CsPbBr$_3$ Nanocrystal Induced Bilateral Interface Modification for Efficient Planar Perovskite Solar Cells

Jianjun Zhang, Linxi Wang, Chenhui Jiang, Bei Cheng, Tao Chen,* and Jiaguo Yu*

Organic-inorganic halide perovskite solar cells (PSCs) have drawn tremendous attention owing to their remarkable photovoltaic performance and simple preparation process. However, conventional wet-chemical synthesis methods inevitably create defects both in the bulk and at the interfaces of perovskites, leading to recombination of charge carriers and reduced stability. Herein, a bilateral interface modification to perovskites by doping room-temperature synthesized CsPbBr$_3$ nanocrystals (CN) is reported. The ultrafast transient absorption measurement reveals that CN effectively suppresses the defect at the SnO$_2$/perovskite interface and boosts the interfacial electron transport. Meanwhile, the in situ Kelvin probe force microscopy and contact potential difference characterizations verify that the CN within the upper part of the perovskites enhances the built-in electric field, facilitating oriented migration of the carriers within the perovskite. Combining the superiorities of CN modifiers on both sides, the bilaterally modified CH$_3$NH$_3$PbI$_3$-based planar PSCs exhibit optimal power conversion efficiency exceeding 20% and improved device stability.

1. Introduction

Organic-inorganic halide perovskite materials have shown immense potential in the emerging photovoltaic technology, owing to their prominent characteristics such as adjustable bandgap, high absorption coefficient, superb carrier mobility, and small exciton binding energy.[1–3] Due to great research efforts devoted during the past decade, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) have achieved impressive increase from 9.7% to 25.5%.[4,5] Nonetheless, there still exist great challenges to achieve desired PCEs, such as the formation of detrimental defects inside perovskite films and at interfaces during the fabrication of PSCs.[6,7] These defects serve as recombination sites for photogenerated electrons and holes, causing the loss of the effective carriers.[8] In addition, the defects are highly sensitive to moisture, heat, oxygen, and ultraviolet light, leading to decomposition of the perovskite.[9,10] Therefore, defect control is crucial for fabrication of PSCs with high efficiency and long-term stability. Multitudinous strategies have managed to reduce defect levels in perovskite films such as additive passivation, heterojunction engineering, and interface modification.[11–14] These methods mainly focus on modification of perovskites using salts, polymers, and molecules. However, the modifiers have completely different components and structures from perovskites and hence are immiscible. In this regard, modifiers with better physicochemical compatibility with perovskite will be more desirable.

Recently, lead halide perovskite nanocrystals and quantum dots (QDs) have been widely utilized in the field of light-emitting diodes, attributed to their high photoluminescence (PL) quantum yields (nearly 100%), outstanding processability, and simple preparation.[15–17] The perovskite nanocrystals still retain the superb optoelectronic properties of their bulk counterpart and possess similar characteristics in stoichiometry and crystal structure.[18] Hence, the perovskite nanocrystals can be a brilliant candidate for the modification in perovskite films and at interfaces. Previous studies have already verified the significance of perovskite nanocrystals and QDs in passivation. Concerning bottom modification of perovskite films, CsPbBr$_3$ nanocrystals (CN) based interlayer could serve as the seed-mediated layer for the subsequent crystallization of perovskite, leading to fewer defects in the perovskite and retarded charge recombination.[19] As for the top modification, C$_{0.95}$(MA$_{0.17}$FA$_{0.83}$)$_{0.05}$PbI$_3$ QDs were introduced into the perovskite film through solid-state
interdiffusion process, which passivated the ionic defects at the surface and grain boundaries.\(^{[20]}\) CsPbBrCl\(_2\) QDs were exploited as the molecular surface modifiers, realizing decreased tail states and reduced trap-state density.\(^{[21]}\) CN or nanowires based surface modifier successfully constructed a graded heterojunction at the upper part of perovskite film to ameliorate interfacial band alignment.\(^{[22,23]}\) CsPbBr\(_2\) QDs were utilized to construct a graded dimensional perovskite interface in all-inorganic PSCs, contributing to enhanced hole extraction and conduction efficiency.\(^{[24]}\) However, it has been neglected that bottom and top modification of perovskite film by perovskite nanocrystals can be achieved simultaneously. Besides, compared to the conventional hot-injection procedure, the preparation of perovskite nanocrystals can be simplified and conducted under much milder conditions.

In this work, CN is successfully synthesized via a simple one-step injection method at room temperature and applied as the bilateral interface modifier for CH\(_3\)NH\(_3\)PbI\(_3\) (MAPbI\(_3\)) perovskite film. To fulfill the CN bottom modification, CN is spin-coated on the SnO\(_2\) electron transport layer (ETL). CN can serve as the seed crystal to facilitate the seed-mediated growth of perovskite, which effectively passivates the SnO\(_2\) ETL/perovskite interface and reduces ionic defects in the perovskite film. Meanwhile, the CN can also decrease the energy barrier between the SnO\(_2\) ETL and the perovskite layer, enabling more efficient electron extraction. As for the CN top modification, toluene (TL) containing dispersed CN is utilized as the antisolvent during the spin-coating process of the perovskite film to realize gradational incorporation of CN at the upper part of perovskite film. Apart from passivating the surface and strengthening the moisture resistance, CN top modification can also shift down the Fermi level at the perovskite surface and thus enlarge the difference between Fermi levels in the surface and bottom layers. The increased gap between Fermi levels reinforces the built-in electric field, leading to boosted separation and oriented transport of carriers inside the perovskite film. Ultimately, by integrating the advantages in CN bottom and top modification, MAPbI\(_3\)-based planar PSCs with CN bilateral interface modification exhibit an average PCE of 20.1% and boosted device stability. Our findings have systematically revealed the functions of CN modification in the bilateral surface of perovskite film, which also provides guidance for the utilization of perovskite nanocrystals in perovskite-based devices.

2. Results and Discussion

The CN was prepared through a simple and fast one-step injection method in air at room temperature.\(^{[25]}\) The detailed synthesis process can be found in the Supporting Information. According to the transmittance electron microscopy (TEM) images (Figure S1a,b, Supporting Information), the as-prepared CNs possess an average size of \(\approx 10\) nm and the lattice spacing in the high-resolution TEM image corresponds to the (200) plane. The X-ray diffraction (XRD) results in Figure S1c, Supporting Information further verify that CN is well-crystallized into orthorhombic structure (PDF#18-0364).\(^{[26]}\) As exhibited in Figure S1d, Supporting Information, the UV–vis absorption and PL emission spectra illustrate the absorption edge of CN at \(\approx 524\) nm, equivalent to a band gap of \(\approx 2.37\) eV.\(^{[27]}\) The CN suspension (in TL) emits bright green light under 365 nm light excitation, which matches the band gap of CN.\(^{[28]}\)

Considering the superior dispersibility of CN in TL, we prepare CN/TL suspension for modification of perovskite films. Figure 1a depicts the steps of the CN bottom modification of pristine perovskite film (PSK). The CN is introduced onto the SnO\(_2\) ETL via spin-coating a CN suspension for two, four, and six times. All the solvents and ligands in the suspension evaporate quickly during the spin-coating. The obtained SnO\(_2\) ETLs after different cycles of spin-coating are marked as SnO\(_2\)/2-CN, SnO\(_2\)/4-CN, and SnO\(_2\)/6-CN, while the MAPbI\(_3\) perovskite films subsequently deposited on these ETLs are respectively labeled as 2-CN/PSK, 4-CN/PSK, and 6-CN/PSK. The surface morphology of the SnO\(_2\) ETL hardly changes with increasing times of CN bottom modification, but the root-mean-square roughness (\(R_s\)) of SnO\(_2\) ETLs gradually enlarges upon the introduction of CNs (Figures S2–S4, Supporting Information). As shown in Figures S3 and S5, Supporting Information, CN begins to aggregate after six cycles of CN bottom modification, leading to the nonuniform SnO\(_2\) surface. The agglomerating CNs will influence the normal crystallization process of perovskite, which is disadvantageous to the uniformity of perovskite layer. In addition, EDX mappings of Cs, Pb, and Br in the SnO\(_2\)/4-CN film reveal that the CNs are still uniformly distributed on the SnO\(_2\) surface after four times of CN bottom modification (Figures S6 and S7, Supporting Information). The XRD characterizations in Figure S8a, Supporting Information further confirm the presence of CN on the SnO\(_2\) film. During the wavelength region of 300–500 nm, the transmittance of the SnO\(_2\) films decreases with increasing contents of CN (Figure S8b, Supporting Information). This suggests that CN modified SnO\(_2\) films can absorb certain amount of ultraviolet (UV) light, which is potentially useful in alleviating decomposition of the perovskite film induced by UV radiation.\(^{[29]}\)

After CN bottom modification, the contact angles for SnO\(_2\) films decrease from \(\approx 55^\circ\) to \(\approx 45^\circ\) (Figure S9, Supporting Information and Figure 1b), which is beneficial for spreading the perovskite precursor solution onto the SnO\(_2\) ETL.\(^{[30]}\) During the spreading of perovskite precursor, the CN on the surface of SnO\(_2\) film are partially dissolved by N,N-dimethylformamide and dimethyl sulfoxide. Dissolved CsPbBr\(_2\) will recrystallize and incorporate into the MAPbI\(_3\) lattice at the bottom of perovskite film. The perovskite film grown on the CN modified SnO\(_2\) ETL has a nearly identical morphology to that on the pristine SnO\(_2\) ETL (Figure S10, Supporting Information), but its surface roughness slightly decreases (Figures S11–S13, Supporting Information). The XRD patterns in Figure S14a, Supporting Information further prove high crystallinity of the deposited perovskite films on the CN modified SnO\(_2\) ETLs. The slightly enhanced absorbance in the visible light region (Figure S14b, Supporting Information) also confirms improved crystallinity after CN bottom modification.\(^{[31]}\) Previous article has reported that the uniformly distributed nanocrystals are capable of adjusting the nucleation rate and new phase formation of the perovskite film.\(^{[32]}\) Hence, all the aforementioned improvements can be attributed to the reason that CN serves as the seed crystal to impel seed-mediated growth of the perovskite, which decreases the interfacial trap sites and reduces defects inside the perovskite film.\(^{[33]}\)

The electron extraction capability between the SnO\(_2\) ETL and the perovskite film is characterized by steady-state PL and
time-resolved transient PL (TRPL) on the FTO/SnO₂/CN/PSK sample. When all the samples are illuminated from the FTO-glass side, a blue shift of the PL peak is observed for the samples with CN bottom modification (Figure 1c), which does not happen when the samples are illuminated from the perovskite film side (Figure 1d). The blue shift reveals that the CN has directly become the structural component at the bottom of perovskite film. In comparison to pristine PSK, the 4-CN/PSK possesses the lowest PL intensity and shorter average lifetime (Figure S14c, Supporting Information), indicating more efficient...
electron transfer after moderate CN bottom modification.\textsuperscript{[34–36]} This is due to the capability of CN to reduce the ionic defects and suppress the interfacial charge recombination between SnO\textsubscript{2} ETL and perovskite film. The energy level alignment is another essential factor for efficient electron extraction.\textsuperscript{[37,38]} Based on the information of the ultraviolet photoelectron spectra (UPS) in Figure S15a–d, Supporting Information, the position distributions of the conduction bands (CB), valence bands, and Fermi levels (E\textsubscript{F}) for PSK and CN are calculated (Figure S15e, Supporting Information).\textsuperscript{[39]} As shown in Figure S15f, Supporting Information, the CB of CN is located between the CB of SnO\textsubscript{2} and MAPb\textsubscript{I\textsubscript{3}} perovskite, implying CN bottom modification is able to decrease the energy barrier between the SnO\textsubscript{2}/perovskite interface and reduce the energy loss during the electron transport.\textsuperscript{[40,41]}

To further understand the kinetics of charge transfer at the SnO\textsubscript{2}/perovskite interface, ultrafast transient absorption (TA) characterizations are conducted on the FTO/SnO\textsubscript{2}/(CN)/PSK sample with a 400 nm pump laser pulse. Figure 1e–h exhibits the representative pseudocolor 2D and transient TA spectra at different delay times. Two photobleaching (PB, ΔA < 0) signals and one photoinduced absorption (PIA, ΔA > 0) signal can be distinguished. The broad positive ΔA peak (PIA) from 550 to 600 nm corresponds to the absorption of certain transient species.\textsuperscript{[42]} The negative ΔA peaks at ≈ 480 nm (PB1) originate from the integration of PB and stimulated emission signals.\textsuperscript{[43]} Importantly, the PB2 signals approach to the absorption edge of MAPbI\textsubscript{3} and reflect the photo-induced carrier population in the MAPbI\textsubscript{3}, which can be well utilized to analyze the process of exciton generation and transport. The PB2 peak emerges quickly in just 1 ps (Figure S16, Supporting Information), because the MAPbI\textsubscript{3} possesses the Wannier–Mott type excitons with low binding energy and produces free charge carriers with high generation rate.\textsuperscript{[44]}

Owing to the hot carrier cooling, the PB2 peak rapidly intensifies within 5 ps.\textsuperscript{[45]} The following relaxation of the excited carriers is basically divided into two representative processes: solid lines in Figure 1e,f are ascribed to the bimolecular recombination induced pump-fluence dependent lifetime during a few hundred picoseconds, and the dotted lines in Figure 1e,f belong to the trap-assisted monomolecular recombination during thousands of picoseconds.\textsuperscript{[46]} Furthermore, the normalized decay kinetic curves at 759 nm are finely fitted by a bi-exponential function (Figure 1i) and their corresponding kinetic parameters are listed in Table S1, Supporting Information. The longer decay time (τ\textsubscript{L}) represents the excited-state decay or carrier recombination in perovskite films, while the shorter decay time (τ\textsubscript{S}) reflects the electron injection from photoexcited MAPbI\textsubscript{3} to the CB of SnO\textsubscript{2}.\textsuperscript{[47,48]}

Consequently, the electron injection time (τ\textsubscript{injection}) for the pristine PSK is calculated to be ≈ 611 ps (Figure 1j), which remarkably decreases to ≈ 258 ps with CN bottom modification (Figure 1k). The reduced τ\textsubscript{injection} verifies that CN bottom modification can effectively passivate the SnO\textsubscript{2}/perovskite interfacial defects and expedite interfacial electron transport.

Finally, the planar PSCs with the structure of FTO/SnO\textsubscript{2}/MAPbI\textsubscript{3}/Spiro-OMeTAD/Au are fabricated, and improved photovoltaic performance is observed after CN bottom modification (Figure S17a, Supporting Information). Benefiting from reduced defects and boosted electron extraction at the SnO\textsubscript{2}/perovskite interface, the 4-CN/PSK based PSCs demonstrate an average PCE of 19.4%, higher than ≈ 18.2% for pristine PSCs (Figure S17b and Table S2, Supporting Information). The PCE of the 6-CN/PSK based PSCs decreases owing to increased defects caused by agglomeration of the CN. Besides, electrochemical impedance spectroscopy (EIS) under dark condition (Figure S17c, Supporting Information) shows that the 4-CN/PSK based PSC possesses the largest semicircle, which also reveals that the charge recombination is significantly retarded inside the device.\textsuperscript{[49]} In conclusion, CN bottom modification can successfully ameliorate the interfacial contact between the SnO\textsubscript{2} ETL and the perovskite film.

In addition to controlling defects at the bottom of perovskite film, CN also possesses great potential as a surface modifier for perovskite films. The schematic of CN top modification is presented in Figure 2a. During the spin-coating process of perovskite, TL with dispersed CN is utilized as the antisolvent. The antisolvent is diluted to 5%, 10%, and 20% of its original concentrations to deposit the perovskite film, which are respectively marked as PSK(5%CN), PSK(10%CN), and PSK(20%CN). The distribution of CN within the perovskites is characterized by the glancing-angle XRD, whose schematic diagram is depicted in Figure 2b. X-ray with different glancing-angle (ω) is utilized to obtain the 2θ information for the (110) lattice plane at various depths. An increasing ω allows probing into deeper regions. With ω increasing from 0° to 2°, the position of the (110) peak gradually shifts to lower 2θ angle, suggesting a gradual expansion of lattice from the surface to the interior of the perovskite film (Figure 2c).\textsuperscript{[23]} This phenomenon also elucidates that the doping concentration of CN gradually decreases with increasing depth into the perovskite film. When ω increases from 2° to 4°, the 2θ angle for the (110) peak barely changes, illustrating that little CN exists at the bottom of the perovskite film. Therefore, a gradational incorporation of CN is constructed at the upper part of perovskite film. The surface roughness of the perovskite films slightly increases with CN top modification, while the typical compact and polycrystalline grain morphology remain (Figures S18–S20, Supporting Information). Meanwhile, the size of perovskite grains slightly decreases and the surface undulation mildly increases (Figure S21, Supporting Information). This can be interpreted as CN provides additional heterogeneous nucleation sites for the crystallization of MAPbI\textsubscript{3} perovskite.\textsuperscript{[50,51]}

As exhibited in Figure 2d, the peak intensity of (110) and (220) lattice plane is significantly enhanced with moderate CN top modification, and PSK(10%CN) sample possesses the strongest peak intensity. This confirms that CN facilitates the formation of ordered perovskite crystalline structure that is preferentially oriented along the (110) lattice plane, which is advantageous to the charge transport within the perovskite film.\textsuperscript{[15]} Thanks to improved crystallinity of the perovskite film, the light absorbance is also enhanced (Figure S22a, Supporting Information). Compared to the PSK, the PSK(10%CN) exhibits higher steady-state PL intensity (Figure S22b, Supporting Information) and longer average lifetime both in TRPL test (Figure S22c, Supporting Information) and TA measurement (Figure S23 and Table S3, Supporting Information), elucidating that non-radiative recombination sites are effectively minimized. The cations and anions from the CN can occupy the ionic vacancies at the upper part of MAPbI\textsubscript{3} film through solid-state interdiffusion, so the ionic defects at the surface and grain boundaries are significantly repaired.\textsuperscript{[20]} Ultimately, the PSK(10%CN) based PSC shows an
average PCE of 18.9% with increased open-circuit voltage ($V_{oc}$) and short-circuit current ($I_{sc}$) (Figure S24a,b and Table S4, Supporting Information), attributed to the ameliorative quality of the perovskite film and suppressed charge recombination (Figure S24c, Supporting Information). Consequently, the CN top modification is proved to be a brilliant ionic defect passivation strategy for perovskite films.

Another effect of CN top modification is tuning the surface potential of perovskite films, which can be investigated by Kelvin probe force microscopy (KPFM).

To acquire more specific information, the average surface work function ($W$) of the perovskite films is measured by the Kelvin probe instrument. Figure 4a exhibits the stable contact potential difference (CPD) values of the PSK, PSK(10%CN), and CN under dark condition and 461 nm light illumination. The related parameters including work function ($W$), Fermi level ($E_f$), and SPV can be calculated through the following equations:\[56]\]

$$SPV = CPD_{illumination} - CPD_{dark} \quad (1)$$

$$W = W_{tip} + e \cdot CPD_{sample} \quad (2)$$

$$E_f = -W \quad (3)$$

where CPD$_{illumination}$ and CPD$_{dark}$ represent the CPD of samples under dark condition and 461 nm light illumination, $e$ is the electron charge, and $W_{tip}$ is the standard $W$ of the gold probe (established to be 4.25 eV). Results of these surface characteristic parameters are listed in Table 1. The PSK and PSK(10%CN) have similar SPV, which is in consistent with the aforementioned KPFM results. According to the position of Fermi levels in PSK, CN, and PSK(10%CN), a schematic of Fermi level distributions is presented in Figure 4b. The Fermi level of the PSK is higher than that of the CN under both dark conditions and 461 nm light illumination. As discussed above, CN top modification can achieve a gradational incorporation of CN at the upper part of the
perovskite film and the doping concentration of CN gradually decays at deeper regions. Hence, a gradual downshift of Fermi level near the surface of PSK(10%CN) film is proposed. According to the CPD results, the Fermi level of PSK(10%CN) surface under dark condition and 461 nm light illumination is calculated to be $-4.64$ and $-4.74$ eV respectively, lower than the Fermi level of PSK surface. This is consistent with the aforementioned UPS results. As shown in Figure 4c, when the perovskite film is sandwiched between SnO$_2$ ETL and Spiro-OMeTAD HTL, a stabilized Fermi level is formed at the bottom ($E_{\text{F bottom}}$) and surface
Figure 4. 

(a) In situ CPD detection of PSK, CN, and PSK (10% CN) under dark condition and 461 nm light illumination. 

(b) Schematic for the Fermi level of PSK, CN, and PSK (10% CN) under dark condition and 461 nm light illumination. 

(c) Schematic for the changes of Fermi level at the interfaces of PSK/ETL and PSK/HTL.

(E_{surface}) of perovskite film after interfacial charge transfer.\(^{[57,58]}\) The difference in Fermi levels (E) at the bottom and surface of the perovskite film is the source of the built-in electric field, which is the driving force for the separation of electrons and holes inside perovskite film.\(^{[59]}\) Hence, the built-in electric field can be enlarged by increasing the difference in Fermi levels.\(^{[60]}\) With CN top modification, an increased difference in Fermi levels (ΔE) is achieved under both dark and illuminated conditions, resulting in a stronger built-in electric field that better orients charge transfers to further enhance the photovoltaic performance of PSCs. In conclusion, the ameliorative oriented charge transfer also contributes to the optimal PCE of PSK (10% CN) based PSCs.

In order to study the synergy of CN bottom and top modification, the planar PSCs with bilateral interface modification are fabricated (Figure 5a). The optimal concentration of CN bottom modification and top modification is chosen for the bilateral interface modification, and the obtained bilaterally modified perovskite film is labeled as 4-CN/PSK (10% CN). The photovoltaic performance of the planar PSCs composed of FTO/SnO\(_2\)/4-CN/PSK(10% CN)/Spiro-OMeTAD/Au has also been investigated (Figure 5b) with corresponding photovoltaic parameters listed in Table 2. The 4-CN/PSK (10% CN) based planar PSCs demonstrate an average PCE of 20.1%, higher than that of the PSK, 4-CN/PSK, and PSK (10% CN) based PSCs. All the related photovoltaic parameters including \(V_{OC} \), \(J_{SC} \), and \(FF \) are improved through bilateral interface modification. Especially, the incident photon-to-current conversion efficiency results in Figure S26a, Supporting Information further confirm that 4-CN/PSK (10% CN) based PSC displays a reinforced photoelectric response during the wavelength of 400–700 nm. This distinguished photovoltaic performance results from the combined effects of higher quality of perovskite film and more efficient charge extraction. To further verify the enhancement of PCE, stabilized photocurrent density and power output with a bias of maximum power point (MPP) voltage (0.88 V for PSK and 0.91 V for 4-CN/PSK (10% CN)) are exhibited in Figure 5c. The 4-CN/PSK (10% CN) based PSC demonstrates excellent \(J_{SC} \) of 21.65 mA cm\(^{-2}\) and PCE of 19.7% at steady state, whereas the pristine PSK based PSC only shows inferior \(J_{SC} \) of 20.23 mA cm\(^{-2}\) and PCE of 17.8%. The results of the stabilized PCE are close to the values extracted from the \(J-V\) curve.

Table 2. Detailed photovoltaic parameters for PSCs based on diverse CN modification (25 devices are fabricated for each sample).

| Samples            | \(V_{OC} \) [V] | \(J_{SC} \) [mA cm\(^{-2}\)] | \(FF \) [%] | PCE [%]  |
|--------------------|-----------------|-------------------------------|-------------|----------|
| PSK                | 1.11 ± 0.01     | 23.07 ± 0.37                  | 71.1 ± 1.6  | 18.2 ± 0.6 |
| 4-CN/PSK           | 1.12 ± 0.01     | 23.88 ± 0.26                  | 71.3 ± 1.4  | 18.9 ± 0.5 |
| PSK (10% CN)       | 1.12 ± 0.01     | 24.08 ± 0.24                  | 71.6 ± 1.1  | 19.3 ± 0.4 |
| 4-CN/PSK (10% CN)  | 1.13 ± 0.01     | 24.35 ± 0.16                  | 73.0 ± 1.2  | 20.1 ± 0.5 |

On the basis of the \(J-V\) curves under illumination (Figure 5b) and dark condition (Figure S26b, Supporting Information), the exciton dissociation probabilities in PSK and 4-CN/PSK (10% CN) based PSCs can be analyzed by photocurrent density \(J_{ph}\) and effective voltage \(V_{eff}\).\(^{[61]}\) They are calculated through the following formulas:\(^{[62]}\)

\[
J_{ph} = J_L - J_D \tag{4}
\]
\[
V_{eff} = V_0 - V \tag{5}
\]

where \(J_L \) and \(J_D \) are the current density under illumination and dark condition; \(V_0\) represents the compensation voltage when \(J_{ph} = 0\) and \(V\) signifies the applied voltage bias. As reflected in Figure 5d, \(J_{ph}\) increases sharply at the low \(V_{eff}\) and attains a
Figure 5. a) Schematic for CN bilateral interface modification of perovskite film. Characterizations of PSK and 4-CN/PSK(10%CN) based planar PSCs: b) $J$–$V$ curves under simulated AM 1.5 illumination; c) steady-state photocurrent and PCE measured at the maximum power point; d) plots of photocurrent density ($J_{ph}$) with regard to the effective bias ($V_{eff}$); e) normalized photocurrent ($J_{ph}/J_{sat}$) with regard to $V_{eff}$; f) EIS plots tested under dark condition. g) $J$–$V$ curves of the electron-only devices based on PSK and 4-CN/PSK(10%CN) active layer.

The PSK device shows higher $J_{sat}$ at higher $V_{eff}$. The 4-CN/PSK(10%CN) based PSC reaches $J_{sat}$ earlier than the pristine PSK based PSC, elucidating that more efficient charge separation is achieved through bilateral interface modification. In addition, the light-harvesting ability of perovskite layer can be revealed via the maximum exciton-generation rate ($G_{max}$), as obtained by the following equation: \[ G_{max} = \frac{J_{sat}}{q \cdot L} \]
where $q$ represents the charge quantity of one electron (1.6 × $10^{-19}$ C) and $L$ is the thickness of perovskite film (≈400 nm). Intriguingly, the 4-CN/PSK(10%CN) demonstrates superior $C_{\text{max}}$ of $3.92 \times 10^{27}$ m$^{-3}$ s$^{-1}$, whereas pristine PSK film exhibits inferior $C_{\text{max}}$ of $3.51 \times 10^{27}$ m$^{-3}$ s$^{-1}$. The boosted $C_{\text{max}}$ also indicates that the light harvest and utilization of perovskite film are effectively improved through bilateral interface modification. Moreover, the normalized photocurrent density $J_{\text{ph}}/J_{\text{sat}}$ in Figure 5e can manifest the exciton dissociation probability ($P_{\text{d}}$) \cite{64}. When $V_{\text{oc}}$ is 0.1 V, the $P$ values of PSK and 4-CN/PSK(10%CN) based PSCs are 50% and 66%, respectively. The increased probability implies the exciton recombination is suppressed inside 4-CN/PSK(10%CN) based PSC, consequently proving that CN bilateral interface modification contributes to more efficient charge separation and extraction. An enlarged semicircle is observed for the 4-CN/PSK(10%CN) based PSC in the EIS test (Figure S5), illustrating the recombination of carriers is effectively suppressed owing to the reformative interface and decreased defects induced by the CN bilateral interface modification. To measure the trap density of the perovskite films, space charge limited current (SCLC) test is conducted on a device composed of FTO/SnO$_2$/perovskite/PCBM/Au. The trap-filled limit voltage ($V_{\text{TFL}}$) is acquired through the intersection voltage of ohmic and trap-filled limit region, and the trap-state density ($N_{\text{traps}}$) can be determined by the following equation\cite{65,66}:

$$N_{\text{traps}} = \frac{2 \varepsilon_0 \varepsilon_r V_{\text{TFL}}}{qL}$$  \hspace{1cm} (7)

where $\varepsilon_0$ signifies the vacuum permittivity, $\varepsilon_r$ represents the relative dielectric constant of MAPbI$_3$. The $N_{\text{traps}}$ of PSK and 4-CN/PSK(10%CN) are calculated to be $3.10 \times 10^{16}$ cm$^{-3}$ and $2.04 \times 10^{16}$ cm$^{-3}$, respectively. The reduced $N_{\text{traps}}$ intuitively proves that the defects inside the perovskite film and at the interfaces are significantly passivated through CN bilateral interface modification.

Apart from the enhancement of photovoltaic performance, the device stability is another critical factor for planar PSCs.\cite{67,68} It has been previously reported that multiple types of defects, such as vacancies of Pb$^+$ or I$^-$, grain boundaries and dangling bonds, are more likely to form at the interfaces between perovskite film and its adjacent layers than the bulk perovskite.\cite{69,70} The lattice in these positions is extremely fragile and effortlessly destroyed by moisture and heat, thus the decomposition of perovskite film generally begins at the interface.\cite{71,72} As shown in Figure S27, Supporting Information, the moisture resistance of perovskite film has been reinforced by CN top modification. Except for passivating the defects at the surface, the incorporation of Cs$^+$ and Br$^-$ with smaller radii in the lattice also strengthens the ionic and covalent bonding of perovskite.\cite{73} Therefore, these two features slow down the moisture ingress and kinetic behavior of perovskite film, leading to superior moisture stability. Moreover, the long-term stability test of PSCs is performed in atmosphere at a humidity of 60% ± 5%. As shown in Figure S28, Supporting Information, the PCE of 4-CN/PSK(10%CN) based PSC still maintains above 90% after 36 days, whereas the pristine PSK based PSC dramatically drops below 80%. This further confirms that the CN bilateral interface modification can reduce the defect density inside the device and increase its tolerance to moisture.

3. Conclusion

In summary, we have demonstrated a simple and effective strategy to ameliorate the perovskite active layers through bilateral interface modification using room-temperature synthesized CN. Through CN bottom modification, CN is uniformly introduced on the surface of SnO$_2$ ETL, where CN based seed crystal can initiate the seed-mediated growth of perovskite to reduce the innate defects in perovskite films and facilitate interfacial electron transport. With CN top modification, a graded heterojunction is constructed at the upper part of perovskite film, which increases the difference between Fermi levels at the bottom and surface of perovskite film. This results in a stronger built-in electric field which is advantageous for the separation and oriented migration of electrons and holes inside the perovskite film. Combining the merits of CN bottom and top modification, the CN bilateral interface modified MAPbI$_3$-based PSCs demonstrate an average PCE exceeding 20% and ameliorative device stability. Consequently, our work provides significant insights into the systematic utilization of perovskite nanocrystal to boost the photovoltaic performance of planar PSCs, which facilitates the advancement of perovskite based optoelectronic devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51961135303, 51932007, U1905215, 21871217, 52073223, and U1705215), the National Key Research and Development Program of China (2018YFB1502001), and China Postdoctoral Science Foundation (2021TQ0311).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

built-in electric field, CsPbBr$_3$ nanocrystals, defect passivation, gradational incorporation, interface modification

Received: July 9, 2021
Revised: August 10, 2021
Published online: September 13, 2021
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