Recent achievements in perovskite solar cells

Hybrid (organo-inorganic) perovskite materials are potential candidate as a photoactive materials for photovoltaics. Currently, many research groups have been focused on designing the perovskite materials in such a way so that it can harness the broad spectrum of visible light wavelength. Hybrid perovskites such methylammonium lead halides reveal unique photovoltaic and charge transport properties. The main objectives of this article are to provide some recent research progress on perovskite nanomaterials for solar cell application. Therefore, this mini review paper summarizes some recent development of organic-inorganic perovskite materials of different research groups and provides some useful insights for its future improvement.

Key words: photoactive materials, photovoltaics, hybrid perovskites, nanomaterials, sunny batteries.

Introduction

The world’s growing population and industrialization result in a constantly rising demand for energy. Uses of fossil fuels as an energy source produce greenhouse gases which have detrimental effect on the environment, especially global warming [1–3]. Are we willing to accept the effect of greenhouse gases on climate change in order to meet our energy demand? If we are not we need to urgently solve the challenging problem of developing alternative sources of energy that can make a difference. Harnessing energy directly from sunlight can be an alternative approach to fulfill the clean energy need with negligible environmental effect. Developing of photovoltaic (PV) and water splitting devices based on the remarkable perovskite materials are one of the important step toward achieving that goal.

Organic-lead halide perovskites have the potential to be such an alternative technology for energy production. Power conversion efficiencies (PCE) of PV devices based on these materials have increased from around 4 % to a certified 20.1 % in the last three years [4–7]. Due to their high efficiency, perovskite solar cells are already competing established thin-film technologies, such as those based on inorganic semiconductor CdTe and CIGS [8]. These organic-lead halide perovskites show high photon absorptivity in optical range, and a sharp optical band edge, which suggests low levels of disorder.[9, 10] They also exhibit long charge-carrier diffusion lengths (>1 mm) relative to the absorption depth of incident light (~100 nm) [11–14], meaning that almost all photoexcited charge carrier in the perovskite are able to reach the interfaces from where the charges are then transported through suitable hole and electron-transporting layers to the electrodes.

Despite progress in the efficiency of PCSs, there is still challenges to commercialization because of the toxicity of Pb atoms, longterm stability, and (3) cost-effectiveness. We have extremely large field for researching to improve and optimize perovskite solar cells in order to soon as possible see these remarkable solar cells on the market.

In this review paper, it is intended to provide the recent progress in perovskites for the application in photovoltaics. In the first section, we introduce the perovskite structure. In Section 2, recent progress in organolead halide perovskite, deposition processes of organolead perovskite for solar cells and the operation principles of perovskite solar cells are discussed. Finally, in Section 3, some conclusions are drawn on future perspective of perovskite materials.

1. The structure of perovskites materials

Perovskite materials have similar crystal structures to calcium titanate (CaTiO₃). The compounds with perovskite structure exist widely in earth, and some researchers believe that magnesium silicate perovskite (MgSiO₃) is the most prevalent mineral in the mantle of the earth [15]. Perovskite materials have various interesting properties and practical applications such as large magnetoresistance, superconductivity, ferroelectricity, transport properties, optical properties, etc. which can be utilized in designing effective devices for photovoltaic and photocatalysts for water splitting. The perovskite structure can be expressed...
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by generalized formula of $ABX_3$, where the B atom is usually a metal cation and $X$ is an anion ($O^{2-}$, $I^-$, $Br^-$, $Cl^-$, etc.) [16]. They form the $BX_6$ octahedral where $X$ lies in the corner around B located at the center of the octahedral (Figure 1a). The $BX_6$ octahedral form an extended three dimensional space network with all-corner connected each other (Fig. 1b). The symbol A is assigned to a metal cation that fills the vacancy among the octahedral and balances the charge of the whole network. The larger A cations (Ca$^{2+}$, K$^+$, Na$^+$, Sr$^{2+}$, Pb$^{2+}$, Ce$^{3+}$) occupy the 12 coordinated sites between the octahedral. In the idealized cubic unit cell, the position of cation A sites, cation B sites and anion X sites are at cube corner positions (0,0,0), body center position ($1/2,1/2,1/2$) and face centered positions ($1/2,1/2,0$), respectively. The examples of ideal cubic perovskite structure (undistorted cubic structure) are SrTiO$_3$ [17], CsSnBr$_3$ [18].

![Figure 1](image.png)

Figure 1. ABX$_3$ perovskite structure showing $BX_6$ octahedral geometry (a) and their extended network structure connected by the corner-shared octahedral (b). Reprinted from [15] and [19].

In most cases, the perovskites have distorted type of cubic structure. These distortions are enormous in number and have complex details. Even the CaTiO$_3$ mineral has pseudo-cubic structure due to the tilting of the octahedron. According to Ziyong Cheng and Jun Lin [16] the various distortion mechanisms can be classified into five types: (1) distortion of the $BX_6$ octahedron by the Jahn-Teller effect, (2) off-center displacement of the B cations in the $BX_6$ octahedron, this effect is responsible for possible ferroelectricity, (3) so-called tilting of the octahedra framework, typically occurring as result of a too small A cation at the cuboctahedral site, (4) ordering of more than one kind of cations A or B, or of vacancies, (5) ordering of more than one kind of anions X, or vacancies. Physical properties of perovskite materials depend crucially on these distortions, particularly the electronic, optical, transport, magnetic and dielectric properties which are significant for many applications of perovskite materials. Therefore, the distortions as a result of cation substitution can be used for tuning physical properties exhibited by perovskites.

2.1 Recent progress in organolead halide perovskite for solar energy conversion

The prevalent perovskite materials used in solar cells to date are three-dimensional hybrid perovskites. These perovskites have short-chain organic cations, such as methylammonium (CH$_3$NH$_3^+$, MA), metal cations such as lead (Pb$^{2+}$), and halides ($X = I^-$, $Br^-$, $Cl^-$ or mixtures). For efficient devices, cation B has been Pb$^{2+}$. Although, Sn$^{2+}$ forms similar structure with lower and naturally more ideal bandgaps [20], with lower stability. In this Section, we will focus on the MAPbI$_3$ and the mixed-halide analogue, MAPbI$_3$$_x$Cl$_{3-x}$ perovskite films. We will present a recent progress in organolead halide perovskite, the different methods for the formation of films and consider the operation principles of perovskite solar cells which are not fully understood yet.

In 2013, one of Science's Top 10 Breakthroughs of 2013 has become highly efficient organolead halide perovskite solar cells [21]. In perovskite solar cell (PSCs), the organolead halide perovskite, CH$_3$NH$_3$PbX$_3$ (where $X = I^-$, $Br^-$, $Cl^-$), is used as a photoactive layer to harvest sunlight. In 2009, Miyasaka et al. first published a report on using perovskite nanoparticles as visible light sensitizers in liquid DSSC based on mesoporous TiO$_2$ scaffold yielding efficiencies of 3.81% [22]. However, these first DSSCs sensitized by perovskite nanoparticles had poor stability because of liquid electrolyte which corrupts perovskite sensitizer. In 2009, Grätzel's group also used the perovskite nanoparticles to sensitize mesoporous TiO$_2$ films in a solid-state mesoscopic solar cell and delivered power conversion efficiency (PCE) of up to 9.7% [23]. They used hole-conductor spiro-MeOTAD instead of liquid electrolyte. Soon, Snaith’s group employed mesoporous Al$_2$O$_3$ as a scaffold and a mixed halide perovskite, CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$, as sunlight absorber.

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The insulting Al₂O₃ scaffold supports the formation of continuous thin films of CH₃NH₃PbI₃Cl, and extremely decreases the energy costs associated with separating tightly bound excitons (photoinduced electron-hole pairs) and extracting free charges from highly disordered low-mobility networks such as mesoporous TiO₂. That so-called «meso-superstructure» PCS had a PCE as high as 10.9 % and generated open-circuit photovoltage of more than 1.1 volts [24]. This study for the first time demonstrated that the mixed halide perovskite could be as both a sunlight absorber and a charge carrier transporter. The PCE of the perovskite solar cell was further increased up to 12 % by the infiltrating the pores of the mesoporous TiO₂ film with CH₃NH₃PbI₃ perovskite, and overlayers of CH₃NH₃PbI₃ co-exist on top of the mp-TiO₂ film [25]. This study implied that the perovskite performs a double role as light harvester and hole conductor. A significant improvement in the PCSs fabrication and reproducibility of their performance was achieved introducing a two-step sequential deposition technique. PbI₂ was first introduced from solution into an mp-TiO₂ film and subsequently transformed into the perovskite by exposing it to a solution of CH₃NH₃I, resulting in a cell with a PCE of 15 % [26]. Further, Snaith’s group showed that nanostructuring is not necessary to achieve high efficiencies with this material [27]. They obtained PCE of 15 % in simple planar heterojunction solar cell incorporating vapour-deposited perovskite as the absorbing layer, a compact layer of n-type TiO₂ as an electron-collecting layer, and spiro-MeOTAD as a p-type hole conductor. This study demonstrated that perovskite absorbers can function with the highest efficiencies in simplified device architectures, without the need for complex nanostructures. Y. Yang et al. reported a planar PSC with a PCE of 19.3 % using the efficient interface engineering technology. By controlling the formation of the perovskite layer and careful choices of other materials, they suppressed carrier recombination in the absorber, facilitated carrier injection into the carrier transport layers, and maintained good carrier extraction at the electrodes [28]. Recently, the certified PCE of PSC has been boosted up to 20 % [29], which is the most promising competitor to silicon-based solar cells.

2.2. Deposition processes of organolead perovskite for solar cells

In the first reports on CH₃NH₃PbI₃ and CH₃NH₃PbI₃Cl, solar cells, spin-coating technique was used to prepare the photoactive absorbers from a single precursor solution. A solution of CH₃NH₃I and PbI₂ (stoichiometric ratio) in polar solvents such as GBL or DMF was used to form CH₃NH₃PbI₃ films [7, 25]. For forming CH₃NH₃PbI₃Cl, a solution of PbCl₂ and CH₃NH₃I (a molar ratio of 1:3) in DMF was usually used [30, 31]. The perovskite absorber can be deposited either within the pores of the mesoporous layers or be formed as uniform films on TiO₂ compact layers in a case of planar solar cells by proper optimization of the precursor concentration and spin-coating conditions. For planar cells, the deposition of a uniform perovskite layer by spin-coating demands the optimization of various parameters including post-deposition treatment [32, 33]. Since wettability of underlying layer is different, the deposition of perovskite must need to be separately optimized for each of ones. The degree of infiltration within the mesoporous layer depends crucially upon the solution concentration, spin-coating rate and the properties of solvent used. The roughness of surface which could cause shunts in the solar cells depends on the tendency perovskite films to crystallize [25].

An important achievement in solution based deposition has been the development of the sequential deposition method for the preparation of perovskite solar cells by Grätzel and coworkers [26]. These deposition method is composed of spin-coating PbI₂ layer on the TiO₂ mesoporous layer from a solution under proper conditions (solution concentration, spin-coating rate) that allow to qualitatively infiltrate PbI₂ within the mesoporous layer (first step) (Fig. 2a). Subsequently, the substrates with formed PbI₂ which has yellow color are dipped in a CH₃NH₃I solution in 2-propanol solvent. Over the dipping, the yellow PbI₂ layer converts forming the dark brown CH₃NH₃PbI₃ that occurs in a few seconds (Fig. 2b). It is worth to mentioning that the conversion time can depends on different PbI₂ deposition conditions. It has been reported on a 20-minute conversion time [34], though the original work by Mitzi and co. informed that the conversion took 1–3 h [35]. It is probable that the PbI₂ layer deposited on top of mesoporous layers has increased roughness that promotes the conversion reaction [26]. The conversion of PbI₂ into CH₃NH₃PbI₃ occurs with volume expansion [36] (~75 %) therefore it is believed that the mesoporous layer would be better infiltrated by the sequential deposition process. The SEM top view of samples deposited by this process show a highly crystalline film with complete coverage (Fig. 2c).
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Cross-sectional SEM image of a mesoporous TiO₂ film infiltrated with PbI₂

Changing in absorbance at 550 nm of such a film monitored during the conversion from PbI₂ to CH₃NH₃PbI₃

SEM top view of the CH₃NH₃PbI₃ film prepared utilizing the sequential deposition method

Figure 2. Reprinted from [26]

Vapour deposition techniques have also been used to form perovskite solar cells along with the extensively applied solution based deposition processes. Efficient planar solar cells (15.4 %) of CH₃NH₃PbI₃−ₓClₓ fabricated by dual source evaporation of PbCl₂ and CH₃NH₃I (Figure 3a) were showed by Snaith and coworkers [27]. The evaporated perovskite film was sandwiched between a compact TiO₂ layer and a spin-coated spiro-OMeTAD layer performing as electron and hole transporters, respectively. The vapour-deposited perovskite films are extremely uniform and compact, with crystal grains of hundreds of nanometers. By these vapour deposition technique, Bolink and coworkers [37] managed to fabricate device with efficiency 12.04 % utilizing different electron and hole transporters, organic electron and hole transport layers such as PCBM and PEDOT: PSS. In both cases, in order to yield the desired perovskite layers and efficient solar cells, careful optimization of dual source evaporation process was required. Chen et al. has demonstrated a combined approach in which both solutions based deposition and vapour phase transformation has been utilized [36]. In these so called vapour-assisted solution process (VASP), PbI₂ solution was first spin-coated on a compact TiO₂ substrate. Subsequently, the yellow colored films underwent a vapour of CH₃NH₃I at 150 ºC in N₂ for 2 h (Fig. 3b). Due to the slow rate of conversion, VASP produced CH₃NH₃PbI₃ films with micron sized grains and with very low surface roughness of ∼20 nm. Perovskite solar cells fabricated from such films had an efficiency of 12.1 %.

A schematic illustration of dual-source thermal evaporation equipment for depositing the perovskite films; the organic source was methylammonium iodide and the inorganic source PbCl₂. Reproduced from [27]

A schematic illustration of the vapour assisted conversion of PbI₂ to CH₃NH₃PbI₃ by exposure to CH₃NH₃I vapour. Reproduced from [36]

Figure 3
2.3. The operation principles of perovskite solar cells

As mentioned above the perovskite nanoparticles were first used as 'sensitizers' on mesoporous TiO₂ and their role in the solar cell was supposed to be similar to the dye in a DSSC. Sunlight is absorbed by the perovskite nanoparticles, producing electrons in the conduction band of the TiO₂, across which electrons are transported to the anode. The holes remaining on the perovskite bulk are then transferred to a redox electrolyte, or solid-state hole-transport materials, and further transported to a cathode [38] (Fig. 4a). Further studies revealed that the perovskites can function as both hole and electron transport material [5, 39], and that a thin perovskite film with a thickness of few hundred nanometer can even perform charge generation and transport [5, 31, 40–42]. The cell architectures are similar to a planar heterojunction architecture, where a perovskite layer is sandwiched between p- and n-type selective contacts [27] (Fig. 4b). This simple planar architecture can be assembled by different preparation methods and strongly attracted attention of photovoltaic [30–60].

Figure 4. (a) Mesoscopic perovskite solar cell with mesoporous TiO₂ layer and (b) planar structure without a mesoporous TiO₂ layer. Thin film on fluorine doped tin oxide (FTO) is an n-type semiconductor. HTM stands for hole transporting material. In the mesoscopic structure, electrons can be collected directly and/or via TiO₂ layer

In planar perovskite solar cells, the charge generation mechanism and dynamics are not completely clear yet. It is not understood what is photoexcited species, free electrons and holes or bound excitons? In the room-temperature, the upper bound of exciton binding energy in the perovskite materials with tetragonal phase is ~50 meV [43]. However, in these computation dielectric constant is supposed to be 6.5, but according to Even J. et al., the effective dielectric constant is probably much greater. In that case, exciton binding energies in the tetragonal phase is probable ~1–10 meV [44]. Though, even for the exciton binding energy of ~50 meV, free charge carriers are generated spontaneously after light harvesting, that controversial to a large concentration of bound excitons [43–46]. According to ultrafast spectroscopy studies (Fig. 5a), dissociation of exciton occur during 2 ps after photoexcitation [48, 49]. For confirmation of these features it is required thorough interpretation of these transient spectra. The mobilities of free electrons and holes are approximately equal and lay in the range ~10–30 cm² V⁻¹ s⁻¹ [49–51] (Fig. 5a inset). Stranks S.D. et al. studied recombination kinetics in organic-inorganic perovskites under high light intensities, according to them; recombination is bimolecular [46]. This indicates that the prevalent relaxation pathway is recombination of free electrons and holes [48, 52]. The recombination in these perovskite is mainly radiative as well. At room temperature, photoluminescence quantum efficiencies reach value of 70 % (Fig. 5b) [46, 48] and at low temperature even 100 % [58]. This high luminescence efficiency ascribes perovskite solar cells to the efficiency limit Shockley–Queisser. In that case all recombination is supposed to be radiative [53–55]. It is worth mentioning that there are monomolecular trap-assisted recombination pathways that can predominate under normal solar cell operating conditions [45, 46].
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Photoluminescence quenching measurements which will tend to give an underestimate due to the assumptions of perfect quenching and homogenous recombination throughout the bulk of the film.

The perovskite film morphology and the defect density within the films strongly influence on the charge carrier lifetime in the perovskite. According to recent research on single crystals of MAPbI₃ and MAPbBr₃, defect densities in such crystals are lower ~10¹⁰ cm⁻³ [59, 60], in comparison to the polycrystalline perovskite films where ones are ~10¹⁶ cm⁻³ [45, 46, 57]. In these single crystals, an estimated charge carrier lifetime and a corresponding charge carrier diffusion length reach value of a few hundred microseconds and of 175 μm, respectively. It is worth to mentioning that here to estimate the charge carrier lifetime electrochemical impedance spectroscopy and photovoltage decay techniques of electronically contacted crystals were used. If charge carrier trapping takes place at the crystal surface, it may overestimate the charge carrier lifetime, and in that case, the results require verification by other techniques.

In polycrystalline thin films, the intergrain potential barriers present obstacles to carrier transport through layer and may reduce the carrier mobility by many orders of magnitude from that found in single-crystal material. In this respect, CIGS has long been regarded a «better material» due to the extremely low intergrain potential barrier of 100 meV [58]. In comparison with CIGS, at the CdTe grain boundaries, depending on processing conditions, intergrain potential barrier is ~100–800 meV [58]. However, intergrain potential barrier in polycrystalline MAPbI₃ perovskite films in the dark is ~ only 45 meV and further decreased under illumination [37]. This implies that charge trapping at grain boundaries in perovskite films must be much less of an obstacle than in CIGS or CdTe. However, cells with large grain size had enhanced device performance and charge carrier diffusion length which imply that the grain boundaries may not be benign [59, 60].

The steepness of the optical absorption edge indicates on the quality of the material. It allows to characterize the energetic disorder by analyzing the exponential decay of the absorption spectra below the bandgap with a characteristic energy, the Urbach energy [61, 62]. The perovskite films have a high absorption coefficient with a sharp absorption edge and a low Urbach energy of 15 meV, that means a low level of energetic disorder. For comparison, values of Urbach energy of GaAs, CdTe, crystalline silicon, MAPbI₃ or MAPbI₃–Clₓ, CIGS are 7, 10, 11, 15, 25 meV, respectively. The Urbach energy of perovskite is lower than CIGS (~25 meV) and somewhat higher than GaAs (~7 meV) [54, 61], that is unbelievable for a solution prepared semiconductor. Despite that perovskite samples fabricated employing most standard solution-processing methods [45, 48, 51, 57] have low densities electronic trap states (~10¹⁶ cm⁻³) in band gap, even the low trap states strongly influence on recombination dynamic [46], cell photovoltage [51], and photoluminescence quantum efficiencies [46, 48, 51] (Figure 6b).

In the most efficient perovskite solar cells using nanoporous TiO₂, the cell is composed of a thin (~200 nm) layer of nanoporous TiO₂ infiltrated and capped with a solid perovskite layer (~200–300 nm) (Fig. 5a) [63–66]. In these nanoporous TiO₂-based perovskite cells, a bottom layer of TiO₂/perovskite perform a role of a bulk distributed heterojunction and a top layer of the perovskite and the hole-transport material operates as a planar heterojunction [63, 66]. Snaith et. al assume that as soon as proper control of the interfacial contact between the perovskite and the compact n-type layers is achieved, the privileged solar cell architecture will be the planar heterojunction one (Fig. 5b) [33, 37, 67].

3. Summary and perspectives

In summary, some major progresses on the development of perovskite based photocatalysts for water splitting have been achieved by following different modification strategies considering the fundamental principle and process of photocatalysis, crystal structure and chemical component characteristics of perovskite materials.

Intense research into perovskite solar cells and other optoelectronic applications has only recently begun, however a great breakthrough in solar cells has been made utilizing organolead halide perovskites as sunlight absorbers with low-cost preparation techniques. Organolead halide perovskites are capable of a high light harvesting, possess excellent electrotransport properties and have a low defect density and low intergrain potential barriers. PCEs of over 15 % have been reached for both mesoscopic architecture and planar heterojunction one. We believe that the increase in the domain size of crystals and the uniformity of perovskite film will be the major factors that will enhance the performance of perovskite solar cells over the next few years.
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