Anti-solvent Engineering for Efficient Perovskite Solar Cell Using PVK as Hole-Transporting Layer

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Abstract. Perovskite solar cells were studied using PVK as hole-transporting layer and different anti-solvent process. We have fabricated CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) photoactive layer using chlorobenzene (CB) solution and PVK in CB solution as the anti-solvent solution, respectively. The results show that the power conversion efficiency is enhanced to 14.7% by using 2.5 mg/mL PVK in CB solution as the anti-solvent, which is significantly improved compared with 12.85% for the device treated using CB. PVK in CB as the anti-solvent solution facilitates the hole transport for MAPbI$_3$/PVK heterojunction as well as good crystallinity and less PbI$_2$ residues in MAPbI$_3$ photoactive layer.

1. Introduction
Semicontacting hybrid organic/inorganic perovskite solar cells (PSCs) have been rapidly developed in past few years due to their excellent performance [1-7]. The power conversion efficiency (PCE) of PSC is reported over 23% as stated by Jeon et al. using a new fluorene-terminated hole-transporting material DM [7]. For PSC, electron-transporting layer (ETL) plays significant roles in transporting electron and blocking hole, as well as hole-transporting layer (HTL) plays significant roles in transporting hole and blocking electron. Most highly efficient PSCs utilize a n-type layer of mesoporous TiO$_2$ and a layer of 2,2’,7,7’-tetrakis-(N,N-di-p-methoxyphenylamine)9,9’-spirobifluorene (spiro-OMeTAD) in CH$_3$NH$_3$PbI$_3$ (=MAPbI$_3$) or CH$_3$NH$_3$PbI$_3$-Cl$_x$ based n-i-p device configuration [8-12]. Lee et al. developed PSCs using spiro-OMeTAD as HTL with a maximum full sun PCE of 8% [8]. Kim et al. demonstrated a PCE of nearly 10% employing MAPbI$_3$ nanoparticles and spiro-OMeTAD as HTL [9]. However, spiro-OMeTAD is reported bad for device stability [12]. Many researches work on developing thermally stable and high-performance alternative HTLs. For example, Seok et al. used poly-[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA) as HTL and a PCE of over 20% has been produced holding the record for the highest PCE reported in 2015 [13].

Conjugated polymer poly(9-vinylcarbazole) (PVK) is an efficient hole-transporting material in organic photoelectronics and can be easily deposited [14-17]. On the other hand, recently researchers employed anti-solvent approach for high efficient PSCs utilizing a few drops of nonpolar solvent during spin coating. This approach makes the precipitation process uniform across the whole surface, giving rise to a smooth crystalline film with large grains [18-20]. Based on these considerations, we have developed a simple way for high efficient PSCs using PVK as HTL and controlling anti-solvent engineering in this work. Under the optimal condition, the PSC device displays a PCE of 14.7%.

2. Material and Methods
FTO glasses (20×20mm$^2$) were sequentially cleaned with standard procedure, and dried in N$_2$.

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atmosphere. Then, a 500°C spray pyrolysis method was employed to deposit TiO$_2$ compact layer (c-TiO$_2$). The mesoporous TiO$_2$ (m-TiO$_2$) layer was spin-coated on the top of the c-TiO$_2$ layer. PbI$_2$ (650 mg/mL) and MAI (220 mg/mL) were dissolved in dimethyl sulfoxide (DMSO) and N,N-Dimethylformamide (DMF) (1:9), and the mixed solution was spin-coated at 4000rpm for 30s to deposit the perovskite absorber layer. As anti-solvent engineering, 70μl of CB solution or PVK in CB solution with different concentration were cast on the top of MAPbI$_3$ layer at 4000 rpm for the last 24s without stop during spin-coating, respectively. The substrates were dried at 65°C for 3 min and then dried at 100°C for 5 min to form the MAPbI$_3$ film. For the sample with CB as the anti-solvent, PVK was dissolved in CB to prepare 2.5mg/mL solution. The mixed solution was spin-coated at 4000 rpm for 24s and annealed at 100°C for 10 min to fabricate the HTL film on the top of the MAPbI$_3$ absorber layer. Finally, a 120 nm Au metal electrode was deposited by thermal evaporation method. Figure 1 presents the schematic of detailed fabrication steps of the perovskite device with a structure of FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$/PVK/Au.

3. Result and Discussion

To explain the effect of the anti-solvent engineering on the characteristic of the perovskite absorber layer, we conducted UV-vis absorption spectroscopy, XRD patterns and PL spectra measurement of perovskite layer with a structure of FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$ using CB solution and 2.5 mg/mL PVK in CB as the anti-solvents, respectively. Figure 2a shows the absorption curves with different anti-solvent. Both absorption curves exhibit broad band absorption characteristics from visible to NIR wavelength region. Compared to that of the perovskite layer treated with CB anti-solvent, the absorbance of the perovskite layer treated with PVK in CB as anti-solvent with a concentration of 25 mg/mL increases at 300-470 nm, which is due to the absorption of PVK. This phenomenon indicates that PVK in CB anti-solvent has negligible effects on the absorption of MAPbI$_3$ thin film in the range of visible light.

XRD measurement is conducted to elucidate the effect of various anti-solvents on the lattice structure of MAPbI$_3$ thin films. As shown in figure 2b, XRD patterns of MAPbI$_3$ thin film with CB anti-solvent reveal a nearly identical crystalline structure as reported in the previous literature [4]. It can be seen that the intensity of the (220) peak at 28.71 and the (310) peak at 32.01 decreased a little for the MAPbI$_3$ thin film with PVK in CB as the anti-solvent. This shows that the crystal grains in perovskite film with PVK in CB anti-solvent have oriented grains and that the orientation intensities change a little which may be caused by the formation of grain boundaries or vacancies which origin from the partly extruded and segregated of the amorphous PVK during the MAPbI$_3$ formation.
procedure [21]. It should be noted that there was no peak pertain to MAI and PbI$_2$, that is to say, MAI and PbI$_2$ were almost completely converted into MAPbI$_3$.

Figure 2. UV-vis absorption spectra (a), XRD patterns (b), and PL spectra (c) of the cells with a structure of FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$ with different anti-solvents.

Figure 2c emerges the photoluminescence spectra measured for FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$ with different anti-solvents. It was worth noting that the PL intensity of MAPbI$_3$ with PVK in CB anti-solvent was much weaker than that treated with CB at an excitation wavelength of 526 nm, although both films exhibited strong PL peak at about 750 nm. These results demonstrated that PL quenching was occurring in the MAPbI$_3$/PVK heterojunction due to the efficient charge transfer from MAPbI$_3$ to PVK [22].

Figure 3. (a) J-V curves for the perovskite solar cells with different anti-solvents; (b) the schematic charge transporting at heterojunction of the perovskite and PVK with deep penetration.

Figure 4. PCE as a function of time for the perovskite solar cell using PVK in CB anti-solvent with a concentration of 2.5mg/mL without encapsulation.
In summary, we demonstrated the perovskite photovoltaic devices using PVK as HTL. We concluded that PVK in CB solution, the heterojunction of the perovskite and PVK is also formed which will facilitate hole transporting in all device resulting a higher performance. The concentration of PVK has a dramatic influence on the device performance and the optimized concentration of PVK is 2.5 mg/mL. The optimal device with a concentration of 2.5 mg/mL has an excellent $J_{sc}$ reached 22.76 mA/cm$^2$ which is larger than that of the devices with other concentrations. The results show that the device fabricated with 2.5 mg/mL PVK in CB solution has a highest PCE of 14.7% which is enhanced compared with 12.85% of the device with CB anti-solvent, which may be due to enhanced photogenerated carriers transporting by the formation of heterojunction between the perovskite and PVK in perovskite bulk. Figure 3b shows the schematic charge transporting at heterojunction of the perovskite and PVK. With the anti-solvent of PVK in CB solution, the heterojunction of the perovskite and PVK is formed penetrating deeply in perovskite bulk and it will facilitate hole transporting in all device resulting a higher $J_{sc}$. With the anti-solvent of CB solution, the heterojunction of the perovskite and PVK is also formed when spin coating PVK after the perovskite absorb layer. However, the depth of penetration of heterojunction may not be enough and impede the hole transporting from the perovskite into PVK HTL layer.

Figure 4 depicts the stability of the optimal perovskite solar cell with PVK in CB as anti-solvent without encapsulation. PCE of the device decreases to 13.3% from 14.7% after 168 h with a droop rate of 9.5%, which may be caused by the high hydrophobicity of PVK. From above evaluation, it is concluded that PVK in CB solution as anti-solvent effectively increases performance of the n-i-p perovskite photovoltaic devices using PVK as HTL.

4. Conclusions
In summary, we demonstrated the function of anti-solvent engineering in n-i-p PSCs with PVK as HTL. A PCE of 14.7% has been achieved using PVK in CB as anti-solvent with a concentration of 2.5 mg/mL. Finally we researched the stability of the optimal PSC and confirmed that the HTL solution can be ideal anti-solvent candidate to fabrication n-i-p perovskite photovoltaic devices.

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