells have already been commercialized based on silicon and compound semiconductors,^{1–4} the manufacturing processes are still relatively expensive in terms of both materials and techniques. Driven by the demand for inexpensive, clean, and renewable energy sources, emerging photovoltaic devices are being developed at a rapid pace, most of which differ from traditional solar cells in their unique mesoscopic structural features, such as dye-sensitized solar cells (DSSC),^{5–8} quantum dot sensitized solar cell (QDSC),⁹ and organic solar cells.¹⁰

Recently, high efficiency solar cells based on organic–inorganic hybrid perovskite methylamine lead halide

(MLH) have been being reported far and wide.^{11–14} Their power conversion efficiency (PCE) progressively set records in a few months and this greatly inspired many researchers in this domain. MLH has direct band gap and shows impressive photovoltaic properties, with high extinction coefficient,^{15,16} carrier mobility,^{17,18} wide spectrum absorption range (from visible light to near infrared)¹⁹ and convenient synthesis method. Therefore, its potential application in optoelectronic field is beyond doubt. Here, we introduce the structure and preparation of organic–inorganic hybrid perovskites MLH, review its latest research progresss in photovoltaics devices specifically, and give a comparative analysis of some controversies and issues such as materials selection, architecture of device etc., which is crucial to the further development of MLH-based solar cells.

2. STRUCTURE AND PREPARATION OF MLH

In 1978 Weber synthesized and characterized methylamine perovskite lead iodide (CH₃NH₃PbI₃),²⁰ the one of MLH hybrid perovskites (CH₃NH₃PbX₃) family, which is

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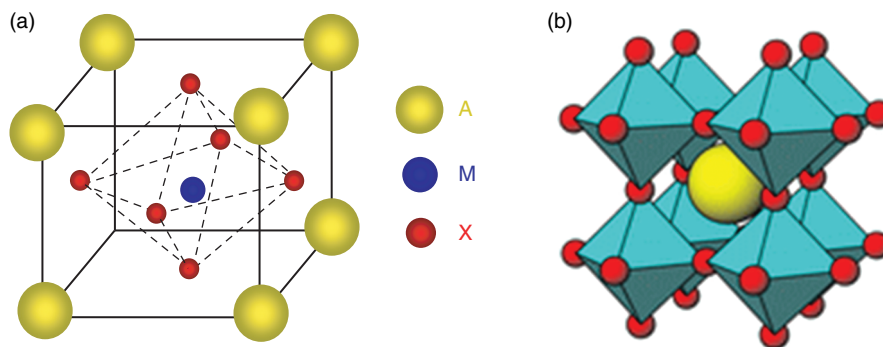


Fig. 1. (a) Crystal structure of perovskite and (b) their extended network structure connected by the corner-shared octahedra.

derived from the structure of inorganic perovskite AMX_3 . Wherein, the halogen anion is represented by X ($= I^-$, Br^- , Cl^-), the metal cation Pb^{2+} corresponds to M and methylamine cations ($CH_3NH_3^+$) corresponds to A. They form the PbX_6^{4-} octahedra where Pb^{2+} is located at the center of the octahedra and halogen anion X lies in the corner around $CH_3NH_3^+$ (Fig. 1(a)). The PbX_6^{4-} octahedra form an extended three-dimensional (3D) network by all-corner-connected type (Fig. 1(b)). The $CH_3NH_3^+$ fills the hole among the octahedra and balances the charge of the whole network.^{21–23} Previous experiments demonstrate that the symmetry and structure of $CH_3NH_3PbI_3$ crystals are highly dependent on the temperature.²⁴

Furthermore, the position of the halogen atom X can be replaced by different types of atoms in a certain ratio randomly, thereby forming organic–inorganic mixed perovskite phase crystalline materials, for instance methylamine lead bromide chloride ($CH_3NH_3PbBr_{3-x}Cl_x$) and methylamine lead iodide chloride ($CH_3NH_3PbI_{3-x}Cl_x$). Employing this mixture phase, the properties of material (such as band gap) can be adjusted or optimized.^{12, 14, 19}

3. PREPARATION METHOD HYBRID PEROVSKITE

As for current reports, the preparation methods of MLH hybrid perovskites mostly involve solution or solvent evaporation, which has a simple process and easy synthesis characteristics. Taking monocrystalline $CH_3NH_3PbI_3$ as an example, the preparation is as follows:²¹

Under ice-water bath condition ($0^\circ C$), slowly add hydroiodic acid (HI, 40% aqueous solution) to methylamine (CH_3NH_2 , 57 wt% methanol solution), keep stirring for 2 h for sufficient reaction. Heat the mixture to $50^\circ C$ in a rotary evaporator, handle it with vacuum distillation and the crude product (the colour is yellow due to impurities) is obtained. Then wash 3–5 times with diethyl ether, utilize suction filtration, dry in vacuum condition at $60^\circ C$ for 24 h, so as to get the white iodide methylamine (CH_3NH_3I) powder crystallines. Next, weight the same molar mass of CH_3NH_3I and PbI_2 (99%) into γ -butyrolactone to make the reaction sufficient ($60^\circ C$, continuous stirring, 12 h), spread the solution onto the glass substrate, heat to $100^\circ C$ and anneal for

30 min and eventually after cooling down, the $CH_3NH_3PbI_3$ monocrystalline powder is obtained. Followed by process similar to this, methylamine lead bromide ($CH_3NH_3PbBr_3$) and methylamine lead chloride ($CH_3NH_3PbCl_3$) can be prepared with proper hydrohalic acid instead of HI.^{25–27}

To prepare MLH perovskite film,²⁸ four methods have been reported so far, including spin-coating,²⁹ vacuum vapour deposition,³⁰ two-step deposition technique (TSD)^{13, 31–33} and patterning thin film.³⁴ Initially, one-step spin-coating was used to fabricate the solar cells, but it was difficult to obtain a high quality film, let alone to get an appropriate solvent that can dissolve both organic and inorganic part. In addition, perovskite particles could not effectively fill the mesoporous metal oxide (MMO), which inevitably led to a less light absorption. Mitzi and co-workers³¹ created the TSD technique to prepare hybrid perovskite. When it was used to coat $CH_3NH_3PbI_3$ layers, the film quality was significantly improved, moreover, the large characteristic differences among devices during preparation was reduced.¹³ Vacuum evaporation is considered as a good technique to grow oriented thin films of layered perovskites with a precise control of the film property. However, the preparation of various perovskites using different organic components is expected to be limited, and this technique demands high vacuum, which is too energy consuming and hinders mass production. A very recently report demonstrate use of the vapor-assisted solution process to fabricate planar perovskite thin films and their corresponding solar cells.³⁵ The key step is film growth via in situ reaction of the as-deposited film of PbI_2 with CH_3NH_3I vapour. This method is conceptually different from the current solution process and vacuum deposition, by avoiding co-deposition of organic and inorganic species. The perovskite film derived from this approach exhibits full surface coverage, uniform grain structure with grain size up to micrometers, and 100% precursor transformation completeness.

4. APPLICATION PROGRESS OF MLH IN SOLAR CELLS

Organo-lead halide perovskite solar cells have emerged as one of the most promising candidates for the next

generation of solar cells. Recently, especially in the year of 2012 and 2013, solar cells based on such materials have shown an unprecedented improvement of performance, with a PCE increase from less than 10% to over 15%,^{11–14} and this has led to increased research interest. Despite these remarkable achievements, multifarious controversies about such perovskite-based solar cells are going, which involve some crucial factors that related to the promotion and development of devices, and it is urgent and important for these to be clarified.

4.1. Materials: Iodide, Bromide and Chlorine, Which is the Better One

In conventional DSSC, it was deemed that the selection or optimization of dyes is crucial for efficiency promotion,^{36–41} so MLH were used initially in nanostructured solar cells as a more effective sensitizer, and exhibits almost ideal light absorption characteristics. In 2009, Miyasaka research group, for the first time, introduced hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ in place of traditional N719 dyes into the DSSC, and attained 3.8% conversion efficiency.²⁵ Within the following 3–4 years, $\text{CH}_3\text{NH}_3\text{PbI}_3$ as light harvesters in solar cells has led to reports of impressive efficiency values of up to 15%.¹³ Therefore it is a fascinating and important question that what render them possessing such an unique photoelectric characteristics. According to Xing and co-worker's report, by using femtosecond transient optical spectroscopy of $\text{CH}_3\text{NH}_3\text{PbI}_3$ heterojunction with selective electron and hole extraction, they decoupled electron and hole dynamics and show evidence of long electron- and hole-transport lengths (both over 100 nm), and the high PCE of these systems stem from the comparable optical absorption length and charge-carrier diffusion lengths, transcending the traditional constraints of solution-processed semiconductors.⁴² When chloride is incorporated into $\text{CH}_3\text{NH}_3\text{PbI}_3$, a mixed perovskite phase crystalline $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ is formed.¹² Despite the little change of band gap, both electron and hole diffusion length are $> 1 \mu\text{m}$; in contrast, $\text{CH}_3\text{NH}_3\text{PbI}_3$ shows a comparable effective diffusion length for holes but a shorter one for electrons.⁴³ It is still not explicit that what reason lead to this, but it can be used to explain why $\text{CH}_3\text{NH}_3\text{PbI}_3$ if used as an absorber in a flat design (i.e., without mesoporous scaffold) has efficiencies of 2–3%, while with $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ nearly 16% can be reached. Whether the difference between the tri-iodide material and its chlorine incorporated counterpart is a result of, for example, different internal electric fields, crystal orientation or doping (without ruling out other possible reasons) requires more research.⁴⁴

Additionally, it was notable that employing $\text{CH}_3\text{NH}_3\text{PbBr}_3$ as the sensitizer can obtain a device with higher open-circuit voltage but the short-circuit current dropped significantly.²⁵ Edri et al. used $\text{CH}_3\text{NH}_3\text{PbBr}_3$ as sensitizer and obtained open-circuit voltage up to

1.3 V and deemed that with more optimal work function values of the electron and hole conductors, both a further increase in V_{OC} and improved charge separation should be possible.²⁶ Soon after, they employed methylamine lead bromide chloride ($\text{CH}_3\text{NH}_3\text{PbBr}_{3-x}\text{Cl}_x$) as the absorber in a mesoporous p-i-n device configuration with $V_{\text{OC}} = 1.5 \text{ V}$.⁴⁵

4.2. Structure: Perovskite-Sensitized Mesostructure or Planar Heterojunction

In general, there are two different device architectures have appeared, which correspond to two types of solar cells operation mechanism: perovskite-sensitized and planar heterojunction (PHJ). The former one possessed a mesoporous metal oxide (MMO) framework infiltrated with perovskite sensitizer aiming to maximize the interfacial area between the two materials, upon which solid-state hole transporter layer (HTL) was deposited, and it was named mesostructure solar cell (MSSC)¹² (Fig. 2(a)).

The latter one was constructed similar to a PHJ-based solar cell (PJSC), where the perovskite film was sandwiched between selective electrodes, and MMO was removed (Fig. 2(b)).¹⁴ It is quite intriguing that the highest reported PCE value of MSSC and PHJ-based solar cell is 15.7%,⁴⁶ 15.4%,¹⁴ respectively, which almost equals each other. Speaking only in efficiency, it seemed that MSSC is not inferior to PJSC; as a whole, however, because of the need of complex nanostructure in MSSC, this not only lead to complexity of process and technology, but also cause some excess cost of energy and materials, so PJSC is more promising comparatively. While, PJSC is also suffering from some serious issues, such as hard to preparation of perovskite thin film with good homogeneous and full coverage, uncontrollable efficiency fluctuations etc.⁴⁷ Several previous works reported MLH PJSC with a low PCE, but its maximum IPCE can reach as high as 100% in the visible light range.^{48,49} This implied that the perovskite could probably have functioned well and pointed that PHJ architecture is potentially efficient. Eperon et al. analyzed that the poor performance of PJSC may arise from pin-hole formation, incomplete coverage of the perovskite resulting in low resistance shunting paths and lost light absorption in the solar cell;⁴⁷ as in other technologies the issue of film formation is likely to be extremely important in the PHJ.^{50–52} This limitation mainly resulted from severe constraints in film thickness, where thicker

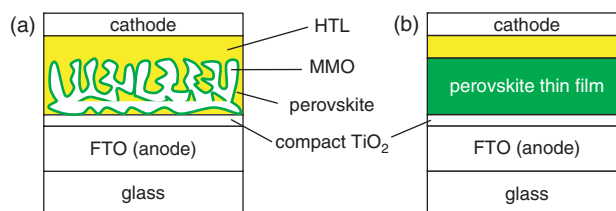


Fig. 2. Schematic device configuration of (a) MSSC and (b) PJSC.

films were found to be too coarse for successful solar cell operation. Literature⁴⁷ demonstrated more efficient PJSC based on $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ (11.4% for the best device) by optimizing perovskite coverage, and found the highest efficiencies are achievable only with the highest surface coverage; however standard deviations are observed of up to almost 50% of the average value. Docampo et al.⁵³ demonstrate that a PHJ device with the structure of (FTO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ /PCBM/ TiO_x/Al) can deliver up to 10% PCE. A recent report⁵⁴ fabrication of solar cells based on the mixed metal halide perovskite absorber $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$, with reasonably smooth films with up to >95% coverage and thicknesses exceeding 200 nm, thus enabling light absorption close to 100%, and resulting in very reproducible efficiency values. Another very recent report⁵⁵ demonstrated a low-temperature vapor-assisted solution process to construct polycrystalline perovskite thin films with full surface coverage, small surface roughness, and grain size up to microscale; and solar cells based on the as-prepared films achieve PCE of 12.1%. Flexible PJSC based on MLH were also be attempted, and the reported PCE value from 6% to 9%.^{53,55} So far, the highest efficiency record of perovskites PJSC is reported by Liu et al.¹⁴ which has PCE of over 15% and open-voltage of 1.07 V. They used $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ as the absorbing layer, and fabricated it by vapour deposited method.

Further more, some literature reported a very interesting structure of perovskite-based PJSC, in which the HTL was removed and the perovskite active layer served as hole transporter.⁵⁶⁻⁶⁰ This HTL-free device attracted much attention because it would benefiting to simplify the fabrication and reduce cost greatly. Meng and co-workers fabricated efficient $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Au}$ solar cells with a sequential deposition method, and achieved a highest efficiency of 10.49%.⁵⁹ They applied the ideal model for a single PJSC and clarify the cell characteristics, meanwhile, the cell parameters derived from the model indicate that the performance of this HTL-free PJSC is comparable to that of the high-efficiency thin-film solar cells.

4.3. MMO and HTL, What Effect on MSSC

As described above, despite MSSC is not as simple and less cost for fabrication as PJSC, it is must be admitted that MSSC represents a type of high efficiency architecture. In fact, MSSC was believed to operate based on sensitized mechanism, so performance promotion strategies for solid-DSSC also adapt to it. Thus, the existing issues and effects of different MMO and HTL in MSSC became two important respects of this study domain.

Generally, the requirements for an ideal MMO involves reasonable energy band, large specific surface area, high electron mobility, easy and low cost for fabrication etc. For evolved from solid-DSSC probably, MMO was considered to be a scaffold on which MLH light absorber

can be grown and an essential transporter for accepting photoelectrons from the absorber and transporting them to the electrode surface, and Titania was mostly investigated for at the beginning.¹¹⁻¹³ Kim et al. synthesized a length-controllable submicron anatase TiO_2 nanorod to replace porous TiO_2 layer, by which they expected to solve the problem that $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite particles could not effectively fill the MMO, but did not achieve a more desirable result.⁶¹ Zhao et al. fabricated a MSSC with liquid electrolyte and $\text{CH}_3\text{NH}_3\text{PbI}_3$ sensitizer.⁶² They found its charge collection characteristics and optical absorption properties have an obvious dependence with the thickness of porous TiO_2 film that exerts significant influence on the current density, photovoltage, fill factor and PCE. Bi et al. reported MSSC based on ZnO nanorod arrays for the first time, considering that vertically aligned ZnO nanorod arrays exhibited unique material properties, and as well as easy availability.⁶³

When using the insulating Al_2O_3 was used as MMO, the resulting MSSC with an absorber layer of $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$, achieved a higher PCE of 10.9% and V_{OC} in excess of 1.1V.¹² This also demonstrated that the electrons are able to transport through the $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$ phase without significant charge recombination. In fact, a higher electron diffusion rate was found in the $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$ phase than that in mesoporous TiO_2 films, revealing that it possesses an ambipolar transport property. The device efficiency was further improved to 12.3% by optimizing the film thickness of the Al_2O_3 layer.⁴⁸ Carnie et al. proposed an alternative method of Al_2O_3 -perovskite deposition whereby the two step deposition process can be performed in a single step.⁶⁴ This has the advantage of combining two manufacturing steps into one and negates the need for a high temperature (550 °C) sintering step, and results in devices that have a lower embodied energy with a relatively more simple manufacturing process. Similarly, ZrO_2 also possess a larger band gap, and the conduction band is most probably much higher in energy than the perovskite conduction band, and electron injection into them is therefore not possible, and the excited electron stays in the perovskite. Several literatures reported the use of ZrO_2 instead of TiO_2 can lead to either slightly better (10.8% instead of 9.5%)³³ or significantly worse (4.2% instead of 7.8%)⁶⁵ photovoltaic performance. The reason for different result of them might be related to the method of absorber deposition and is the subject of ongoing research. Additionally, some MMO with functionalized or composite structure also achieved considerable performance,⁶⁶⁻⁶⁸ especially Wang et al. demonstrated the successful combination of graphene and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ in MSSC, and a remarkable PCE of 15.6% was obtained.⁶⁸ State-of-the-art perovskite solar cells based on a mesoporous ZnO scaffold, a $\text{CH}_3\text{NH}_3\text{PbI}_3$ light-absorption layer and spiro-OMeTAD hole transport layer have achieved PCEs as high as 15.7% when measured under AM1.5G illumination, which is the highest-performing perovskite solar cells reported to date.⁴⁶

As for HTL, no doubt it must possess appropriate photoelectric characteristics, meanwhile the cost, stability, preparation process etc. should be considered seriously. A variety of organic polymer materials such as spiro-OMeTAD, poly(3-hexylthiophene-2,5-diyl)(P3HT), poly[*N*-9-heptadecanyl-2,7-carbazole-*alt*-3,6-bis(thiophen-5-yl)-2,5-dioctyl-2,5-di-hydropyrrolo[3,4-]pyrrole-1,4-dione] (PCBTDPP), poly-[2,1,3-benzothiadiazole-4,7-diyl][4,4-bis(2-ethylhexyl)-4H-cyclopenta 2,1-b:3,4-b']dithiophene-2,6-diyl]] (PCPDTBT), poly-[[9-(1-octylonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]] (PCDTBT), poly-(triarylamine) (PTAA), 4-(diethylamino)-benzaldehyde diphenylhydrazone (DEH), *N,N*-di-*p*-methoxyphenylamine-substituted pyrene derivatives (Py) and swivel-cruciform 3,3'-bithiophene (KTM3) have been used as HLL,^{69–74} and an inorganic hole conductors, copper iodide (CuI) HTL was reported also.⁷⁵ However, these hole conductors are either expensive or poor performance. Despite some of them had achieved the highest PCE (e.g., the efficiency of solar cells with spiro-OMeTAD as a HTL reached almost 16%), it is essential to explore newer HTL for advancement of cost-effective and practical perovskite solar cells. Previous work shown that interfacial chemical interactions may play a significant role in determining efficiencies in solid state sensitized solar cells.⁷⁶ Additionally, the design of the HTL with the appropriate structure can inhibit back electron transfer, which will result in a solar cell with higher fill factor and open circuit voltage.²⁶ Tuning the energetic levels of the HTL is also a methodology to enhance the V_{oc} . shifting the highest occupied molecular orbital level of the HTL towards that of the lead iodide perovskite will result in higher open circuit potentials.⁷⁷ Previous studies on perovskite solar cells using different HTL have indicated that polytriarylamine PTAA and spiro-OMeTAD,^{69,72} which contain amine group, have shown the best performance. This has been tentatively attributed to the favorable molecular interaction between the amine groups and the lead perovskite.

5. CONCLUSIONS AND OUTLOOK

In summary, we introduced the structure and preparation of organic–inorganic hybrid perovskite MLH (films), and reviewed its latest investigation in solar cell application, especially compared and analyzed some different views and key issues, including selection of halogen materials as well as MMO, advantages or disadvantages of two types of device architecture—MSSC and PJSC, effects of varied or no HTL etc. To conclude, MLH along with their mixed-halide crystals, corresponding to three-dimensional perovskite structures, have been used as effective light harvesters for solar cells, benefiting from the advantages of direct band gap, large absorption coefficient, and high ambipolar carrier mobility. PJSC possess a more promising architecture owing to simple fabrication and less cost.

Meanwhile it is must be admitted that MSSC represents a type of high efficiency device configuration, and too early to say that MMO and HTL is necessary or not. Although MLH-based solar cells have reached a PCE almost as high as 16%, one has to keep in mind that these studies are still at the very initial stage, and many theoretical and technical issues need to be explicated or solved, such as systematic and comprehensive study of materials characteristics and device operating mechanism, stability enhancement of both of them, environmental friendliness (as perovskite cells contain lead, it is not a critical, scarce metal but a toxic one, and definitely needs to be kept out of the environment). Given the relatively short period of time in developing MLH perovskite solar cell, and it was widely and intensively investigated, we have every reason to believe that the remaining issues, including scaling up of cell area and further promotion of PCE, will be satisfactorily resolved in the near future, and MLH-base solar cell will certainly possess wide application prospects.

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