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CuI/Spiro-OMeTAD Double-Layer Hole Transport Layer to Improve Photovoltaic Performance of Perovskite Solar Cells

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Abstract: The hole transport layer (HTL) is one of the main factors affecting the efficiency and stability of perovskite solar cells (PSCs). However, obtaining HTLs with the desired properties through current preparation techniques remains a challenge. In the present study, we propose a new method which can be used to achieve a double-layer HTL, by inserting a CuI layer between the perovskite layer and Spiro-OMeTAD layer via a solution spin coating process. The CuI layer deposited on the surface of the perovskite film directly covers the rough perovskite surface, covering the surface defects of the perovskite, while a layer of CuI film avoids the defects caused by Spiro-OMeTAD pinholes. The double-layer HTLs improve roughness and reduce charge recombination of the Spiro-OMeTAD layer, thereby resulting in superior hole extraction capabilities and faster hole mobility. The CuI/Spiro-OMeTAD double-layer HTLs-based devices were prepared in N₂ gloveboxes and obtained an optimized PCE (photoelectric conversion efficiency) of 17.44%. Furthermore, their stability was improved due to the barrier effect of the inorganic CuI layer on the entry of air and moisture into the perovskite layer. The results demonstrate that another deposited CuI film is a promising method for realizing high-performance and air-stable PSCs.

Keywords: hole transport layer; CuI/Spiro-OMeTAD; perovskite solar cells



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1. Introduction

Perovskite, an organic–inorganic metal halide, which acts as a light absorber for solid film solar cells, has attracted extensive attention lately as a result of its excellent photoelectric properties, such as direct band gap, low exciton binding energy, wide light absorption spectrum range, long electron/hole diffusion length and high absorption [1–6]. In just a few years, perovskite solar cell efficiency reached 25.5% [7,8]. In the process of fabricating PSCs, we use upright structure or inverted structure. The upright structure is deposited perovskite films on electronic transport materials (ETMs) on FTO substrates, while the inverted structure is composed of perovskite films deposited on HTM on FTO substrates [9,10]. In many related research studies, organic hole transport layers, including Spiro-OMeTAD, are the most commonly used in NIP structures [11–14]. Though Spiro-OMeTAD is the most popular, the Li-TFSI in acetonitrile corrodes perovskite film, resulting in a rough Spiro-OMeTAD film, and a large number of pinholes appear; through these pinholes the perovskite film contacts water and oxygen in the air directly [15].

In recent years, CuI, CuO, CuCrO₂, NiOx, Cu₂O and CuSCN have been used as hole transporting layers to improve device stability [16–23]. Vahid et al. introduced a new method of depositing CuI, using a CuI/Cu structure as a hole transport and buffer layer at the same time, to achieve a PCE of 9.24% [24]. Hong et al. inserted a p-type cesium (CS: NiOx) layer, which yielded an optimum efficiency of 19.24% [19]. Shao et al. improved the PCE to 16.47%, by coating NiOx nanoparticles on the surface of organic–inorganic hybrid perovskite solar cells without using any other post-treatment [25]. Chen et al. obtained

19.0% high steady state PCE of perovskite solar cells by low-temperature CuCrO nanocrystals as HTL [26]. The CuI Island modified TiO₂ ETL in planar PSCs prepared by Park et al. obtained high efficiency, with the PCE of the planar PSCs reaching 19.0% [27]. Therefore, it can be concluded that CuI is a cheap, promising material. Yu et al. added CuSCN to CuI HTL, and the perovskite PCE was shown to reach 18.76%, which is higher than that of pure CuI (14.53%) and CuSCN (16.66%)-based perovskite solar cells [28]. Copper salt has good electrical conductivity, can be dissolved in solution, and has good stability. Doping is for the sake of combining Spiro levels with CuI stability. Inorganic salts prevent perovskite film decomposition to a certain extent. Zhang et al. prepared Spiro-OMeTAD doped with CuI (20% mol ratio), and it was shown that CuI could effectively oxidize Spiro-OMeTAD and obtain the best PCE of 12.8% [29]. However, the efficiency based on copper iodide is relatively low. In addition, experience has shown that the Spiro-OMeTAD layer contains many holes derived from lithium bis(trifluoromethanesulfonyl)imines (LiTFSI) dopants, and these pinholes are found between the perovskite layer and the air or electrode, thereby leading to a poor stability or efficiency. Few researchers inserted the CuI into the absorption layer and the transport layer as a buffer layer by solution spin coating, which is convenient and cost-effective. CuI is not.

Perovskite coating technology includes magnetron sputtering technology, ion diffusion, evaporation in specific environments, plasma enhanced atomic layer deposition (PEALD), high temperature coating and precursor spin coating technology. In view of the characteristics of perovskite thin film materials, in most cases, researchers use precursor technology and co-evaporation technology due to the fact that the cost of coating technology is relatively low compared with co-evaporation technology, and the precursor spin coating technology has the lowest cost, is easy to control, and the required environment and equipment are relatively simple. Most importantly, the control of the amount of solvent in the solution is relatively simple. Therefore, we chose solvent spin coating technology.

In this study, we applied CuI solution by dissolving copper iodide in 1:39 di-n-propyl to chlorobenzene. CuI has long been used as a hole transport layer because of its appropriate energy level, which is very suitable for perovskite solar cells. Additionally, we deposited the CuI next to the perovskite layer, on account of the Spiro-OMeTAD-layer, which does not require annealing. In order to resolve the existing pinholes, we considered the two CuI and Spiro-OMeTAD materials together, and prepared CuI/Spiro-OMeTAD-based double hole transporting layers. We successively spun CuI on perovskite and Spiro-OMeTAD on CuI, to form a double hole transport layer-based device. We demonstrated that the CuI layer was able to stop perovskite corrosion caused by acetonitrile from Spiro-OMeTAD solution. Therefore, it can improve efficiency to some extent. In addition, more matching of energy levels is conducive to hole extraction, which results in a better VOC (voltage of open circuit) and FF (fill factor). Finally, we achieved a 17.44% PCE for double HTLs based devices, and the VOC was 1.10 V, which was 0.05 V higher than a single Spiro-OMeTAD HTL based device. The stability of perovskite solar cells was thus further improved.

2. Materials and Methods

2.1. Cleaning Glass

First, we dealt the FTO (fluorine-doped tin oxide) (150 nm) substrate with detergent. Next it was washed with deionized water, followed by ultrasonic cleaning. We ultrasonic cleaned the FTO glass with absolute ethyl alcohol, isopropanol and acetone for 30 min, respectively. Lastly, we took out the FTO glass from the acetone and blow-dried it with N₂, then placed it in an ozone processor for 30 min ozone treatment.

2.2. Preparation of the HTL Solution

72.3 mg of Spiro-OMeTAD, Li-TFSI (bistrifluoromethanesulfonimide lithium salt) solution, and 28.8 µL tBP mixed in 1 mL of chlorobenzene. Deposited at 4000 rpm for 30 s.

2.3. Preparation of the Perovskite Precursor Solution

1.1 M FAI (formamidinium iodide), 1.1 M PbI_2 , 0.2 M MABr (methylazanium bromide) and 0.22 M PbBr_2 and 1 ml DMF:DMSO (4:1). Lastly, 52.6 mL CsI.

2.4. Fabrication

SnO_2 was deposited on the FTO. SnO_2 electron transport compact layer was deposited on FTO coated glass substrate by a two-step spin-coating process, first at the spin speed of 1500 rpm for 30 s, leading further to 2500 rpm for next 30 s for compact layer. The SnO_2 film was finally annealed at 150 °C in air for 1 h. The Cs/MA/FA perovskite solution was spin-coated onto the SnO_2 layer at 1000 rpm for 10 s, then at 3000 rpm for 20 s, and a chlorobenzene (CB) antisolvent was used in the last 10s to obtain a perovskite/ SnO_2 /FTO substrate. These substrates were then heated to 100 °C for 60 min. Next, the hole transport layer Spiro-OMeTAD or CuI/spiro-OMeTAD was deposited on top of the Cs/MA/FA perovskite layer at 4000 rpm for 30 s. For CuI/Spiro-OMeTAD double hole transport layers, the perovskite film was first coated with CuI solution at 4000 rpm for 30 s, then annealed at 130 °C for 20 min and cooled. The CuI surface was then coated with a spiro-Meotad solution at 4000 rpm for 30 s. It was put in a drying oven for 12 h. Finally, the gold electrode was evaporated by hot evaporation.

2.5. Characterizations

The SEM images were observed by the FEI NOVA NANOSEM 450 cold field scanning electron microscope (FEI Company, Hillsboro, TX, USA). The atom force microscopy (AFM) (Thermomicroscopes, Sunnyvale, CA, USA) analysis of the Cs/MA/FA films, Cs/MA/FA/Spiro-MeOTAD films and Cs/MA/FA/CuI/Spiro-MeOTAD films were obtained on a Dimension Icon. The roughness value, and images processing were taken on a NanoScope (Nanoscope V, Veeco) while the J-V plots of Cs/MA/FA/spiro-MeOTAD and Cs/MA/FA/CuI/Spiro-MeOTAD devices were characterized by Keithley 2400 Source in dark conditions, measured by an Agilent B1500A Semiconductor (Abet Technologies, Milford, MA, USA). The PL spectra were recorded by an Edinburgh Instrument FLS920 (PICOQUANT, Berlin, Germany). The TRPL spectra were measured by an Edinburgh Instrument FLS920 (PICOQUANT, Berlin, Germany). The space-charge limited current (SCLC) and EIS were obtained using a multi-channel potentiostat (Biologic, Paris, France).

3. Results and Discussion

We referred to the NIP structure planar PSCs (Figure 1a) based on $\text{Cs}_{0.05}(\text{FA}_{0.87}\text{MA}_{0.13})_{0.95}\text{PbI}_{2.55}\text{Br}_{0.45}$ as the photoactive layer, wherein Spiro-OMeTAD and SnO_2 were spun as the HTL and ETL [30]. The CuI film was deposited on perovskite by spin coating, and then annealed. Then we spun Spiro-OMeTAD solution and oxidized it naturally in dry air. The cross-section of the perovskite sample can be seen in Figure 1a, which corresponds to the structural diagram of the device. From the figure, we observed that there were obvious boundaries between the different layers. Figure 1b shows the location of the conduction band and the valence band of each layer of the device. For example, the HOMOs of CuI and Spiro-OMeTAD are 5.2 and 5.11 eV, respectively [31], and the $\text{Cs}_{0.05}(\text{FA}_{0.87}\text{MA}_{0.13})_{0.95}\text{PbI}_{2.55}\text{Br}_{0.45}$ is 5.44 eV [32]. The insertion of the CuI buffer layer effectively reduced the energy level mismatching between the transport layer and absorption layer. This method effectively reduced the loss of voltage [33].

AFM was applied to compare the surface morphology of the Spiro-OMeTAD and CuI/Spiro-OMeTAD bilayers (Figure 2a–f) on perovskite films, respectively. Perovskite films were spun on SnO_2 to form a rough film (Figure 2a,d), and CuI was spun on the perovskite layer (Figure 2b,e). Evaporation and chemical methods were not adopted to obtain CuI layers. We did not adopt evaporation and chemical methods to obtain the CuI layer, mainly due to the fact that spin coating will result in a smooth and dense film [29]. We manufactured several devices to compare how the CuI film optimized the Spiro-OMeTAD-based devices, SnO_2 /perovskite, SnO_2 /perovskite/Spiro-OMeTAD and

SnO₂/perovskite/CuI/Spiro-OMeTAD. Figure 1c,f represent the fact that the CuI film is conducive to the Spiro-OMeTAD growing film, and CuI film can fill the pinholes on Spiro-OMeTAD films.

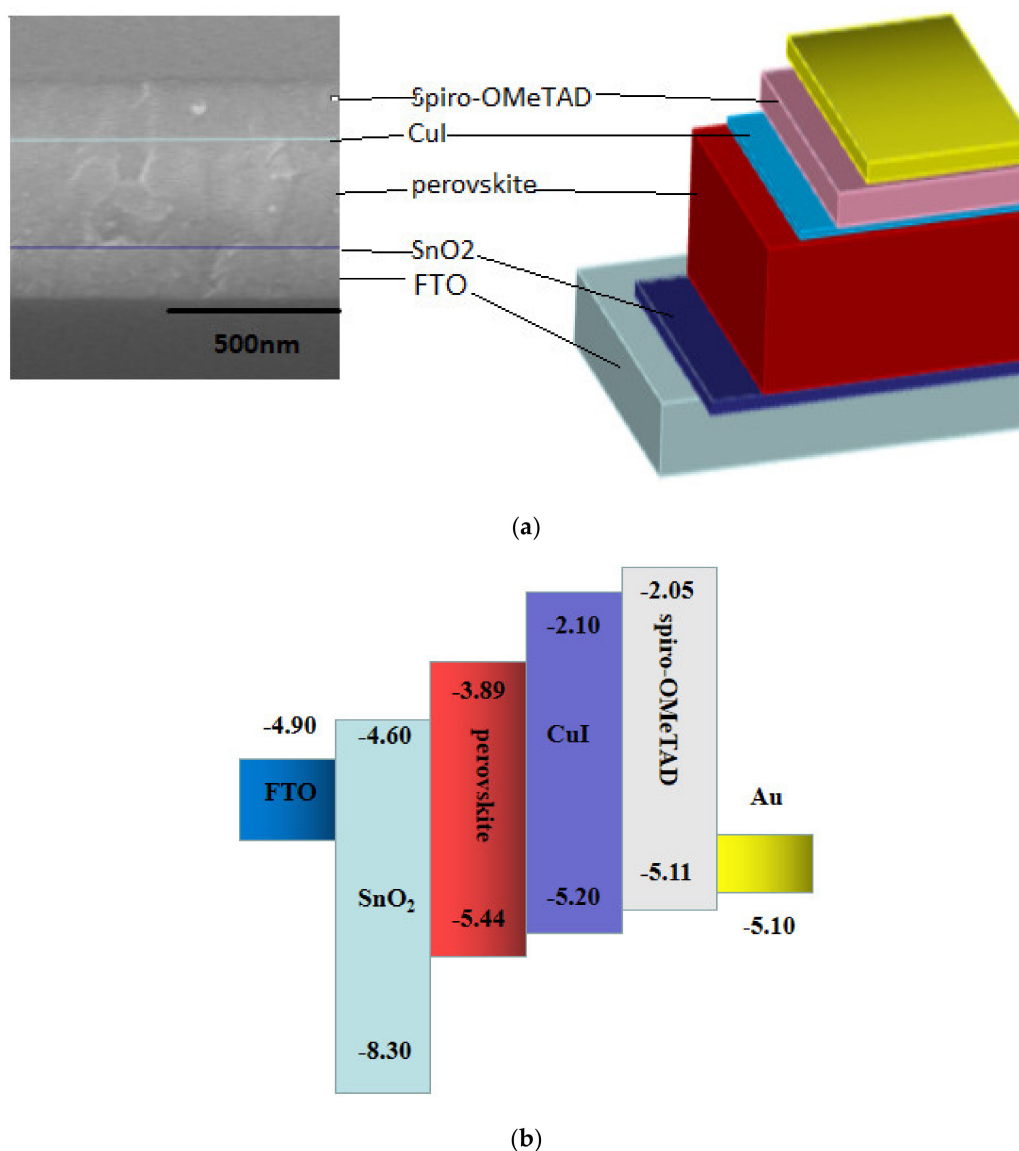


Figure 1. (a) Cross-sectional SEM image and structure of inorganic–organic double hole transporting layer device; (b) device energy level diagrams.

According to the research of Park et al., the Spiro-OMeTAD layer contains numerous of pinholes which lead to a high leakage current and serious electron-hole recombination [14]. The inserted buffer layer CuI can prevent the acetonitrile in Spiro-OMeTAD from corroding the perovskite film, and the pinholes in the Spiro-OMeTAD film are filled. At the same time, the passivation layer can reduce the boundary trap density.

XRD patterns on different substrates of CuI were measured as seen in Figure 3. By testing the XRD of FTO conductive substrate and FTO conductive substrate covering CuI film, and then subtracting the two XRD images, the obtained XRD image is CuI's XRD on the FTO conductive substrate. Similarly, the XRD of CuI on perovskite surface can be obtained. XRD results show that CuI is located on the surface of FTO and FTO/perovskite, respectively. From the XRD pattern of CuI, it can be seen that the (111) peak phase of the annealed CuI crystal based on FTO and FTO/perovskite surface is the same, indicating

that the crystal obtained after annealing before and after spin coating on perovskite surface is the desired structure, and has not been oxidized or decomposed. The only difference is that the (111) peak on the surface of FTO/perovskite is sharper, which indicates that the CuI crystal on the surface of perovskite has a better crystal phase.

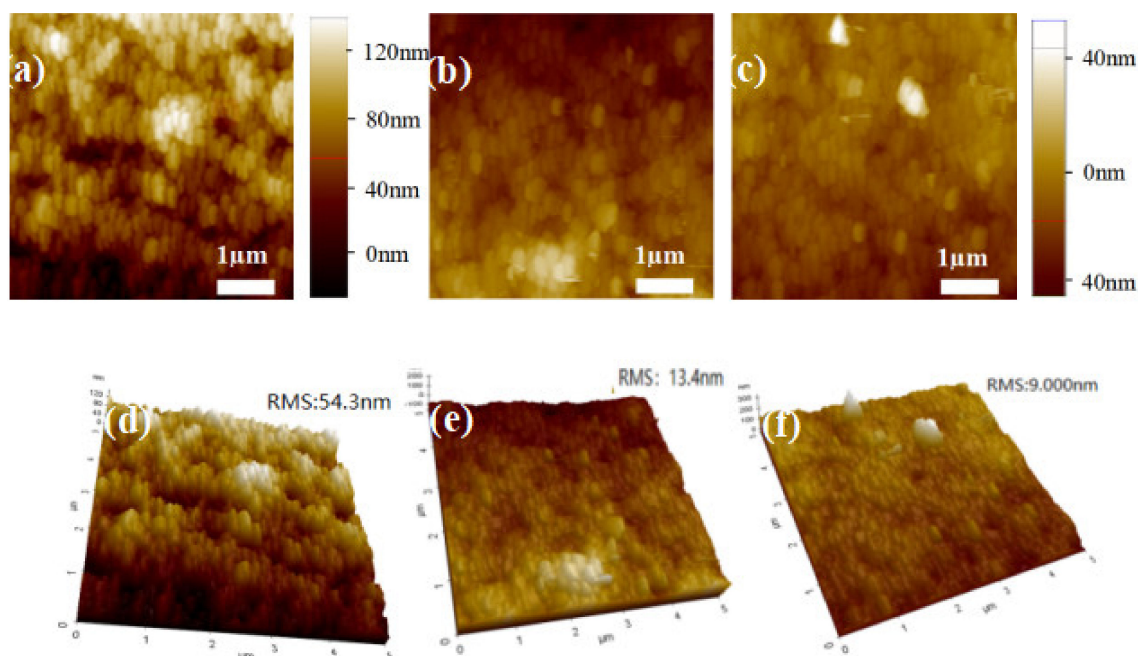


Figure 2. (a,d) AFM of the perovskite films on SnO₂ compact layer; (b,e) AFM images of CuI on perovskite; (c,f) AFM images of Spiro-OMeTAD on the CuI layer.

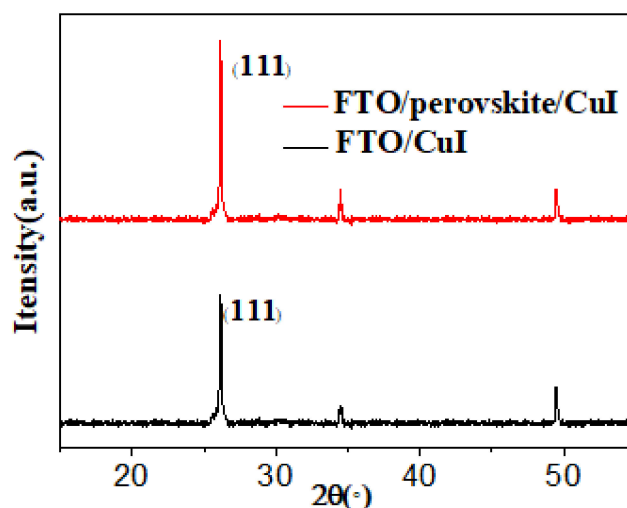


Figure 3. XRD of CuI located on the surface of FTO and FTO/perovskite.

Figure 4 shows the XPS of CuI measured on the surface of perovskite crystal to prove a peak spectrum of Cu 2p of Cu⁺ in CuI. The figure shows the FTO/CuI spectrum. That is to say, after dissolving CuI powder, it was spin coated on the surface of perovskite and then annealed and crystallized to obtain non-oxidized Cu⁺. This is consistent with the (111) phase of CuI crystal measured by XRD. CuI composition did not change before and after treatment. Tzung Fang Guo et al. improved the photoelectric characteristics of perovskite photovoltaic devices by doping CuI in the perovskite absorption layer. CuI does not exchange molecules with perovskite, but only distributes in the perovskite grain

boundary to passivate defects [34]. The crystal plays a positive role in hole transport and electron blocking of perovskite photovoltaic devices.

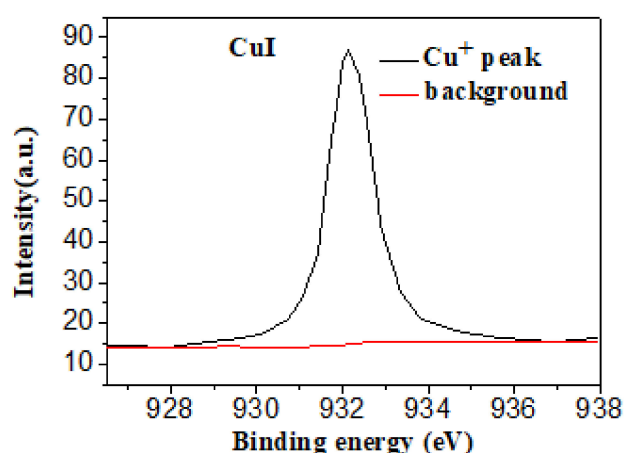


Figure 4. XPS of CuI located on the surface FTO/perovskite.

The compact CuI layer is not only used for transmission, but also used to protect the absorption layer to improve the efficiency of the solar cells. The photocurrent voltage (J-V) curves of champion devices were prepared in N₂ gloveboxes with different thicknesses of CuI, which are compared in Figure 5. The V_{OC}, J_{SC} (short-circuit current), FF and PCE are measured according to the statistical data of 50 independent devices. The results are summarized in Table 1. The different spin coating speed of CuI of organic–inorganic double-layer CuI/Spiro-OMeTAD exhibited an effect on the device efficiency. Based on the single Spiro-OMeTAD HTLs material, the champion device V_{OC} was 1.05 V, J_{SC} was 20.05 mA/cm², FF was 71.99%, and the best PCE was 15.16%. For the devices based on double HTLs, when the CuI solution was 20 mg/mL and spin coating at 4000 r/min, in the optimal data, the best PCE was 17.44%, J_{SC} was 20.10 mA/cm², V_{OC} was 1.10 V and FF was 78.88%, as shown in Figure 5a. Therefore, we used a CuI solution at 4000 r/min spin speed deposited the HTL additive layer. In the following section, we compare the performance of the double-layer hole transport solar cells with that of the single-layer solar cells, based on the device with a spin speed of 4000 r/min.

Table 1. Optimal parameters of CuI/Spiro-OMeTAD devices depending on different rotations of CuI solution.

Devices	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	η (%)
Pristine	1.05	20.05	71.99	15.16
2000 r/min	1.08	20.08	75.49	16.37
4000 r/min	1.10	20.10	78.88	17.44
6000 r/min	1.08	20.06	76.00	16.47

The EQE spectra in Figure 5b were obtained for several PSC devices. The J_{SC} value obtained from the EQE spectral integration was a little smaller than the value obtained from the J-V curve as shown in Figure 5a, and the two values could match well. If the J_{SC} values are different in EQE and the J-V curves do not match well, it can prove that the light response of the solar cells is not very good; the hysteresis is obvious. The enhancement of champion device performance was further confirmed with the EQE spectrum. The integrated J_{SC} calculated from the EQE spectrum of the champion device was 20.00 mA/cm², which is in good agreement with the measured (mA/cm²). More interestingly, the champion cell exhibited a panchromatic plateau of higher average value in the highest part of the 250–800 nm range.

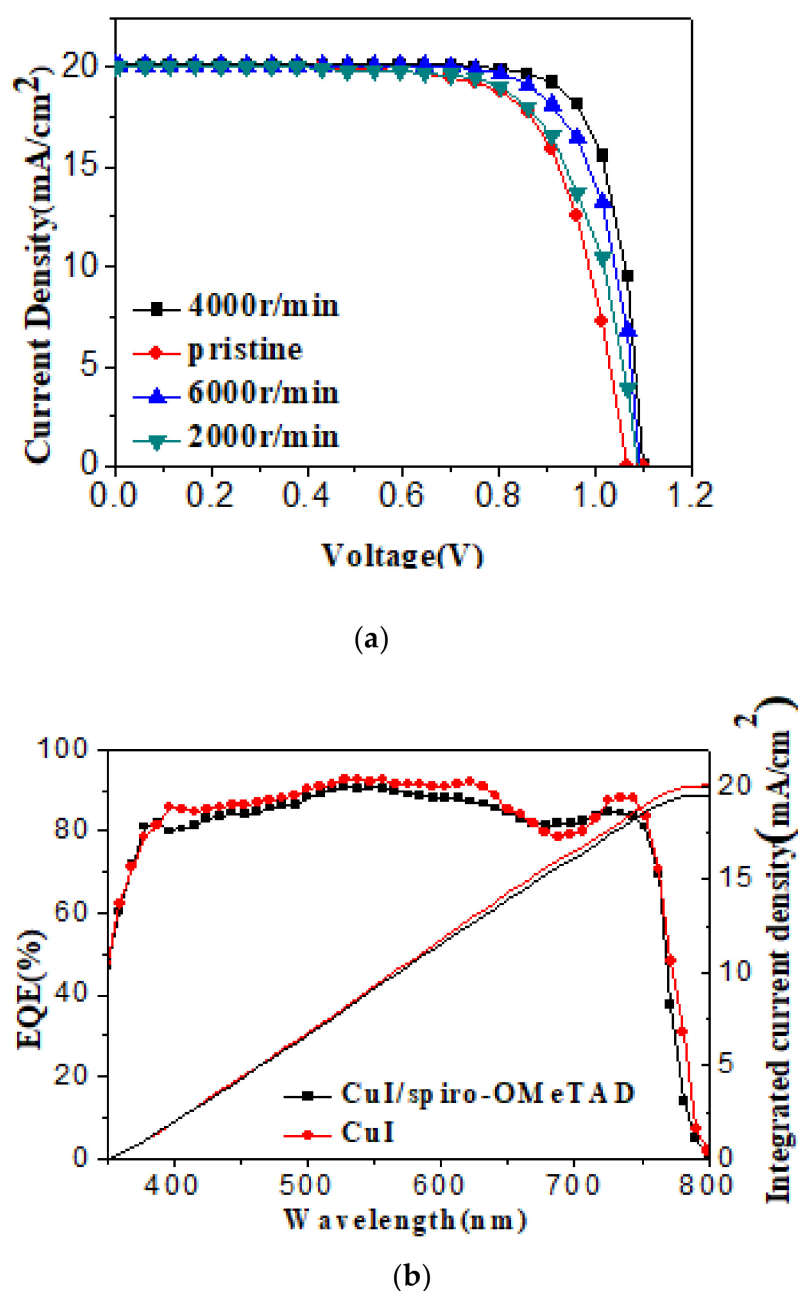


Figure 5. (a) J-V of the Spiro-OMeTAD and the double HTLs devices; (b) EQE of the single HTL devices and the double HTLs devices.

As shown in Figure 6a–d, there were V_{OC} , J_{SC} , FF, PCE box plots based on 20 initially unoptimized and CuI optimized perovskite photovoltaic devices, respectively. It was clearly found that the highest PCE of the optimized perovskite photovoltaic cells was 17.44% and the average PCE was 17.30%, which was much higher than the PCE of the perovskite photovoltaic devices not modified by CuI in any aspect. After analysis, it was further found that the higher PCE was due to the improvement of FF and J_{SC} . The optimized perovskite photovoltaic devices were higher than that of the initial perovskite photovoltaic devices, and the optimized FF and PCE values were more concentrated, while the initial device values were more divergent, which further illustrates the repeatability of optimized perovskite photovoltaic devices.

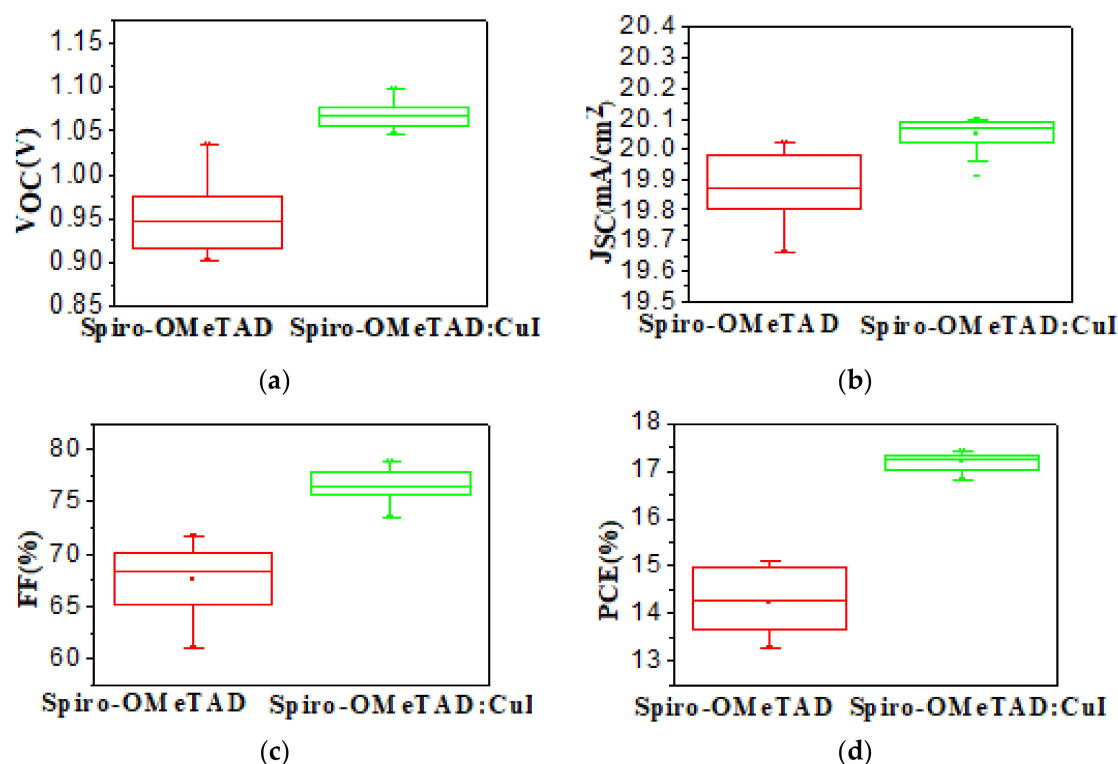
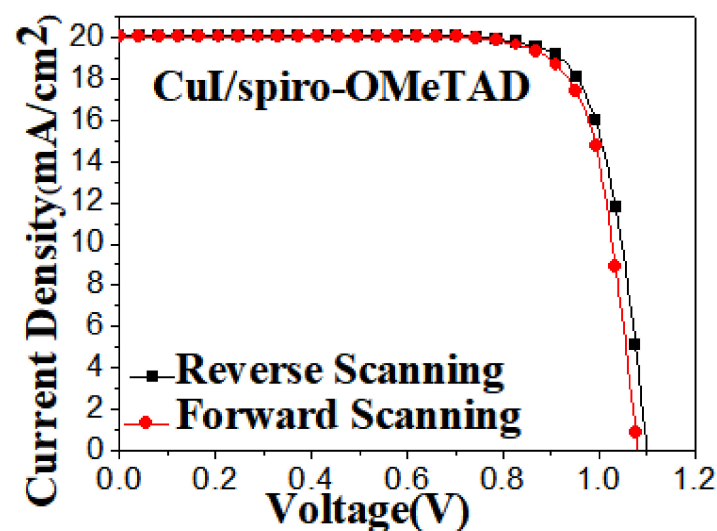


Figure 6. V_{OC} box plots (a), J_{SC} box plots (b), FF box plots (c), PCE box plots (d) for 20 independent pristine and double holes transport layers devices, respectively.

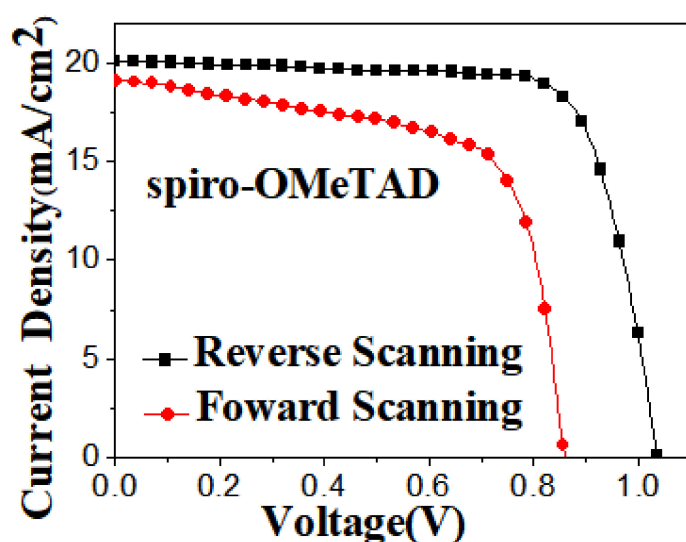
For further study of the solar cells, we prepared the complete solar cells with Spiro-OMeTAD and CuI/Spiro-OMeTAD. From Figure 7, the reverse and forward scanning results, it can be observed that the hysteresis of the single HTL samples was quite serious, while that of the CuI/Spiro-OMeTAD double samples was negligible. Next, we used the hysteresis index [35,36] defined by Equation (1) to quantify the hysteresis change in the photocurrent-voltage (J-V) curve:

$$HI = \frac{J_R\left(\frac{V_{OC}}{2}\right) - J_F\left(\frac{V_{OC}}{2}\right)}{J_R\left(\frac{V_{OC}}{2}\right)} \quad (1)$$

where $J_R(V_{OC}/2)$ is related to the photocurrent and V_{OC} during reverse scanning, and $J_F(V_{OC}/2)$ is the photocurrent during forward scanning. It is generally believed that the smaller the HI is, the smaller the hysteresis of the solar devices will be. The HI is typically between 0 and 1. Here the calculated HI values are 0.17 and 0.005 for devices with single and double HTLs, respectively. As a result of the pinholes between the HTL and perovskite, the perovskite makes contact with the electrode or air directly, resulting in defects. The insertion of CuI avoids the direct contact between Spiro-OMeTAD and perovskite, thereby reducing the number of interface defects, and this is conducive to the collection and transportation of charges, thus reducing recombination. The solar cells hysteresis after optimization is negligible. Therefore, the double HTLs can reduce the hysteresis significantly.



(a)



(b)

Figure 7. J–V curve hysteresis of single HTL devices (a) and double HTL devices (b).

The electron trap-state density between the perovskite layer and HTLs was measured with the aid of a space charge limited current (SCLC) (Figure 8). A regular solar cell of ITO/NiO/perovskite/HTL/Au was prepared, and the corresponding dark J–V curves are shown in Figure 6a,b, for which the trap-state densities were calculated to be $1.4 \times 10^{16} \text{ cm}^{-3}$ and $1.7 \times 10^{16} \text{ cm}^{-3}$ for CuI/Spiro-OMeTAD and Spiro-OMeTAD HTLs, respectively. Such a decrease in the N defect value by around 20% for the CuI/Spiro-OMeTAD cells showed that the defects concentration between the absorption layer and transport layer reduced to a large extent. A persuasive statement for the reduced defect is that the CuI thin layer deposit on the rough perovskite layer filled the small pinholes on the Spiro-OMeTAD HTL, resulting in a more uniform and smoother layer; this was due to the CuI layer leading to the Spiro-OMeTAD layer having intimate contact with the Au electrodes [14]. On the other hand, the addition of CuI film was conducive to hole charge extraction.

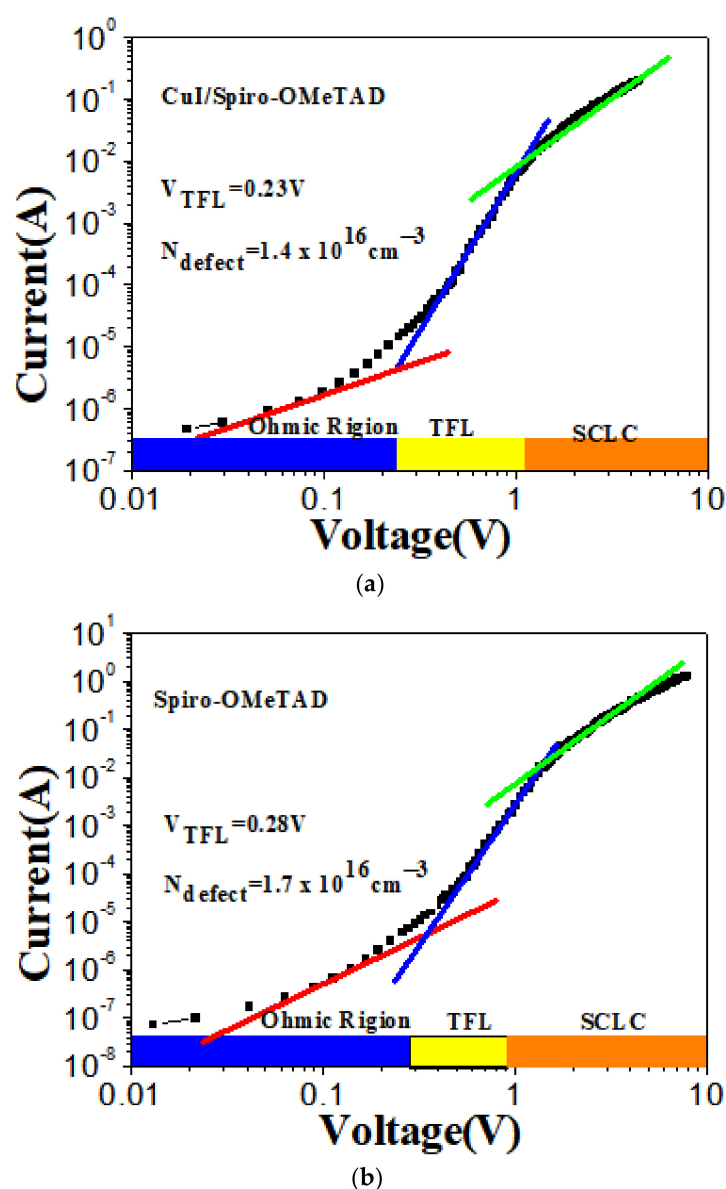


Figure 8. Dark I-V characteristics of devices based on: CuI/Spiro-OMeTAD (a) and Spiro-OMeTAD (b).

Next, the charge carrier recombination dynamics of the two different devices were studied by light intensity dependent V_{OC} . As shown in Figure 9, when the light intensity changes, linear correlation can be obtained. The slopes of the lines for the pristine and double HTLs solar cells near one, thus demonstrate that the charges recombination of the two devices at low light intensity can be ignored [37,38]. The most important recombination is the defect recombination between the perovskite and transport layers [39]. The ideal factors reflect the trap recombination, which describes the relationship between light intensity and voltage, as shown in Figure 9. The N changed from 1.45 of the pristine Spiro-OMeTAD-based solar cells to 1.38 of the CuI/Spiro-OMeTAD-based devices, thereby indicating that the decrease in interface defect density inhibited the trap recombination process. First, the well-matched energy level arrangement at the perovskite/CuI/Spiro-OMeTAD/Au electrode interface enhanced the ability to extract photogenerated holes from perovskite films and inject the holes into the Au electrodes. Second, the CuI intermediate layer prevented the Au electrode particles entering the absorption layer, formed an ideal energy barrier, prevented the flow of electrons to Au electrode, and greatly inhibited the recombination of the perovskite/Spiro-OMeTAD/Au interface. Third, the CuI layer could

passivate the surface defect state of perovskite, thereby greatly reducing the recombination of photocarriers in the devices.

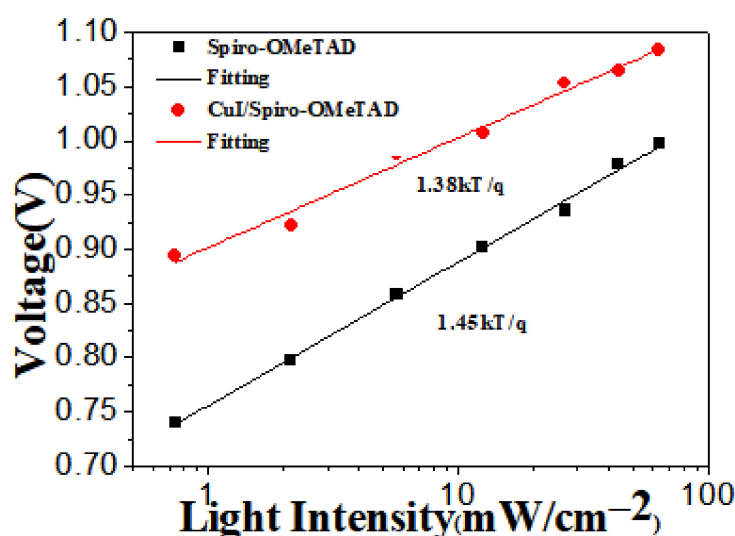


Figure 9. V_{OC} of PSCs plotted against light intensity, together with linear fits.

The steady state photoluminescence (PL) spectra (Figure 10) shows the strong PL emission of perovskite films at 763 nm [40]. Perovskite film on glass substrate has the highest photoluminescence intensity, which indicates that there is serious carrier re-combination in the sample. Clearly, the photoquenching efficiency of perovskite/CuI/Spiro-OMeTAD is greater than that of perovskite/Spiro-OMeTAD, showing effective charge extraction.

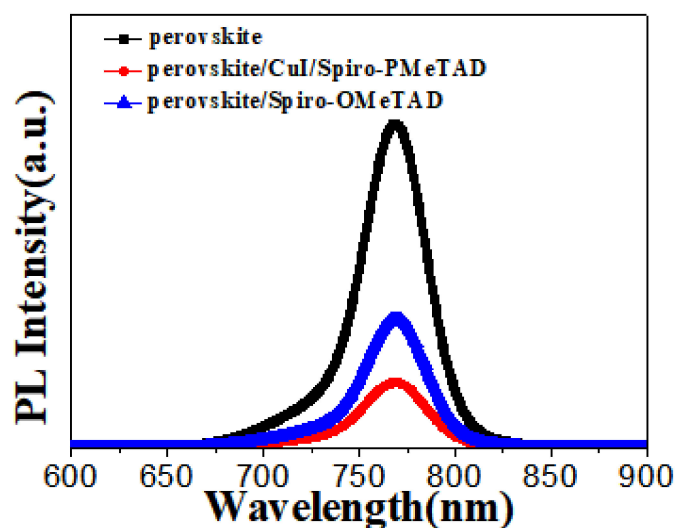


Figure 10. Steady state PL.

The charge recombination lifetime of perovskite solar cells was evaluated by time-resolved photoluminescence (TRPL) (Figure 11) for the structure of single perovskite, perovskite/Spiro-OMeTAD, and perovskite/CuI/Spiro-OMeTAD. The TRPL are fitted by the bi-exponential function:

$$f(t) = Ae^{(-t/\tau_1)} + Be^{(-t/\tau_2)} + C \quad (2)$$

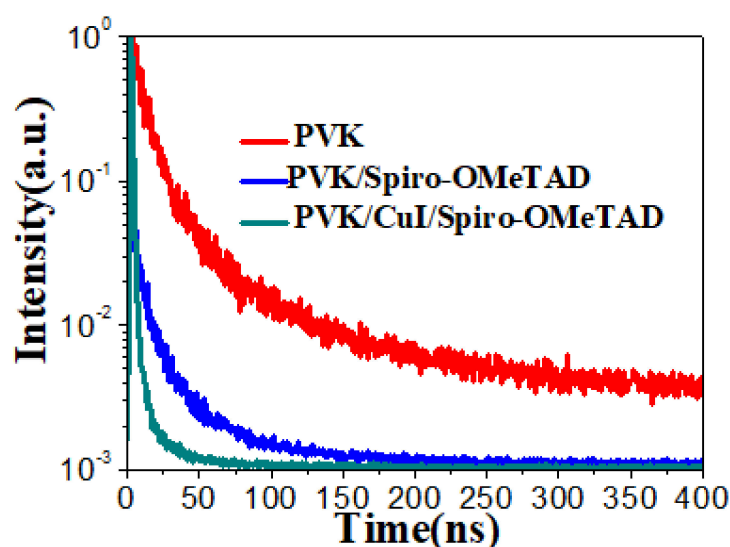


Figure 11. Time-resolved PL spectra of PVK, PVK/Spiro-OMeTAD and PVK/CuI/Spiro-OMeTAD.

In the equation, the fast transient component τ_1 corresponds to the surface characteristics and the slow component τ_2 corresponds to the volume characteristics. A and B represent the contribution of speed. C is a constant [41]. The average decay lifetime is obtained through the following function:

$$\tau_{ave} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \quad (3)$$

Based on single HTL and double HTLs perovskite solar cells, the average photoluminescence lifetime (τ_{ave}) of the extracted perovskite samples (70.4 ns) is greatly reduced to 51.22 and 44.48 ns, respectively (Figure 11).

Compared with single HTL, the PL lifetime of double HTLs samples is much shorter, which signifies that the hole transfer process has been improved. This suggests that light-generated carriers can be effectively transferred to HTL. These results indicate that there is an effective hole transfer and reduction in recombination centers between the perovskite and double hole transport layers, which is necessary for effective charge extraction and collection in perovskite devices.

The EIS was applied studying the carrier transport at the interface. Figure 12 shows the Nyquist plots based on the Spiro-OMeTAD and double CuI/Spiro-OMeTAD HTLs layers. The high frequency arc is due to the transport characteristics of carriers in the bulk layer. The low frequency incomplete semicircle represents the carrier recombination process of carriers at the interface. The values of R_{tr} and R_{rec} were fitted by Z-view software. Compared with the single HTL Spiro-OMeTAD device, the double CuI/Spiro-OMeTAD HTLs device had a smaller R_{tr} and larger R_{rec} . As it had the same preparation conditions except for different HTMs, the shape of the EIS curve depends on the result of HTM and the interface it modified. Additionally, because of the arrangement of energy levels, the CuI layer can prevent the hole diffusion from the Spiro-OMeTAD, which indicates that the interface electron-hole recombination between the ETL and HTL has been reduced. Moreover, a uniform and smoother layer of Spiro-OMeTAD was obtained, which is derived from the fact that the CuI scaffold layer was in close contact with the counter electrode. The results show that the charge carrier transfer rate of double HTLs devices was faster, and the recombination rate was lower, which is consistent with the TRPL results.

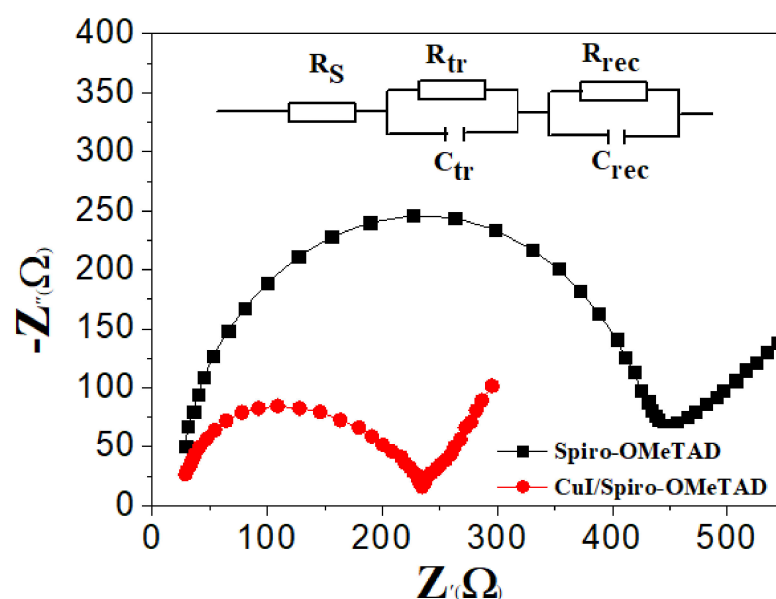


Figure 12. Nyquist plots of PVK/Spiro-OMeTAD, PVK/CuI/Spiro-OMeTAD cells.

According to the equation of $V_{oc} = \frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_0} + 1\right)$ [42], the V_{oc} is related to photocurrent J_{sc} and dark current J_0 , and the V_{oc} decreases as the J_0 increases from the equation. However, the dark current is determined by defects in the perovskite and the interface of the perovskite solar cells. Therefore, the dark state current can be used as a standard by which to evaluate the perovskite solar cells' performance. In order to obtain a better perovskite solar cell V_{oc} , a lower dark current is necessary.

Dark state J-V curves were used to evaluate the quality of the solar cells, which is shown in Figure 13. The current was suppressed with double HTLs. CuI compensated for the defect of Spiro-OMeTAD on the perovskite layer, and impeded the contact between air and perovskite, thereby effectively reducing the defects of the interface and the solar cell, in turn resulting in a reduction in dark current compared to devices of single HTL devices. These results are highly consistent with the EIS measurements.

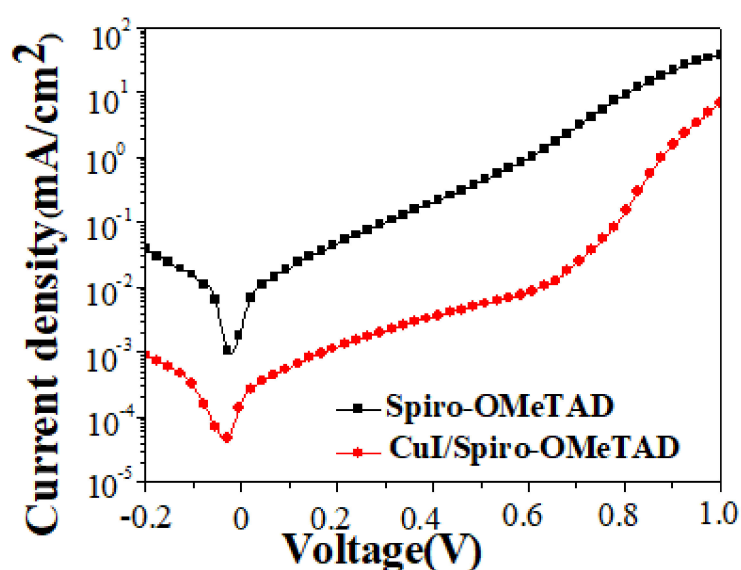


Figure 13. Dark J-V curves of single and double HTLs solar cells.

After a variety of optimization measures, the most important measurement standard of perovskite photovoltaic devices is to improve the stability on the basis of improving

the efficiency, so as to facilitate the practicability of the research results. In this paper, the stability of double hole transport layer perovskite photovoltaic cells optimized by CuI was tested after encapsulation. Under the encapsulation conditions, the perovskite photovoltaic devices can avoid the influence of humidity, mainly due to the influence of temperature and light. Due to the defects and holes in the interface between perovskite and Spiro, the charge recombination and the decomposition of perovskite led to a decrease in the efficiency of perovskite photovoltaic devices, the stability of encapsulation photovoltaic devices (non-optimized and optimized), devices under normal light and temperature, the stability of packaged photovoltaic devices, (non-optimized and optimized), devices under ultraviolet light and normal temperature, and the stability of packaged photovoltaic devices (non-optimized and optimized devices) under normal light and 80 °C.

As shown in Figure 14a, the stability of the encapsulation perovskite photovoltaic devices (non-optimized and optimized devices) under am 1.5 g illumination ($RH \leq 30\%$) in ambient conditions was measured. It can be seen from the figure that under the conditions of laboratory tests and normal illumination, after continuous illumination for 250 h, the photoelectric efficiency of the perovskite photovoltaic device based on CuI/Spiro-OMeTAD double-layer hole transport layer structure became 90% of the beginning structure, while the efficiency of the perovskite photovoltaic device based on single-layer Spiro-OMeTAD hole transport layer decreased to 75% of the beginning photoelectric efficiency. This is due to the defects in the interface between perovskite and Spiro-OMeTAD, and the slight decomposition of perovskite under continuous illumination, which leads to the degradation of perovskite properties.

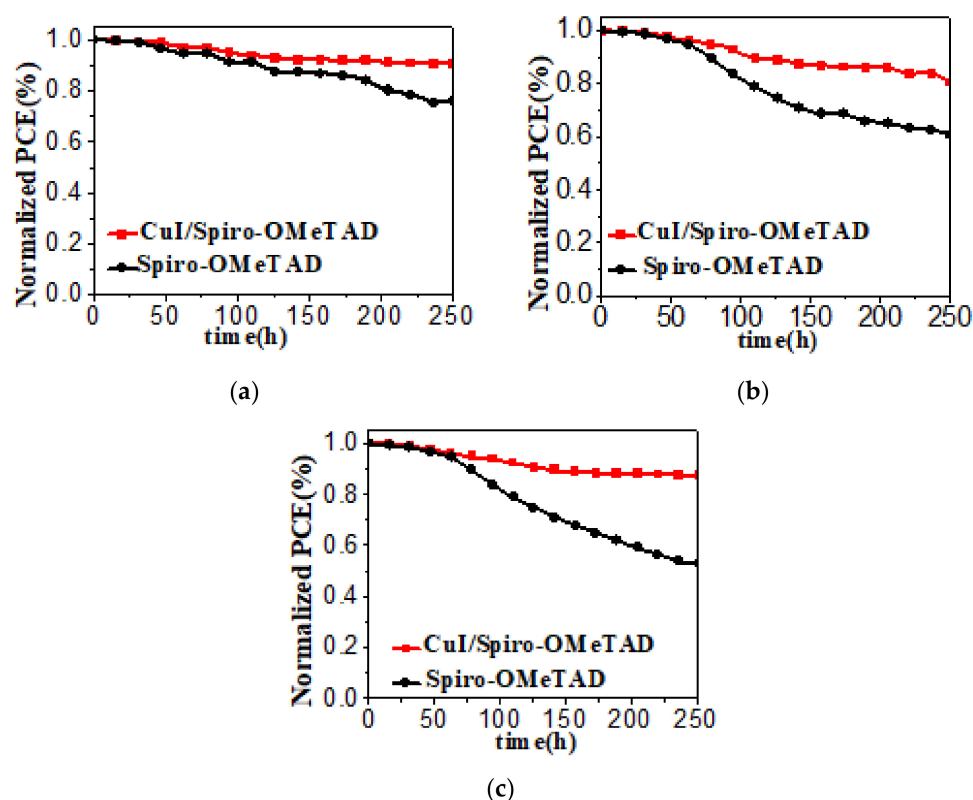


Figure 14. Stability test (a) under ambient conditions ($RH \leq 30\%$); (b) UV irradiation; (c) 80 °C.

As shown in Figure 14b, under laboratory conditions, the temperature was kept at room temperature, and the light was changed to ultraviolet light. The stability of the encapsulation perovskite photovoltaic device (non-optimized and optimized devices) was improved. It can be found that under the influence of ultraviolet light, after 250 h of continuous irradiation, the efficiency of the photovoltaic device based on CuI/Spiro-OMeTAD double-layer hole transport layer was 80% of the original efficiency, while the

efficiency of the perovskite photovoltaic solar cell based on single-layer Spiro-OMeTAD hole transport layer was 60%. This is due to the accelerated decomposition of the perovskite absorption layer under UV irradiation, and the defects in the perovskite crystal and Spiro-OMeTAD interface also led to the decomposition of perovskite photovoltaic devices. This led to a decrease in the efficiency of photovoltaic devices.

As shown in Figure 14c, under am 1.5 g illumination ($RH \leq 30\%$) in ambient conditions and at 80 °C, the stability of the encapsulation perovskite photovoltaic devices non-optimized and optimized devices was compared. Under certain conditions, after 250 h of continuous irradiation, the efficiency of the photovoltaic device based on CuI/Spiro-OMeTAD double-layer hole transport layer was 85% of the original efficiency, while the efficiency of the perovskite photovoltaic solar cells based on single-layer Spiro-OMeTAD hole transport layer was 55%. At a high temperature, the perovskite absorption layer will also accelerate the decomposition of the absorption layer components and become a toxic material which is not conducive to perovskite photoelectric conversion. Thus, the performance of perovskite photovoltaic devices is reduced.

4. Conclusions

In this study, we adopted a perovskite solar cell device with an upright structure. We inserted a CuI layer between perovskite and Spiro-OMeTAD by means of the one-step method prepared in N₂ gloveboxes. The CuI layer deposited on the perovskite surface was annealed by solution spin coating, because liquid spin coating is a low-cost and easy to control means. The CuI layer and Spiro-OMeTAD layer produced by spin coating formed a double-layer hole transport layer. The CuI on perovskite layer reduced the perovskite roughness, and also reduced the Spiro-OMeTAD roughness, resulting in a better connection between the Au electrode and Spiro-OMeTAD. In addition, CuI reducing defect density is conducive to hole extraction, and improves the collection of hole carriers at the Au electrode. For these reasons, the CuI/Spiro-OMeTAD double HTLs devices achieved an improved PCE of 17.44%. More importantly, without encapsulation, a PCE degradation of only 10% was shown in the aging test for 250 h. Meanwhile, the hysteresis of perovskite solar cells modified by double cavity transport layer can be ignored. The double HTLs model offers an easy means by which to realize high-quality and stable perovskite films for optoelectronic applications. Our work demonstrates that double HTLs can be the promising HTLs for high performance and environmentally stable PSCs.

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