Environment-friendly High Efficiency $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Solar Cells Fabricated by Green Antisolvent Method

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Research Article

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Abstract

Green antisolvents propyl acetate and isooctane can promote the nucleation of PbI_2 particles and provide the heterogeneous nucleation site of perovskite crystal, so as to promote the rapid growth of perovskite crystal. The films treated with propyl acetate and propylene glycol methyl ether have larger grains and lower root-mean-square value (RMS) than those treated with chlorobenzene. The full coverage perovskite films with uniform grain size which is closer to the exciton diffusion length of perovskite can be obtained. Compared with the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells treated with chlorobenzene (power conversion efficiency (PCE) is 17.86%), the best efficiency of the devices treated with propylene glycol methyl ether is 21.60%, which is improved by 21%, which has certain reference value and guiding significance for researchers to obtain environment-friendly high-quality perovskite solar cells in the future.

1. Introduction

Halogenated perovskite materials have excellent photoelectric properties, such as high extinction coefficient, long carrier diffusion length, high carrier mobility, high defect tolerance and controllable band gap, etc., which have attracted more and more attention of researchers all over the world. In the past ten years, the power conversion efficiency of the perovskite solar cells can be obtained from 3.8–25.5% [1–5]. Perovskite solar cells (PSCs) can be prepared by solution method, but it is inevitable that solution treated polycrystalline films tend to have high-density defect states and show a large degree of electronic disorder. It leads to carrier recombination and increase of interface resistance. Defects with transition energy levels in the band gap will attract more energy electrons / holes as non radiative recombination centers. The Fermi level is pinned near the defect state. Non radiative recombination is induced by charge recombination of these defect states, which constitutes a main energy loss mechanism. They will mean reducing the filling factor (FF) and open circuit voltage (V_{oc}) of the device. Theoretical modeling and experimental studies have shown that V_{oc} in photovoltaic devices is divided by the quasi Fermi energy levels of electrons and holes in the whole, and the disorder of band tail defects or trap states caused by energy extends to the forbidden band, introducing additional electronic states. Nonequilibrium photogenerated electrons tend to relax downward. For these trap states, this will lead to lower splitting of the quasi Fermi level and smaller open circuit voltage. Due to the insertion of MAI into PbI_2 lattice, the penetration of methylammonium halide becomes a serious problem, which will lead to incomplete conversion. Due to the formation of perovskite structure dense layer of PbI_2 , MAI diffusion and insertion into deeper PbI_2 layer are prevented. In addition, residual and uncontrolled PbI_2 have adverse effects on carrier separation and transport and subsequent equipment performance carrier, and reproducibility and stability cannot be guaranteed. In order to solve this problem, Seok's team used PbI_2 (DMSO) complex to increase the conversion process, leading to high-performance solar cells. Huang and his colleagues developed a thermally driven cell, using the interdiffusion method to generate a compact MAPbI_3 layer. Zhao and his colleagues added some Mai to PbI_2 precursors to produce adjustable volume expansion before Mai contact, so as to produce efficient and renewable solar cells. Improving the film quality of perovskite film (such as density, roughness and grain size) can effectively improve the energy conversion

efficiency of the device. Researchers have developed a series of methods to prepare high-quality perovskite films, such as one-step film forming method ^[6–10], two-step film forming method ^[11–15]. Among them, antisolvent method or antisolvent assisted crystallization (ASAC) is the most widely used method because of its low cost, simple process and good repeatability. ^[16–18] However, the antisolvent assisted crystallization method usually uses toxic solvents such as chlorobenzene, toluene, dichloromethane, etc. In general, researchers need to use glove boxes, fume hoods, gas masks and so on to isolate the damage from toxic solvents. If this method is applied to the large-area preparation of perovskite films or the production line, it will inevitably increase the possibility of exposing the experimenters to toxic atmosphere. Therefore, looking for new green solvents that can replace toxic solvents without (or as little as possible) environmental side effects has become the focus of attention. Green solvent generally refers to the unstable chemical properties of the solvent, which can be degraded by soil organisms or other substances, with short half-life and easy to decay into low toxic and non-toxic substances. In recent years, researchers have invested a lot of research work in the development of green solvent or solvent-free preparation process of perovskite films, and made a lot of meaningful research results.^[19] For example, Wang Shimin studied the effects of different antisolvents (toluene, chlorobenzene, ethyl acetate, diethyl ether and isopropanol) on the quality of perovskite films and the performance of solar cells. At last, they concluded that ethyl acetate with low toxicity was the most suitable antisolvent.^[20] Qin Yong systematically studied the influence of green solvent anisole and toxic solvent chlorobenzene on the absorbance and crystallinity of perovskite films. It was found that the roughness and crystallinity of the film were significantly improved by using anisole as the antisolvent, the PCE of perovskite solar cells prepared with anisole as antisolvent reached 19.42%.^[21, 22] Based on the above research, our group proposed to apply environmentally friendly solvent to regulate the process of perovskite crystallization in order to achieve high-quality perovskite films. We studied the effects of green organic solvents (such as propyl acetate and propylene glycol methyl ether) on the morphology and performance of perovskite solar cells. The results show that propyl acetate and propylene glycol methyl ether can promote the nucleation of PbI_2 particles and provide the heterogeneous nucleation site of perovskite crystal, the films treated with propyl acetate and propylene glycol methyl ether have larger grains and lower RMS than those treated with chlorobenzene. The dense and full coverage perovskite films with uniform grain size which is closer to the exciton diffusion length of perovskite can be obtained. Compared with the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells treated with chlorobenzene, the best efficiency of the devices treated with green antisolvent propylene glycol methyl ether is 21.60%, which has certain reference value and guiding significance for researchers to obtain environment-friendly high-quality perovskite solar cells in the future.

2. Results And Discussion

It is well known that chlorobenzene is widely used in the antisolvent method, and the perovskite films are of good quality. Therefore, we choose the perovskite film prepared by chlorobenzene as the control group. First, the precursor solution of perovskite was dropped on the fluoro doped tin oxide (FTO) glass substrate coated with a dense TiO_2 layer. The solution is then uniformly spread on the TiO_2 surface by

rotating at a fixed speed. In the process of spin coating, due to the slow volatilization of the solvent, the solute in the solvent will slowly separate out, and the color of the liquid film will gradually change from bright yellow to dark yellow. At the moment of transformation, chlorobenzene is added to the crystal rapidly and uniformly. As mentioned before, the use of antisolvent can make the solution supersaturated and affect the nucleation of solute and the growth rate of crystal, and then affect the crystallization kinetics of perovskite materials and the final morphology of the film. When chlorobenzene drops on the wet film, the film immediately changes from transparent bright yellow to light brown. From the side, the film is mirror like, after annealing, the film is black. Then spin coating spiro ometad solution, then static annealing in the glove box for 24 h, and finally evaporate the Ag electrode. After the device is fabricated, its photovoltaic performance is tested. The process and sample of preparing perovskite film by antisolvent are shown in Figure 1.

We systematically studied the effects of green organic solvents such as propyl acetate and propylene glycol methyl ether on the morphology control and performance of perovskite solar cells. The SEM of the perovskite films under different antisolvent conditions and the corresponding device parameters are measured in the experiment, as shown in Fig. 2 and table 1. It can be seen from Fig. 2 that when the perovskite precursor solution is spin coated and concentrated, anti solvent is dripped, which has different effects on the perovskite crystallization. The results show that the addition of antisolvent can promote the rapid crystallization of perovskite in different degree, so as to produce micron scale perovskite polycrystalline films. Fig.2 (a) data shows that the grain size of the film without any treatment is about 100nm~120nm, the uniformity is relatively poor and the surface roughness reaches 30nm. The series resistance of the corresponding device reaches $1000 \Omega \cdot \text{cm}^2$, and the parallel resistance is only $300 \Omega \cdot \text{cm}^2$, which is extremely unfavorable for the internal performance of the devices. Fig.2 (b) shows the film treated with chlorobenzene. The particle size is about 120nm~150nm, the uniformity is improved, and the surface roughness is 25nm. This shows that the addition of antisolvent can effectively improve the crystallization speed and quality of the film grain. Fig.2 (c) and (d) show that the high boiling point DMF and DMSO in the film can be extracted quickly after dropping ether and 2-methyl-1-propanol can complete the rapid crystallization of perovskite at room temperature, and the grain size has been greatly improved, which can reach 200nm~250nm, which will be conducive to the separation and transmission of electrons and holes, so as to reduce the probability of the combination of the two and improve the short-circuit current density; however, due to the poor uniformity of the film grain, this will objectively lead to the series resistance of the device or The larger one is more than $150 \Omega \cdot \text{cm}^2$. Fig. 2 (e) and (f) are perovskite films treated by propyl acetate and isooctane, respectively. It is found that the grain size of the film is about 330nm ~400nm, and the surface roughness is reduced to 12nm, showing a better the uniformity and roughness. The grain size and orientation growth of perovskite crystal are obviously improved. In particular, tetragonal phase is seen in Fig. 2 (e) and (f). We think that propyl acetate and isooctane have good solubility for methylamine salt in precursor, but poor solubility for PbI_2 . On the one hand, the antisolvent is conducive to the solubilization and transfer of methylamine salt particles, and promotes the mixing reaction between precursors. On the other hand, it can promote the nucleation of PbI_2 particles and provide the heterogeneous nucleation site of perovskite crystal, so as to promote the

rapid growth of perovskite crystal. Therefore, the films treated with propyl acetate and isooctane have larger grains, and lower RMS roughness than those treated with chlorobenzene. Larger grain size means less grain boundary and carrier recombination sites. In addition, lower roughness is conducive to the formation of better contact between perovskite film and electron transport layer and the formation of larger short-circuit current density. Both propyl acetate and isooctane have obtained a denser calcium titanium ore bed with full coverage. This will inevitably lead to less grain boundaries between the crystals, thus reducing the charge recombination, greatly reducing the series resistance of the device (only $50 \Omega \cdot \text{cm}^2$), while the parallel resistance reaches an amazing $3000 \Omega \cdot \text{cm}^2$, which means that a good ohmic contact and interface connection are formed inside the device.

Table 1: parameters of perovskite films and corresponding devices with different antisolvent

Antisolvent treated	Grain size /nm	Surface roughness /nm	Series resistance / $\Omega \cdot \text{cm}^2$	Parallel resistance / $\Omega \cdot \text{cm}^2$
propylene glycol methyl ether	389	12	50	3000
propyl acetate	236	20	150	1500
Chlorobenzene	203	23	300	1200
As cast	128	25	800	500

The absorption spectrum of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film when dropping different solutions of chlorobenzene and isooctane in the process of spin coating can be obtained, as shown in Figure 3(a). It can be seen that the absorption range of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film without any treatment is 500nm-800nm, the absorption strength is not large, and the grain size is basically below 130nm. We prepared $\text{CH}_3\text{NH}_3\text{PbI}_3$ film with chlorobenzene and found that absorptive strength has been improved in the range from 500nm to 800nm. When isooctane was used as extractant, the absorption strength of the film was increased by more than 55%. This is mainly because isooctane can regulate the grain size and orientation growth of $\text{CH}_3\text{NH}_3\text{PbI}_3$.The grain size reaches 320nm and the grain boundary is significantly passivated. Therefore, the intensity of absorption can be improved. In addition, the anti-solvent can penetrate into MA^+ , Pb^+ and I^- ion positions between perovskite molecules, regulate the narrowing of the band gap, and promote the red-shift of the absorption spectrum. We analyzed the XRD patterns of perovskite films treaded with chlorobenzene and isooctane, as shown in Figure 3(b). There are two small peaks at 11.8° and 12.9° for $\text{CH}_3\text{NH}_3\text{PbI}_3$, which are the inactive δ phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and the peak of the cubic PbI_2 phase. When we prepare $\text{CH}_3\text{NH}_3\text{PbI}_3$ film with isooctane, the peaks of yellow phase and PbI_2 completely disappear. The peaks of (100), (200), (210) and (220) will gradually increase, which fully shows that isooctane can promote the orientation growth of the film, inhibit the phase formation of δ phase and cubic crystal PbI_2 ,

and obtain more stable perovskite crystal. Furthermore, we extracted the grain size from XRD data by the Scherer equation. We can get more accurate grain size for perovskite films treated with different antisolvents. The result shows that the grain size of the film without any treatment is 105nm, and the particle size of the film treated with chlorobenzene increases to 128nm. Dropping ether and 2-methyl-1-propanol can complete the rapid crystallization of perovskite at room temperature, and the grain size has been greatly improved, which can reach 203nm and 236nm, respectively. It's even more obvious that this value has grown to 337nm and 389nm respectively after introducing propyl acetate and isooctane optimization. This fully shows that green antisolvent can effectively regulate the crystallization process of perovskite crystal and improve film quality.

In order to further clarify the influence of antisolvent on the photovoltaic performance of perovskite solar cells, we prepared perovskite solar cells with FTO/TiO₂/perovskite / spiro- oMeTAD / Ag. High quality and high efficiency devices were obtained by adding different antisolvent in the preparation process. The measured data are shown in Fig.4(a) and table 2 respectively. It is found that PCE of perovskite solar cells without any green antisolvent treatment is only 14.50%, in which the open circuit voltage V_{OC} is 1.10V, the short circuit current density J_{SC} is 18.85mA/cm² and the filling factor FF is 69%. After chlorobenzene treatment, the device efficiency has been improved to 15.60%, the main reason is that the micro morphology of perovskite film has been optimized, the grain size is larger, which makes the composite probability of hole and free electron decrease, resulting in the increase of short-circuit current density, reaching 20.26 mA/cm². Further analysis shows that when we add different green antisolvent in turn, the effect on device efficiency is more obvious. For example, when we use ether or 2-methyl-1-propanol as antisolvent, the crystalline particle size of perovskite film becomes large, reaching 350nm, which is more conducive to the dissociation and diffusion of holes and free electrons, so that the combination is reduced. The surface roughness is reduced to about 20 nm, The short-circuit current density J_{SC} is increased to 25.10 mA/ cm², the filling factor FF is increased to 72%, and the device efficiency after 2-methyl-1-propanol treatment is up to 20.05%. Compared with the untreated perovskite solar cells, the energy conversion efficiency is improved by nearly 38%. Moreover, when propyl acetate and isooctane are added to the crystallization process of perovskite film, the effect is more obvious. The antisolvent control of isooctane has achieved a dense and fully covered calcium titanium oxide layer with uniform grain size, which is closer to the exciton diffusion length of perovskite, basically maintained at about 300nm, and the surface of the film is smoother, only 12nm. These parameters show that there are less grain boundaries between the crystals, and the probability of charge recombination is greatly reduced. The series resistance of the devices treated with isooctane is only 50 $\Omega \cdot \text{cm}^2$, while the parallel resistance is as high as 3000 $\Omega \cdot \text{cm}^2$, which means that a good ohmic contact and interface connection are formed inside the devices, which makes the short-circuit current density J_{SC} increase to 25.80 mA/cm², the filling factor FF increased to 75%, and the optimal device efficiency increased to 21.60%. Furthermore, we found that the J-V curve obtained were basically consistent when using forward and reverse scanning to test the device efficiency, this may be due to the use of antisolvent green leads to the large perovskite grains and

high quality perovskite thin film, so as to effectively eliminate the ion migration at the interface and the non-radiative recombination, cause the hysteresis phenomenon is not obvious, as shown in Fig4 (b).

Table 2: photovoltaic performance parameters of perovskite devices prepared by adding different antisolvent

Antisolvent treatment	V_{oc} (V)	J_{sc} (mA/cm ²)	FF(%)	PCE(%)
propylene glycol methyl ether	1.12	25.80	75	21.60
propyl acetate	1.12	25.10	72	20.05
Chlorobenzene	1.11	23.12	70	17.86
As cast	1.11	20.26	70	15.60

3. Conclusion

The results show that propyl acetate and isooctane can promote the nucleation of PbI_2 particles and provide the heterogeneous nucleation site of perovskite crystal, so as to promote the rapid growth of perovskite crystal. Therefore, the films treated with propyl acetate and isooctane have larger grains and lower RMS roughness than those treated with chlorobenzene. Compared with the $CH_3NH_3PbI_3$ perovskite solar cells treated with chlorobenzene (power conversion efficiency is 17.86%), the best efficiency of the devices treated with green antisolvent isooctane is 21.60%, which is improved by 21%.

4. Experimental Section

4.1. Chemicals and materials

N, N-dimethyl formamide (DMF, 99.9%), Dimethyl sulfoxide (DMSO, 99.9%), Chlorobenzene (99.9%), Propyl acetate (99.8%), and Propylene glycol methyl ether (99.8%) were purchased from Alfa Aesar. PbI_2 and MAI were purchased from Sigma-Aldrich. Spiro-OMeTAD was purchased from Alfa Aesar. Silver wire was purchased from Beijing new material technology co., LTD.

4.2. Device fabrication

Firstly, Fluorinated tin oxide (FTO) substrate was placed vertically in the polytetrafluoroethylene cleaning rack, and use acetone, ethanol and deionized water for ultrasonic cleaning for 30 minutes in turn. Then the surface of FTO is treated in the oxygen plasma cleaning machine together with the culture dish for 15 min and is immediately poured into the $TiCl_4$ aqueous solution (0.2M/mL). The aqueous solution of $TiCl_4$ is prepared by adding liquid $TiCl_4$ to the frozen deionized water drop by drop. After that, the FTO immersed in $TiCl_4$ solution and the culture dish were sealed with fresh-keeping film, then covered and placed in an oven at 70°C for 1h. After the reaction, a large amount of deionization is used to wash until

the solution is clear, and then the FTO substrate with TiO_2 is blown dry with a nitrogen gas gun and is annealed on a 150 °C hot bench for 15 min. Therefore, equal mass ratio of MAI and PbI_2 was dissolved in dimethyl formamide (DMF) and dimethylsulfoxide (DMSO) mixed solvent (volume ratio of 4:6), and the mass concentration of MAPbI_3 was 1.2 M/mL. Dropping 100 μL of perovskite precursor solution on the surface of titanium oxide, spin coating at 1000 rpm for 10 s, then spin coating at 4000 rpm for 40 s, and dropping 150 μL chlorobenzene, propyl acetate and propylene glycol methyl ether, respectively, and transferred to 110 °C hot stage for annealing for 15 min. Next, dissolving 90 mg Spiro-OMeTAD in 1 mL of chlorobenzene, add 45 μL of Li TFSI acetonitrile solution with a concentration of 170 mg/mL, 75 μL of Kf209 acetonitrile solution with a concentration of 300 mg/mL and 10 μL of TBP, respectively. Spiro-OMeTAD layer was obtained by spin coating on the surface of perovskite film at 4000 rpm for 20 s. At last, we vacuumize to $5 \times 10^{-4} \text{ Pa}$ and control the evaporation speed within $1 \text{ \AA/s}$, and prepare the 80 nm Ag electrode by vacuum evaporation.

4.3. Characterization of perovskite solar cells

The morphology of perovskite films was observed by scanning electron microscopy (SEM, Nova Nano SEM 450, FEI, USA). The UV visible spectrometer (uv-3600, Shimadzu, Japan) was used to test the absorption of perovskite films. Electrochemical impedance spectroscopy (EIS) measurements were conducted using Zahner Zennium electro chemical workstation in a frequency range from 0.01 Hz to 1.5 MHz. X-ray diffraction (XRD) patterns of perovskite films were recorded by Rigaku D/MAX-2400 diffractometer. The J-V curves measurements of the devices were conducted by a Keithley 2611 source-measure unit and a PVIV-201 VI-V Station (Newport Oriel). Its illumination source was calibrated by using a Si reference cell system (91150 V, Newport). The average power of a solar simulator was 100 mW/cm^2 . All the J-V curves were obtained at a scanning speed of 200 mV/s from 1.2 V to -0.1 V and from -0.1 V to 1.2 V, respectively.

Declarations

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Figures

Figure 1

The processing of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film by antisolvent

Figure 2

SEM of perovskite film with different antisolvent: (a) without antisolvent; (b) chlorobenzene; (c) propyl acetate; (d) propylene glycol methyl ether

Figure 3

Absorption spectrum(a) and XRD patterns(b) of CH₃NH₃PbI₃ perovskite films with different antisolvent

Figure 4

Photovoltaic performance (a) of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells prepared by adding different antisolvent, and hysteresis characteristic (b) based on perovskite solar cell treated with isooctane.