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IMIDAZOLIUM TETRAFLUOROBORATE INTERFACE-MODIFIED TiO_2 ELECTRON TRANSPORT LAYER OF PEROVSKITE SOLAR CELLS

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Abstract: In this paper, [BMIM]BF4 is used to modify the interface of the TiO_2 electron transport layer for the purpose of passivating the interface. The research shows that the interface modification with [BMIM]BF4 reduces the surface defects of the TiO_2 electron transport layer, increases the Fermi level of the interface, reduces the carrier accumulation between the TiO_2 electron transport layer and the perovskite layer, and promotes charge transport. It enhances the electron extraction ability of the electron transport layer, fills the interface defects, and suppresses the non - radiative recombination of charges at the interface. It is beneficial to the growth of perovskite materials and increases the particle size of perovskite. It also improves the photoelectric conversion efficiency of the battery.
Keywords: Perovskite solar cells; Interface modification; [BMIM]BF4

1 INTRODUCTION

There are many defects at the interface between the absorption layer and the adjacent carrier transport layer in perovskite solar cells, and these defects affect the stability of the cells. Interface modification can effectively passivate the defect states and improve the photoelectric conversion efficiency and stability of the devices [1]. Researchers such as Zang Zhigang inserted a MACl layer between the electron transport layer and the perovskite layer, successfully accelerating the extraction and transport of carriers, suppressing interface recombination, and finally achieving an open - circuit voltage of 1.19 V [2]. Researchers such as Shih introduced PC61BM at the interface between the TiO_2 electron transport layer and the perovskite. By passivating the defect states and enhancing the interface charge transport, they suppressed charge accumulation, reduced the density of defect states, and effectively suppressed device hysteresis. The researchers spin - coated thioacetamide (TAA) on the surface of the TiO_2 electron transport layer and annealed it at 120 °C for 20 minutes, then used it as an interface modification layer. Studies have confirmed that during the low - temperature annealing process, the N and S atoms in the TAA molecule can coordinately bind to Pb^{2+} in the perovskite and Ti^{4+} in the electron transport layer (ETL) synergistically, effectively passivating the interface defects and promoting carrier transport. The solar cell device based on the TiO_2/TAA heterojunction exhibited a peak energy conversion efficiency (PCE) of 21.17%. Compared with the reference device without TAA modification (PCE = 19.52%), the performance improvement rate reached 8.5% [3]. Researchers have explored a variety of passivation materials, such as organic halide salts and fullerene derivatives. However, the conductivity of these passivation materials is usually poor, which affects the inter - layer charge transport. Some researchers have found that when imidazole derivatives are used for interface modification, they can effectively fill the iodine vacancies on the perovskite surface and reduce interface defects. The prepared perovskite solar cells exhibited a photoelectric conversion efficiency as high as 25.3% [4]. In this paper, 1 - butyl - 3 - methylimidazolium tetrafluoroborate ([BMIM]BF4) is used for interface modification to effectively passivate the defect states. [BMIM]BF4 with different concentrations is spin - coated to explore the suitable concentration, optimize the photoelectric performance of the electron transport layer, and further improve the performance of perovskite solar cells.

2 EFFECTS OF [BMIM]BF4 MODIFICATION ON THE ELECTRON TRANSPORT LAYER

This paper mainly introduces [BMIM]BF4 solutions with different concentrations into the electronic transport layer and the perovskite material layer to investigate their effects on interface modification and surface defect passivation. Figure 1 shows the schematic structure of the prepared battery device.

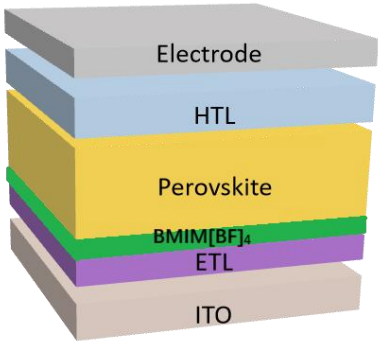


Figure 1 Structural Diagram of the Battery Device Modified with [BMIM]BF4

2.1 Influence of [BMIM]BF4 Modification on the Photoelectric Properties of TiO2 Electron Transport Layer

As shown in the figure, Figure 2 shows the transmittance curves of TiO_2 electron transport layers modified with different concentrations of [BMIM]BF4. As the concentration of [BMIM]BF4 increases, the transmittance gradually decreases. When the spin - coated [BMIM]BF4 concentration is 2.5 mg/mL, the transmittance of the TiO_2 electron transport layer is the lowest, about 88%, which is also higher than that of the initial TiO_2 electron transport layer, meeting the basic requirements for the transmittance of the electron transport layer.

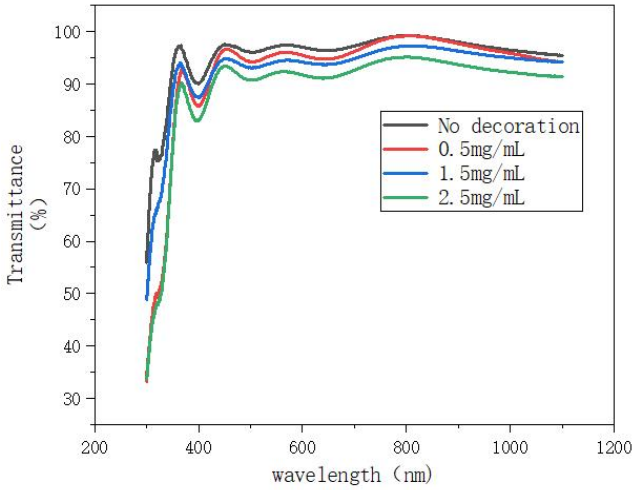


Figure 2 Transmittance of TiO_2 Electron Transport Layer Modified with Different Concentrations of $[BMIM]BF_4$

In order to investigate the influence of [BMIM]BF4 modification on the electrical properties of the TiO_2 electron transport layer, a diode structure of conductive substrate/TiO_2 electron transport layer/silver electrode was prepared, as shown in the device structure in Figure 3. Then, the I-V test of the device was carried out in the dark state. The conductivity curve shown in Figure 3 was obtained. Under an applied electric field, the charges in the device.

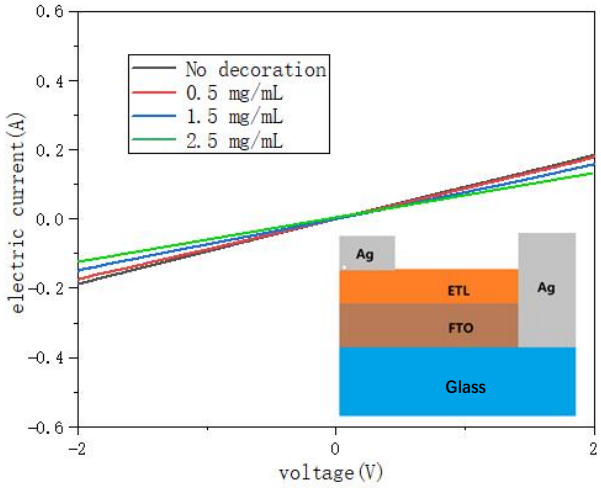
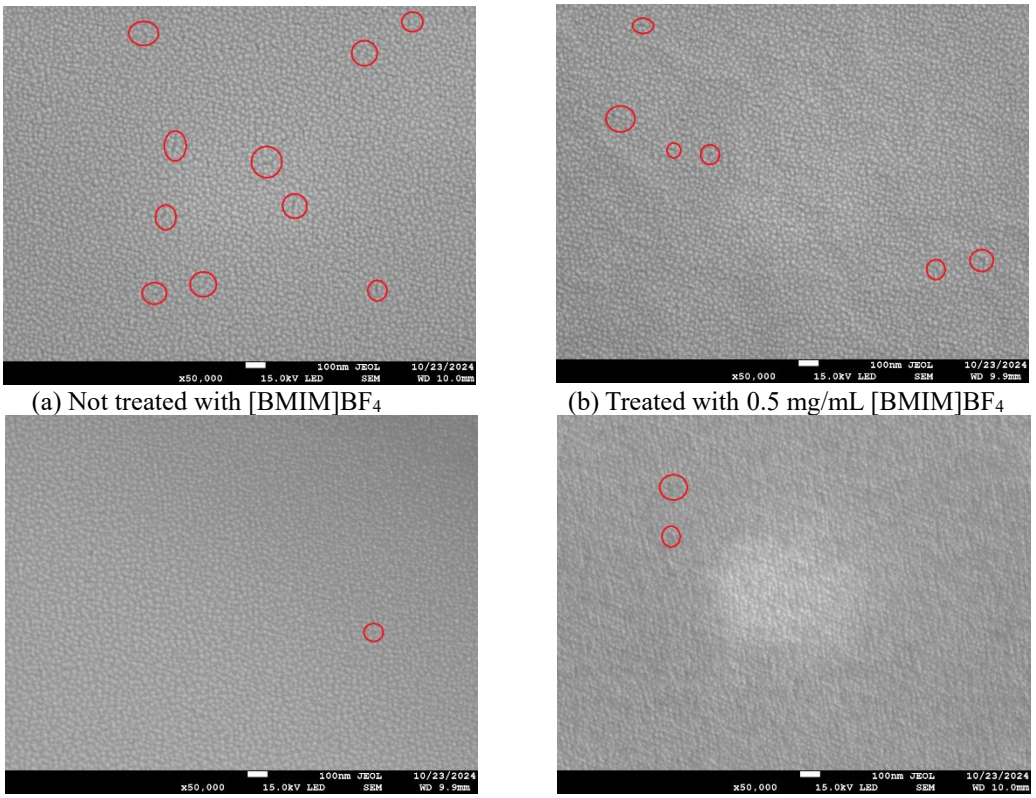


Figure 3 Electroconductibility

Since the [BMIM]BF4-modified TiO_2 electron transport layer covers the surface of the thin film, the conductivity of the surface thin film is measured by the four-probe method, and the sheet resistance cannot accurately reflect the conductivity of the modified TiO_2 electron transport layer. As can be seen from Figure 3, with the increase of the [BMIM]BF4 modification concentration, the conductivity of the thin film decreases slightly, and the change in conductivity is not significant, which has little influence on the electrical properties of the thin film.

2.2 Influence of [BMIM]BF4 Modification on the Microscopic Morphology of TiO_2 Electron Transport Layer

In order to investigate the influence of [BMIM]BF4 modification on the surface micromorphology of the TiO_2 electron transport layer, thin films before and after modification with different concentrations of [BMIM]BF4 were prepared on the surface of the glass layer. As shown in Figure 4, they are the electron microscope images of the TiO_2 electron transport layer before and after modification with different [BMIM]BF4 concentrations. The surface of the unmodified TiO_2 electron transport layer thin film is rough with many pore defects (indicated by the red circles in the figure). After being modified with [BMIM]BF4, the pores on the surface of the TiO_2 electron transport layer are significantly reduced. When the modification concentration of [BMIM]BF4 is 1.5 mg/mL, the thin film surface has the fewest pores and is the most dense and flat. The main reason may be that the [BMIM]BF4 modification fills the surface pores, making the surface smooth and flat, which is beneficial to the subsequent growth of the perovskite layer [5].



(a) Not treated with $[BMIM]BF_4$ (b) Treated with 0.5 mg/mL $[BMIM]BF_4$

(c) Treated with 1.5 mg/mL $[BMIM]BF_4$ (d) Treated with 2.5 mg/mL $[BMIM]BF_4$

Figure 4 Electron Microscope Images of K+-doped TiO_2 Electron Transport Layers Treated with Different Concentrations

3 EFFECT OF [BMIM]BF4 MODIFICATION ON DEFECT PASSIVATION AND CARRIER EXTRACTION OF ELECTRON TRANSPORT LAYER

In order to further investigate the recombination of electrons and holes in the TiO_2 electron transport layer and perovskite layer of the device modified by $[BMIM]BF_4$, Mott - Schottky tests were carried out on the electron transport layers modified with different concentrations. The results are shown in Figure 5. The slopes of the Mott - Schottky curves of both the unmodified and $[BMIM]BF_4$ - modified samples are positive, indicating that both are n - type semiconductors, which meets the requirements of the electron transport layer. As the modification concentration of $[BMIM]BF_4$ increases, the slope of the curve first increases, then decreases, and then increases again. When the modification concentration of $[BMIM]BF_4$ is 1.5 mg/mL, the slope is the smallest, and the carrier separation ability is the strongest, reducing the diffusion and migration of electrons [6]. The modification of $[BMIM]BF_4$ causes the flat - band potential of the TiO_2 electron transport layer to shift negatively, injects a large number of additional electrons, reduces the band bending, and raises the Fermi level.

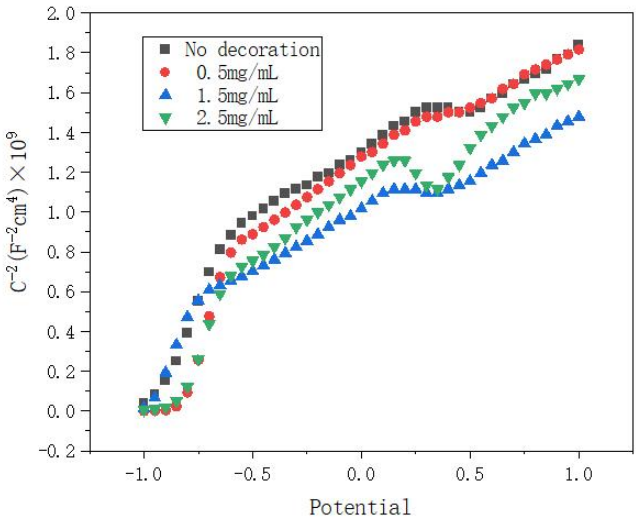


Figure 5 Mott-Schottky Test Curves of TiO_2 Electron Transport Layer Modified with Different Concentrations of $[BMIM]BF_4$

In order to further investigate the recombination of electrons and holes in the TiO_2 electron transport layer and perovskite layer of the device modified by $[BMIM]BF_4$, electrochemical impedance tests were carried out on the films with different modification concentrations. As shown in the figure, Figure 6 shows the Nyquist plots and equivalent circuits of the TiO_2 electron transport layer modified with different $[BMIM]BF_4$ concentrations. The data in Table 1 were obtained by fitting the data through the equivalent circuit in the inset.

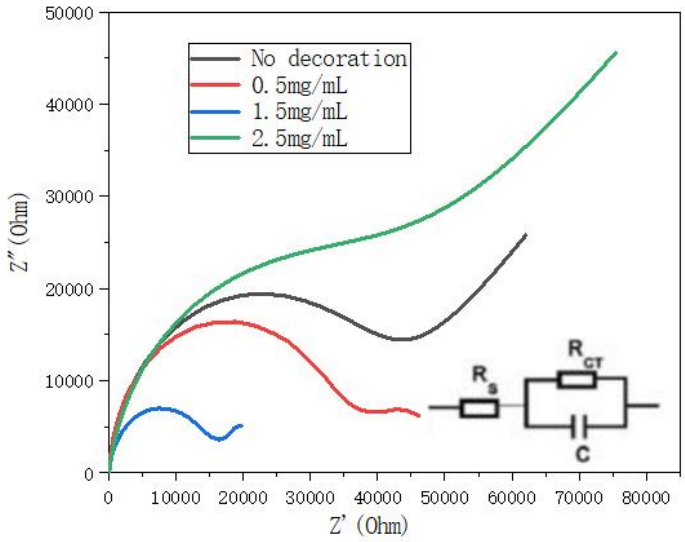


Figure 6 Nyquist Plots and Equivalent Circuits of TiO_2 Electron Transport Layers Modified with Different Concentrations of $[BMIM]BF_4$

As the modification concentration of $[BMIM]BF_4$ increases, the series resistance Rs first increases and then decreases. When the concentration is 1.5 mg/mL, the series resistance Rs reaches the minimum value, which is beneficial for carrier transport and increasing the short - circuit current. The recombination resistance Rrec is obtained by fitting the arc in the low - frequency region, and it represents the carrier recombination between the ETL and the perovskite layer [7]. The recombination resistance represents the ease of carrier recombination in the battery. The larger the recombination resistance Rrec, the less the recombination in the device, which is more beneficial for carrier transport in the device [8]. After the modification with $[BMIM]BF_4$, the recombination resistance Rrec increases, indicating that the $[BMIM]BF_4$ modification effectively suppresses the carrier recombination at the interface. When the modification concentration of $[BMIM]BF_4$ is 2.5 mg/mL, the recombination resistance Rrec decreases, suggesting that a higher $[BMIM]BF_4$ modification concentration is not always better. When the concentration of $[BMIM]BF_4$ is 1.5 mg/mL, the recombination resistance Rrec is the minimum, which is 20.1 ohms. At this concentration, the $[BMIM]BF_4$ modification concentration is appropriate, and the recombination loss is the minimum. By regulating the defects in the device, the non - radiative recombination can be reduced, and the open - circuit voltage of the device can be improved [9-10].

Table 1 Fitting Data of Electrochemical Impedance of TiO_2 Electron Transport Layer Modified with Different

Concentrations of $[BMIM]BF_4$

Sample name	Rs(Ω)	Rrec(kΩ)	CPE-T(F) μMho	CPE-P(F)
Unadorned	14.9	39.1	5.94	0.939
0.5mg/mL	16.4	14.7	14.6	0.94
1.5mg/mL	20.1	35.3	11.7	0.964
2.5mg/mL	17.9	41.5	13.2	0.904

To further investigate the transfer and recombination of interfacial carriers, steady-state photoluminescence spectroscopy (PL) tests were conducted on the TiO_2 electron transport layer before and after $[BMIM]BF_4$ modification. As shown in Figure 7, these are the PL spectra of the perovskite layer under the modification of different concentrations of $[BMIM]BF_4$. By analyzing the quenching intensity of the perovskite thin film, the electron extraction ability of the TiO_2 electron transport layer modified with different concentrations of $[BMIM]BF_4$ can be obtained. By comparing with the unmodified TiO_2 electron transport layer, it can be found that TiO_2 modified with different concentrations of $[BMIM]BF_4$ all exhibits better electron extraction ability. The $[BMIM]BF_4$ modification has a significant impact on the carrier extraction ability at the interface. The PL intensity after $[BMIM]BF_4$ modification shows a trend of first decreasing and then increasing, but the overall PL intensity after modification decreases significantly. When the modification concentration of $[BMIM]BF_4$ is 1.5 mg/mL, the PL peak intensity of the perovskite thin film decreases significantly, which indicates that the modification significantly increases the electron extraction ability of TiO_2. This is because the TiO_2 electron transport layer modified with $[BMIM]BF_4$ has a stronger charge extraction ability. Electrons are rapidly exported from the perovskite layer, resulting in a significant decrease in PL intensity and a reduction in the charge accumulation and recombination at the interface between the TiO_2 electron transport layer and the perovskite layer [11]. It is proven that $[BMIM]BF_4$ modification can reduce the oxygen vacancy defects in the TiO_2 electron transport layer, accelerate the charge transport between the TiO_2 electron transport layer and the perovskite layer interface, and inhibit the recombination between electrons and holes. The interface modification increases the contact area between TiO_2 and the perovskite layer and accelerates the extraction of photo-generated electrons.

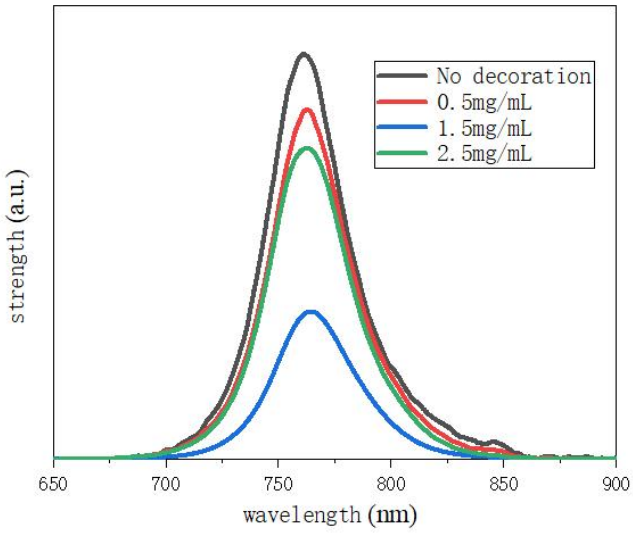
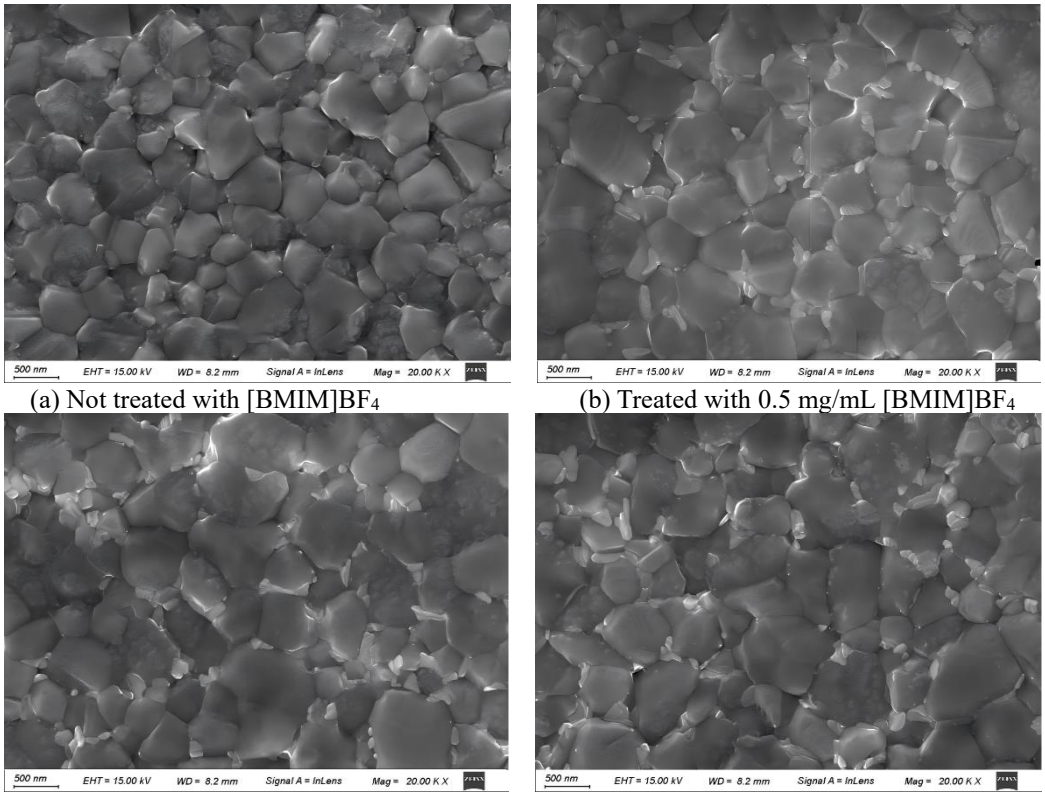


Figure 7 Steady-State Photoluminescence Spectral Curves of TiO_2 Electron Transport Layer Modified with Different Concentrations of [BMIM]BF4

4 EFFECTS OF MODIFICATION WITH DIFFERENT CONCENTRATIONS OF [BMIM]BF4 ON THE MORPHOLOGY OF THE PEROVSKITE LAYER

As shown in the figure, Figure 8 shows the electron microscope images of the perovskite layers prepared on the TiO_2 electron transport layers modified with different concentrations of $[BMIM]BF_4$. After being modified with $[BMIM]BF_4$, the surface of the perovskite layer is smooth without pinholes, dense and uniform. The size of the perovskite particles after $[BMIM]BF_4$ modification becomes larger, significantly exceeding that of the perovskite without $[BMIM]BF_4$ modification, which is beneficial to the transport of carriers [12]. The modification of $[BMIM]BF_4$ has an obvious optimization effect on the growth of perovskite. Through comparison, it is found that the surface of the perovskite layer modified with $[BMIM]BF_4$ at a concentration of 1.5 mg/mL has narrower grain boundaries and closer grain contact compared with the surface of the unmodified perovskite layer, reducing the carrier accumulation at the grain boundaries

and being more conducive to the charge transport and transfer.



(a) Not treated with $[BMIM]BF_4$ (b) Treated with 0.5 mg/mL $[BMIM]BF_4$

(c) Treated with 1.5 mg/mL $[BMIM]BF_4$ (d) Treated with 2.5 mg/mL $[BMIM]BF_4$

Figure 8 Electron Microscope Images of TiO_2 Electron Transport Layers Modified with Different Concentrations of [BMIM]BF4

5 EFFECTS OF MODIFICATION WITH DIFFERENT CONCENTRATIONS OF [BMIM]BF4 ON PEROVSKITE SOLAR CELLS

To investigate the influence of different [BMIM]BF4 concentration modifications on perovskite solar cells, perovskite solar cells modified with different [BMIM]BF4 concentrations were prepared. The photoelectric performance parameters are detailed in Table 2. Through statistical analysis of the data of four groups of devices, after [BMIM]BF4 modification, all performance indicators of the battery devices were significantly improved, including open - circuit voltage (Voc), short - circuit current density (Jsc), and fill factor (FF), indicating that [BMIM]BF4 interface modification effectively optimized the electrical characteristics of the electron transport layer and enhanced the photoelectric conversion efficiency of the devices.

Compared with the unmodified battery devices, [BMIM]BF4 modification significantly improved the photoelectric performance of the batteries. The short - circuit current density (Jsc) of the doped batteries was significantly improved. When the modification concentration was 1.5 mg/mL, Jsc reached 9.29 mA/cm², significantly higher than 4.93 mA/cm² of the undoped device. After [BMIM]BF4 modification, the photoelectric conversion efficiency of the battery devices was significantly improved. Compared with the unmodified device, the efficiency of the device with a modification concentration of 1.5 mg/mL doubled. The device with a modification concentration of 1.5 mg/mL achieved a photoelectric conversion efficiency (PCE) of 3.83%, a short - circuit current density (Jsc) of 9.29 mA/cm², and a fill factor (FF) of 70.29%. These results indicate that [BMIM]BF4 modification effectively optimized the charge transport characteristics of the device and significantly improved the overall performance of perovskite solar cells.

Table 2 Conversion Efficiency of Perovskite Solar Cells with TiO_2 Electron Transport Layer Modified by Different [BMIM]BF4 Concentrations

Sample name	Voc/V	Jsc/mA·cm^{-2}	FF(%)	PCE/%
Unmodified TiO_2	0.54	4.93	66.63	1.77
0.5mg/mL$[BMIM]BF_4$	0.55	6.48	67.23	2.4
1.5mg/mL$[BMIM]BF_4$	0.60	9.29	70.29	3.83
2.5mg/mL[BMIM]BF4	0.53	7.4	65.43	2.57

6 SUMMARY

By using [BMIM]BF4 to modify the interface of the TiO_2 electron transport layer, interface defects are reduced, and the ability of the TiO_2 electron transport layer to extract electrons is improved, which is beneficial to the further growth,

crystallization and film - forming of perovskite materials. Compared with the unmodified device, the efficiency of the battery device with [BMIM]BF4 interface modification has more than doubled. This is mainly because the [BMIM]BF4 modification increases the Fermi level of the interface, reduces the carrier accumulation between the TiO_2 electron transport layer and the perovskite layer, and promotes charge transport. It is beneficial to the transport of carriers inside the device and improves the charge transport efficiency.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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