An Anion-Cation Synergistic Strategy of an Ionic Liquid Additive in Printable Mesoscopic Perovskite Solar Cells: Postprint

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Abstract

To enhance the device performance and long-term stability of printable mesoscopic perovskite solar cells (MPSCs), a cation-anion synergistic strategy is proposed, wherein the ionic liquid additive 1-ethyl-3-methylimidazolium acetate (EMIMAC) is introduced into the perovskite active layer for fabricating efficient and stable MPSCs. Experimental results demonstrate that the imidazolium cation (EMIM+) passivates ionic defects (such as Pb2+ and PbI3-) through coordination effects, promoting perovskite crystallization. On the other hand, the acetate anion (AC-) coordinates with TiO2, simultaneously passivating oxygen vacancy defects on the TiO2 surface, thereby improving the interfacial contact at the TiO2/perovskite interface. Consequently, the synergistic effect of EMIM+ and AC- ions in EMIMAC achieves better perovskite crystallinity, more efficient charge transport, and reduced non-radiative recombination. Ultimately, the power conversion efficiency (PCE) of MPSCs is increased from 13.83% to 15.48%, with negligible hysteresis. Furthermore, unencapsulated MPSCs exposed to air (RH=50$±$5%) retain 90% of their initial PCE after 60 d, demonstrating excellent long-term stability. Experimental results indicate that the ionic liquid additive EMIMAC can effectively enhance the PCE and stability of devices, providing an effective strategy for further improving device performance.

Full Text

Preamble

中图分类号 EMIMAC

Abstract

An Anion-Cation Synergistic Strategy of an Ionic Liquid Additive in Printable Mesoscopic Perovskite Solar Cells

To enhance the device performance and long-term stability of printable mesoscopic perovskite solar cells (MPSCs), we propose an anion-cation synergistic strategy by introducing the ionic liquid additive 1-ethyl-3-methylimidazolium acetate (EMIMAC) into the perovskite active layer. The $EMIM^+$ cation passivates ionic defects through coordination effects, which is believed to be beneficial for perovskite crystallization, while the acetate anion simultaneously passivates oxygen vacancy defects on the TiO_2 surface, thereby improving the TiO_2/perovskite interface contact. This synergistic effect of cations and anions achieves better perovskite crystallinity, more efficient charge transport, and lower non-radiative recombination.

Experimental results demonstrate that the power conversion efficiency (PCE) of MPSCs increases from 13.83% to 15.48% with negligible hysteresis. Furthermore, the unencapsulated devices exhibit excellent long-term stability, maintaining 90% of their initial PCE after exposure to ambient air (RH = 50$±$5%) for 60 days. This work provides an effective strategy for further improving the performance of MPSCs.

Results and Discussion

1. Interaction Mechanism and Film Quality Analysis

Fourier-transform infrared spectroscopy (FTIR) was employed to analyze the interaction between EMIMAC and the perovskite. The C=O stretching vibration peak in the $MAPbI_3$+EMIMAC annealed film shifts to a lower wavenumber compared to the standard sample, which can be interpreted as coordination between EMIMAC and uncoordinated Pb^{2+} in the $MAPbI_3$ film. This effectively passivates ionic defects. X-ray photoelectron spectroscopy (XPS) further confirms this interaction, showing that the binding energy of Pb 4f in $MAPbI_3$ with EMIMAC shifts to higher energy by 0.3 eV. This shift is attributed to the coordination between the nitrogen atoms with lone electron pairs on the imidazole ring and the undercoordinated Pb^{2+} defects. The binding energy of the I 3d spectrum also shifts to higher energy, confirming defect passivation and enhanced coordination.

To evaluate the optical properties of perovskite films, UV-Vis absorption spectra were measured. As shown in [FIGURE:N], the light absorption intensity of $MAPbI_3$ films with EMIMAC is significantly enhanced compared to the standard sample, leading to improved photon harvesting capability. The effect of EMIMAC concentration on crystallization dynamics was analyzed using X-ray diffraction (XRD). The main characteristic diffraction peaks of the $MAPbI_3$ film appear at 13.73°, 28.04°, and 31.45°, corresponding to the (110), (220), and (310) crystal planes, respectively. No additional diffraction peaks are ob-

served, indicating that EMIMAC does not alter the intrinsic crystal structure of perovskite. Notably, the diffraction intensity increases with EMIMAC concentration, demonstrating improved crystallinity. The sample with EMIMAC exhibits the strongest peak intensity and narrowest full width at half maximum (FWHM), indicating optimal crystalline quality with fewer crystal defects.

Since the mp-TiO_2 scaffold serves as the primary support for perovskite nanocrystals and is responsible for electron transfer, its surface chemical state critically affects charge extraction and transport. The acetate group ($-COO^-$) can coordinate with TiO_2 to passivate surface oxygen vacancy defects. XPS analysis reveals that after EMIMAC treatment, the oxygen vacancy content on the mp-TiO_2 surface decreases from 54.23% to 44.15%. The weakened peak intensity and shift in the Ti 2p spectrum confirm the interaction between EMIMAC and the TiO_2 surface, where the acetate anion anchors onto TiO_2, partially shielding the Ti signal. FTIR analysis of TiO_2+EMIMAC films shows the resonance peak of the carboxylate group shifting to lower wavenumbers (1550–1610 cm^{-1}), indicating binding between the $-COO^-$ group and TiO_2. This interaction passivates film defects and improves the TiO_2/perovskite interface contact, thereby promoting charge extraction.

2. Device Structure, Molecular Structure, and Mechanism Model

[FIGURE:N] presents the schematic structure of MPSCs, where the mp-TiO_2, mp-ZrO_2, and mp-Carbon layers are sequentially printed on FTO glass substrates. The perovskite precursor solution infiltrates the entire mesoporous scaffold through drop-casting, followed by annealing and crystallization. The energy level diagram demonstrates proper alignment, enabling effective extraction and transfer of electrons and holes within the mesoporous scaffold for injection into respective electrodes. Enhancing the crystal quality and loading of perovskite in the mesoporous scaffold is crucial for achieving strong photon harvesting and efficient charge transport.

The molecular structure and ball-and-stick model of EMIMAC are illustrated in [FIGURE:N], featuring an imidazolium cation and an acetate anion. [FIGURE:N] depicts the proposed synergistic mechanism: the $EMIM^+$ cation passivates ionic defects through coordination effects, promoting perovskite crystallization, while the acetate anion preferentially anchors to the TiO_2 surface, passivating oxygen vacancy defects and improving the TiO_2/perovskite interface contact. The performance enhancement of MPSCs thus benefits from the anion-cation synergistic action of the EMIMAC ionic liquid.

3. Perovskite Carrier Dynamics Analysis

Time-resolved photoluminescence (TRPL) measurements were conducted to investigate the effects of EMIMAC on electron transfer and non-radiative recombination. Test samples were prepared on mp-ZrO_2/$MAPbI_3$ and mp-TiO_2/$MAPbI_3$ glass substrates. The TRPL curves were fitted using a

bi-exponential function, with fitting parameters and calculated average lifetimes summarized in [TABLE:N]. On mp-ZrO_2 substrates, the average carrier lifetime of perovskite films with EMIMAC is longer than that of the control sample, indicating that EMIMAC passivates recombination centers in the perovskite film and suppresses non-radiative recombination. This is further supported by higher photoluminescence quenching in the steady-state PL spectra.

Conversely, on mp-TiO_2 substrates, the average carrier lifetime decreases from 12.05 ns (control) to 6.41 ns (with EMIMAC), corresponding to accelerated charge transfer from perovskite to TiO_2. The shorter carrier lifetime implies faster charge extraction, which is beneficial for device performance. The PL peak position also blue-shifts from 770 nm to 767 nm due to reduced non-radiative recombination.

4. Device Photovoltaic Performance Analysis

The photovoltaic performance of MPSCs was comprehensively evaluated to assess the impact of EMIMAC' s anion-cation synergistic effect. [FIGURE:N] shows typical current density–voltage (J–V) curves for control devices (PCE = 13.83%) and devices with varying EMIMAC concentrations. The four fundamental photovoltaic parameters affecting device performance are open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF), and PCE. The optimal device with EMIMAC achieves a PCE of 15.48%, with detailed parameters of Voc = 0.94 ± 0.01 V, Jsc = 23.72 ± 0.07 mA · cm^{-2}, and FF = 67.93 ± 0.52%. This enhancement is attributed to improved perovskite crystallinity, reduced film defects, and diminished charge recombination resulting from the anion-cation synergistic effect.

Incident photon-to-current conversion efficiency (IPCE) spectra were compared for devices with and without EMIMAC. The device with EMIMAC shows significant enhancement in the 400–750 nm range, contributing to improved photocurrent and higher Jsc. The integrated current density values of 21.46 mA · cm^{-2} (control) and 22.53 mA · cm^{-2} (with EMIMAC) are consistent with the J–V curve measurements.

Hysteresis is commonly observed in J–V curves during forward and reverse scans, likely arising from interfacial charge transfer and recombination processes. The hysteresis effect index (HEI) was used to quantify hysteresis severity. The control device exhibits an HEI of 0.052, while the EMIMAC device shows a substantially reduced HEI of 0.005, indicating significant hysteresis suppression. This improvement is attributed to faster charge extraction and better interfacial contact.

The steady-state efficiency output of the EMIMAC device was measured under continuous illumination to simulate normal operation. The device maintains a stable output efficiency of 15.25% at the maximum power point (J = 21.5 mA · cm^{-2}), demonstrating high reliability. Electrochemical impedance spectroscopy (EIS) was performed to analyze internal charge transfer characteristics. The

Nyquist plots show a single semicircle representing the overall charge transfer resistance (Rct) of the device. The smaller Rct for the EMIMAC device indicates reduced charge transport resistance from perovskite to the carbon electrode, confirming enhanced charge transfer capability.

Long-term stability is a critical challenge for MPSCs in practical applications. The efficiency evolution of unencapsulated devices stored in ambient air (RH = 50$±5_{2}$/perovskite interface through the anion-cation synergistic effect.

5. Average Photovoltaic Parameters of MPSCs with EMIMAC

[TABLE:N] summarizes the average photovoltaic parameters of MPSCs with varying EMIMAC concentrations:

EMIMAC (mol%)	Voc (V)	Jsc ($mA \cdot cm^{-2}$)	FF (%)	PCE (%)
0 (Control)	0.92$±0.01	23.29±0.09	64.77±1.83	13.89±0.35
0.5	0.93±0.01	23.48±0.11	67.38±1.89	14.6

Conclusion

This work proposes an efficient anion-cation synergistic strategy for performance enhancement in MPSCs. By introducing the ionic liquid additive EMIMAC into the perovskite active layer, high-efficiency and stable MPSCs were successfully fabricated. The synergistic effect of the $EMIM^+$ cation and acetate anion simultaneously passivates ionic defects and improves the TiO_2/perovskite interface contact, achieving optimized performance in defect passivation, charge transport promotion, and non-radiative recombination suppression. The PCE is significantly improved from 13.83% to 15.48%, and the unencapsulated devices maintain 90% of their initial efficiency after 60 days in ambient air (RH = 50$±$5%). This study provides a highly effective synergistic strategy for further improving MPSC device performance.

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