Present Research Progress of Sn Halide Perovskite Solar Cells

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Abstract: As a kind of photoelectric material with high performance, perovskite has drawn wide attention. Since its first application as active layer in solar cell in 2009, the efficiency of perovskite solar cell (PSC) has been raised from 3.8% to 23.3%. As the most efficient Pb-free PSC, Sn halide PSCs attract much attention recently. This review briefly introduces the principle of PSCs, summarizes the methods to improve Sn halide PSCs’ efficiency and makes some outlook of the future of this field.

1. Introduction
Among the common solar cells, silicon solar cell’s cost is too high, which lead to a long payoff period; dye-sensitized solar cell is low in efficiency (<10%). Since 2009, perovskite solar cell (PSC) is increasingly attracting researchers’ interest [1] because its low cost, simple preparation technology and high performance, and PSC’s power conversion efficiency (PCE) has been raised from initial 3.8% to 22.7% [2]. These all indicate that PSC has a great application potential.

Perovskite (ABX₃) is a kind of materials whose structure is the same with perovskite (CaTiO₃), where A can be either a large single atom (Cs) or a monovalent organic cation (e.g., CH₃NH₃⁺ = MA⁺ or NH=CHNH₃⁺ = FA⁺), B stands for a divalent metal cation (e.g., Pb or Sn) and X is halogen anion. The structure is shown on figure.1, B is on the corners of a cube which center on A, while X is on the corners of octahedron which center on B; each X is shared by two nearest B.

Figure 1. Perovskite structure where A stands for monovalent cation, B is Pb(II) or Sn (II) cation, and X is Cl, Br, or I [3]

Perovskite solar cell is commonly composed of perovskite photoactive layer, transporting layer and electrode. The operating principle is shown on Fig.2 [3]. The incidence incomes from the side of transparent electrode, and the perovskite photo active layer absorb photon and generate free excitons. Because the exciton binding energy is relatively low, most of the excitons will separate to be free charge, and the electrons enter the conduction band while the holes enter the valence band. Under the effect of concentration difference and built-in electric field, free electrons and holes diffuse in perovskite and enter the transporting layer. The transporting layer mainly refers to electron transporting layer (ETL) and hole transporting layer (HTL). The ETL can extracts electrons and block
holes, while HTL does the opposite. The carriers extracted by the transporting later is collected by corresponding electrode and enter the external circuit to do work.

Figure 2. Band diagram and main processes in OSCs: 1 Absorption of photon followed by exciton formation; 2 Exciton diffusion; 3 Charge separation; 4 Charge extraction. [3]

PSCs’ performance is commonly described by electric current density-voltage curve under specific light condition (VA characteristic curve). There are four main factors used to evaluate the PSCs’ performance: short circuit electric current density, open circuit voltage, filling factor (FF, the ratio of biggest product of J and V on the curve to the product of Jsc and Voc) and power conversion efficiency (PCE, the ratio of maximum output power to the incidence’s power).

When applied as active layer in solar cells, the advantages of perovskite are as follows:

1. We can adjust its band gap structure by replacing the ion in it with similar ones. For example, by partially or entirely replacing I\(^{-}\)anion with Br\(^{-}\) to make it match the energy level of ETL and HTL, we can improve PSC’s efficiency.

2. Perovskite has a high light absorption coefficient (10\(^{4}\)–10\(^{5}\)), which is larger than that of silicon by an order of magnitude [4], and that means a thinner layer can meet the requirement for making solar cells (~300nm, and for silicon solar cell the number is 3–5μm).

3. Its exciton binding energy is as low as 37–50 eV [5], close to the inner energy in normal temperature K\(_{b}\)T (~26meV). Therefore, separation of electrons and holes can occur under room temperature in perovskite.

4. The carrier mobility in perovskite is relatively high. The electron mobility and hole mobility are 164±25cm\(^{2}\)/V\cdotS\(^{-}\) and 24.8±4.1cm\(^{2}\)/V\cdotS\(^{-}\), respectively, and their diffusion length is over 175μm [6].

5. It has a feature of bipolar transmission, appear to have p-type characteristic when contact with electron transporting material, and show n-type characteristic when contact with hole transporting material.

2. Present research progress of Sn halide PSC

At present, all of the PSCs with top PCE are Pb halide PSCs, however, as a heavy metal element, Pb’s toxicity and stability can do irreversible damage to the environment, so researchers hope to use another element to replace Pb partially or even entirely. As an element belonging to the same family with Pb, Sn has a similar outer electron structure, and its ion radii (Sn\(^{2+}\)) is smaller than that of Pb\(^{2+}\). The optimum band gap for Sn and Pb halide perovskite as active layer is 1.34eV (Shockley–Queisser limit) [7,8], however, among the most frequently-used Pb halide perovskite, FAPbI\(_{3}\)’s band gap is 1.58eV, and the band gap of FAPbI\(_{3}\), which is the smallest, also reaches 1.48eV. In the contrary, MASnI\(_{3}\), FASnI\(_{3}\) and CsSnI\(_{3}\)’s band gap are 1.25-1.3 eV, 1.40 eV, 1.30 eV, respectively, which means it can reach a higher efficiency in theory. Meanwhile, Sn halide perovskite also have a higher carrier mobility, for example, the MASnI\(_{3}\) single crystal’s electron mobility and hole mobility reach 2320 cm\(^{2}\)/V\cdotS\(^{-}\) and 322 cm\(^{2}\)/V\cdotS\(^{-}\), respectively, and its exciton binding energy is also as low as 2-50 meV. Therefore, Sn is regard as one of the most appropriate elements to replace Pb for light absorption. However, there is no report that make the Sn halide PSC’s efficiency reach 10%, and the main causes of the low efficiency are the overly high defect concentration, the high background carrier concentration, and the easy recombination of the photon-generated carrier.
According to the density theory calculation (DFT)\cite{10}, the activation energy of Sn vacancies in Sn halide PSC is low; therefore, the polycrystalline film shows p-type doping properties, and the background hole carrier concentration is as large as $10^{19}$ cm$^{-3}$ (commonly $10^{16}$ cm$^{-3}$ in Pb halide perovskite)\cite{11}. Moreover, without Pb’s inert pair effect, the outmost s orbital electron in Sn is easy to lost, which lead to Sn$^{2+}$’s oxidization\cite{12}. Due to the two aspects, Sn halide perovskite shows heavy p-type doping properties in both intrinsic and extrinsic angle, which results in higher background carrier concentrations. Additionally, the coverage and smoothness of film’s surface can also affect the devices’ efficiency. In order to enhance the Sn halide PSCs’ efficiency, the main directions taken by researchers are: reducing the defects, controlling the perovskite layer’s surface topography and improving the coating method.

In order to reduce defects’ generating, it is easy to consider adding reducing additive or reducing atmosphere. Li W et al. added hypophosphorous acid(H$_3$PO$_2$) into the CsSnI$_3$ precursor solution and formed CsSnX$_{3}$−HPA$_{y}$ cluster in the film\cite{13}. XPS (X-ray photoelectron spectroscopy) measurement directly proved that the amount of Sn$^{4+}$ was much lowered when compared with the pristine sample without H$_3$PO$_2$ addition. With the addition of H$_3$PO$_2$, the PL decay process was dramatically retarded, and the charge carrier density was lowered by one order of magnitude, which both indicated a decrease of Sn defects. Under the optimum H$_3$PO$_2$ concentration 0.5μL·ml$^{-1}$, the champion device reached a $J_{SC}$ of 17.4 mA cm$^{-2}$, a Voc of 0.31V and an FF of 0.56, and consequently a PCE of 3.2%, which was the highest reported PCE for the all-inorganic Sn-based PSCs at that time.

Then, Kayesh et al. used hydrazine dihydrochloride (N$_2$H$_5$Cl) as additive to reduce Sn$^{4+}$. With the addition of hydrazine dihydrochloride, the Sn$^{4+}$ concentration in FASnI$_3$ was dramatically lowered, and the coverage of the film was largely improved. At the same time, the PCE of the device they made reached 5.4%, and the stability was sharply enhanced as well\cite{14}.

At the same time, Gu F et al. reported a method of adding tin powder into FASnI$_3$ solution\cite{15}. Obviously, the tin powder can react with tetravalence Sn (Sn$^{4+}$+Sn→2Sn$^{2+}$). With the addition of tin powder, the hole...
concentration can be lowered from $1.0 \times 10^{18} \text{cm}^{-3}$ to $8.9 \times 10^{16} \text{cm}^{-3}$, showing that the usage of tin powder as additive can also suppress the Sn defects’ generation. They also found that when processing 99% SnI$_2$, it acts as a reducing agent and compensator both; when processing 99.999% SnI$_2$, it mainly acts as a reducing agent. In their experiment, the device made from the solution that had been mixed with tin powder, stilted and filtered reached a highest PCE of 6.75% with a J$_{SC}$ of 17.5 mA cm$^{-2}$, a Voc of 0.58V and an FF of 66.3%.

Different from additive, Song et al. create a reducing atmosphere by adding hydrazine vapor (N$_2$H$_4$) when spin coating to suppress the generation of Sn$^{4+}$ [16]. This method is also effective to the other Sn halide perovskite such as MASnI$_3$, CsSnI$_3$ and CsSnBr$_3$, and the PCE of MASnI$_3$ reached 3.89%.

Adding Sn$^{2+}$ solution as tin compensator is also a common way. In 2014, Kumar M H et al. added SnF$_2$ solution into CsSnI$_3$ precursor solution as tin compensator [17]. They tried SnF$_2$ in several different concentration, finding that a 20%’s concentration of SnF$_2$ can lead to the highest PCE of 2.02% while reducing the carrier density by two order of magnitude, and the absorption wavelength is able to reach 950nm. They thought the addition of SnF$_2$ can raise Sn’s chemical potential, thus raises the formation energy of Sn vacancies and suppresses the formation of defects. In 2016, Yan et al. added SnF$_2$ into FASnI$_3$ precursor solution, which improved the topography of the film and reduced the carrier density. The ITO/PEDOT:PSS/FASnI$_3$/C$_60$/BCP/Ag devices they made could reach a highest PCE of 6.22% and had a high reproducibility [18]. SnI$_2$ and SnCl$_2$ have a similar effect with SnF$_2$.

**Figure 5.** Proposed possible mechanism of hydrazine vapor reaction with Sn-based perovskite materials [16].

Another solution for Sn vacancies is 2D-3D mixing. Low dimensional perovskite like PEA$_3$F$_{3n+1}$Sn$_5$I$_{3n+1}$ ($n$ is the number of the inorganic Sn$_5$I$_6$ octahedra layers encapsulated by the PEA$^+$ (PEA$^+$ = C$_6$H$_5$(CH$_2$)$_2$NH$_3$$^+$) double layer, the increase (decrease) in $n$ value means increase (decrease) in the dimension). The specific structure is shown in figure 7. Compared with more favorable 3D perovskite, 2D perovskite is higher in stability but lower in efficiency. If we mix these two in appropriate proportion, we might gain devices that are fine in both efficiency and stability. More specifically, 2D perovskite have a strong tendency to form a highly ordered structure, thus functions as a seed layer to induce orientation of the 3D perovskite grains and suppresses the formation of tin vacancies. Besides, the addition of hydrophobic component improves the hydrophobicity of the devices, and enhances its stability by this way. Shao S et al. mixed small amount (0.08M) of 2D Sn perovskite with 3D FASnI$_3$ and gained a champion device with a PCE of 9.0%, which is the first report of Sn halide PSC with a PCE of over 9% [19]. In addition, the addition of diamine ions like (ethylenediammoinium) (en), (propylenediammoininium) (pn),...
and (trimethylenediammominium) (tn) can form hollow 3D perovskite, of which the stability and efficiency is improved [20-21].

Figure 7. Schematic crystal structure of a) 3D reference FASnI₃, b) 2D/3D mixture (2D 0.08 m), with the unit cells of each component outlined in red, and c) 2D PEA₂SnI₄.

Except for dealing with Sn vacancies, some researchers seek for higher efficiency by improve the layer’s topography. Liu et al. reported that hot antisolvent treatment (HAT) can improve the film coverage and lower the roughness of the layer [22]. At the meantime, they found annealing under a low partial pressure of dimethyl sulfoxide vapor can increase the average crystallite size and suppress Sn vacancies. Consequently, the PSC they made reached a PCE of 7.2%. Wu et al. presented a method of vapor deposition SnI₂ after spin coating FAI’s aqueous solution to produce FASnI₃ to ensure the purity of SnI₂ [23].

In addition, due to the oxidizable nature of tin-based perovskites, relative to lead-based perovskite VBM and CBM, it is necessary to select suitable HTL and ETL and introduce interface modification layer to assist carrier extraction and transmission. For example, adding ZnS layer between MASnI₃ and TiO₂ reduces the electron transport energy barrier, and inserting LiF between ITO and PEDOT:PSS reduces the PEDOT:PSS work function and facilitates hole extraction [24].

3. Summary and outlook

As we have discussed above, Sn halide PSC is a very potential photoelectric converting device. It is more economical than the solar cells which is universally applied nowadays, and meanwhile more environment-friendly than the Pb halide PSC which has a similar structure with it. However, when it comes to commercial usage, Sn halide PSC still have a long way to go. In view of the known methods to improve the Sn halide PSC, we consider that the Sn halide PSC can be improved in the future by the methods as follow:

1. Continuing enhance Sn halide PSC’s PCE and stability. As we’ve discussed before, the highest PCE for Sn halide PSC now is below 10%, which is far from the PCE that Pb halide PSC can reach. In order to boost the efficiency of Sn halide perovskite active layers, we can search for method to reduce Sn defects continuously, such as trying new reducing agent adding, new film preparation technology and so on. Additionally, improving the device structure, seeking for more suitable charge transport material is also a considerable direction.

2. Lower the Sn halide PSC’s fabricating cost. Recently, most of the Sn halide PSCs with high PCE are made by evaporation, which has relatively high cost and tedious fabricating process, thus unfavorable for commercial applying. In addition, nearly all of area of the Sn halide perovskite films made in laboratory are around 0.1cm², so we also need to expand the films’ area while maintaining the efficiency.

3. Enhance our comprehension about perovskite via theory research. We can alter Sn halide PSCs’ nature more efficiently by studying ionic migration in perovskite and electron-hole pairs’ generation and separation mechanism, thus reach a high efficiency.

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