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Understanding the Passivation Mechanisms and Opto-Electronic Spectral Response in Methylammonium Lead Halide Perovskite Single Crystals

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Supporting Information

ABSTRACT: Attaining control over the surface traps in halide perovskites is critical for the tunability of ultimate device characteristics. Here, we present a study on the modulation of photophysical properties, surface traps, and recombination in MAPbI₃ single crystals (MSCs) with methylamine (MA) vapor surface treatment. Transient photoluminescence spectroscopy in conjunction with density functional theory calculations reveals that nonradiative recombination related to Pb²⁺ becomes mitigated after MA vaporizing while radiative recombination via bimolecular path tends to increase, which originates from the passivation of Pb ions with the Lewis base nitrogen in MA. In contrast to the broad photoresponse in the pristine MSC photodiodes, application of MA surface treatments leads to a spectral narrowing effect (SNE) in MSCs with the response peak width <40 nm. On the basis of the examined photon-cycling effect with MA treatment that indicates a reduction of exciton diffusion into the interior region of MSCs, we attempt to propose an operation mechanism for the SNE which can be related to the overall stronger surface recombination and resulting severe photocarrier losses, such that the charge collection and quantum efficiency from the above-band gap absorption decrease. This work provides a facile approach with chemical means to tune the surface properties and eventual spectral selectivity in MSCs that are promising for photon-detection device applications.

KEYWORDS: spectral narrowing effect, MAPbI₃ single crystal, MA gas surface treatment, surface recombination, traps passivation

INTRODUCTION

In the last couple of years, the emerging methylammonium lead halide (MAPbX₃, MA = methylammonium, X = halide) perovskites have stirred up enormous research interest in optoelectronic applications,^{1–7} achieving record laboratory efficiencies >22% in perovskite solar cells.⁸ The strong oscillator strength, high band gap tunability, and large carrier mobility enable exciting photodetection applications based on these materials. Through state-of-the-art band gap engineering, broadband photodetectors comprising solution-processed MAPbX₃ polycrystalline films have been demonstrated showing fast photoresponse and high photodetectivity.^{6,9,10} In contrast to organic semiconductors or inorganic quantum dots, MAPbX₃ perovskites are generally characteristic of a broad optical absorption. Therefore, realization of the spectral narrowing effect (SNE) in the photoresponse based on perovskite absorbers has stirred up the research attention.

Narrowband photodetectors (NB-PDs) with the SNE are found with wide applications in communication, surveillance, imaging, or biomedical sensors.^{11–13} The realization of NB-PDs often requires to use bulky optical bandpass filters or photoactive layers with intrinsic narrowband absorption, which undesirably increases the fabrication cost or synthetic difficulties to attain photoresponsive materials with truly low bandwidth absorption. Recently, NB-PDs based on polycrystalline films or single crystals of MAPbX₃ have been proposed,^{14,15} which enabled to achieve a full-width at half maximums (FWHMs) less than 20 nm. The SNE can be ascribed to the wavelength-dependent oscillator strength in the perovskite active layer to modulate the surface external

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Figure 1. (A) Lattice structure and photo of MAPbI₃ single crystals (MSCs). (B) The illustrated procedure of methylamine gas surface treatment for MSCs (left panel) and top-view scanning electron microscopy image of MSCs without and after MA gas treatment. (C) Steady-state photoluminescence (PL) spectroscopy of MSCs with various MA surface treatment time. (D) PL peak position of MSCs as a function of MA treatment time. (E, F) PL mapping of various surfaces of MSCs captured by laser confocal microscopy.

quantum efficiency (EQE) via surface charge recombination and resulting spectral width. To achieve the SNE, fine-tuning of the active layer thickness and complex sequential depositions for asymmetric contacts/charge blocking interlayers with sandwich device architecture are required. Alternatively, planar photodiodes with symmetric electrodes have been proposed for NB-PDs which allow for both narrowband and broadband detection modes.¹⁶ In this configuration, the narrowband mode requires that the irradiated surface differs from that for charge collection, which, to some degree limits the flexibility of device operation. To date, there are rare reports on the photoresponse tuning and SNE in perovskite single crystals based on chemical approaches. As key processes of charge transport, all recombination and extraction occur near the surface areas in planar diodes, the application of appropriate surface modification may lead to desired device behaviors.

In this communication, we present a study on the modulation of surface properties by methylamine (MA) gas treatment for MAPbI₃ single crystals (MSCs). We show that the broadband photoresponse in the pristine MSCs can be tuned into a narrowband operation after the MA surface treatment, achieving a response peak with FWHM < 40 and photoresponsivity of ~60 A/W. Photoluminescence (PL) decay kinetics reveal that the surface charge trapping and the resulting Shockley–Read–Hall (SRH) recombination become mitigated after MA gas treatment. We also observe a reduction in red-shifts during the evolution of PL in MA-treated crystals that contrasts with the nontreated MSCs, implying a suppression on the photon-cycling effect (PCE) with MA. On the basis of these results, we propose a mechanism for the spectral modulation with MA treatments that is related to the acceleration of radiative recombination. As a result, charge collection and ultimate external quantum efficiency (EQE)

originating from the above-band gap absorption are effectively suppressed.

EXPERIMENTAL SECTION

Materials. CH₃NH₃I was purchased from Dyesol Limited (Australia). Lead iodide (99%) and γ -butyrolactone (GBL) used for sample preparation were purchased from Sigma Aldrich. Methylamine (40% in water) was bought from Aladdin. All materials were used as received without further purification.

Growth of MAPbI₃ Single Crystals. The precursor solution of MAPbI₃ seed single crystals was prepared by mixing CH₃NH₃I (0.103 g) and PbI₂ (0.297 g) in 0.6 mL of GBL solvent. The solution was heated up to 90 °C and kept for 12 h, leading to the formation of seed crystals. The crystalline seeds were merged in GBL solution (6 mL) with the same concentration (wt) as the precursor solution and was kept at 90 °C. MAPbI₃ single crystals were formed with a dimension of up to 6 mm × 4 mm × 3 mm. The sample was stored in a N₂ purged glow box before use.

Process for MA Gas Treatment and Device Fabrication. Grown MAPbI₃ perovskite crystals without polishing were placed right on top of a vial containing 40% CH₃NH₂ aqueous solution and the treatment was controlled between 3 and 9 s in a fume hood. The samples were then removed quickly to ambient environment. The MA-treated (and pristine) MSC samples were transferred into a thermal evaporator for Au deposition (80 nm) and the electrode pattern was defined through shadow masks with a typical channel length of 70 μ m and a width of 1 mm.

Characterization. Steady-state PL spectroscopy was performed by using a Horiba Fluorolog-III spectrofluorometer sourced by a Xe lamp (slit < 5 nm). PL mapping of MSCs was captured by a Witec Alpha scanning near-field optical microscopic system under the Raman scanning mode. The sample was excited by a laser beam at 432 nm (Omnichrome Series 74) which was focused through a series of microscopic lens (60 $\times$, Nikon Inc.). Time-resolved PL spectra were recorded with a Hamamatsu streak camera working in a single-sweep mode. The excitation source (Spectra-Physics) was the same mode-locked femtosecond laser with a repetition rate of 76 MHz; a pulse picker was inserted on the optical path to decrease the repetition rate

Figure 2. (A, B) Two-dimensional contour image of time-resolved PL spectroscopy measured on freshly grown (A) and mechanically cleaved (B) MSCs with various MA surface treatments. (C, D) Normalized PL decay kinetics of freshly grown (C) and mechanically cleaved (D) MSCs with respective surface treatments.

of the laser pulses when needed. X-ray photoelectron spectroscopy (XPS) was performed utilizing a ThermoFisher ESCALAB 250Xi system. Dark current–voltage characteristics of MSC planar diodes were determined by a Keithley 4200-SCS semiconductor parameter analyzer. The spectral response was measured by shining monochromatic light on top of the MSC crystal facade containing the Au electrodes using a Zolix monochromator and resulting photocurrents were recorded by the parameter analyzer under specific biases. Electrical poling on MSC diodes was performed by applying a constant voltage stress provided by the Keithley 4200-SCS analyzer. All electrical measurements were performed in a LakeShore vacuum probe station at room temperature.

RESULTS AND DISCUSSION

Photoluminescence and Structural Properties in MA-Treated MSCs. MA has been applied to mediate crystallization and defects in MAPbX_3 polycrystalline thin films, enabling to boost the device performance.¹⁷ Here, we tentatively utilized MA gas treatment as a surface mediator for MSCs and investigated how the surface treatment impacts the resulting photoresponse. MSCs (see the tetragonal lattice structure in Figure 1A) were attained by using the inverse temperature crystallization method reported previously.¹⁸ A detailed synthetic procedure can be found in the Experimental Section. The largest natural facade of the studied MSCs has a diagonal length of ~ 6 mm with an average thickness of ~ 2 mm (see the sample picture in Figure 1A). Figure 1B illustrates the procedure of MA gas treatment for MSCs. To start, 9 mL of MA aqueous solution (40%) was pre-prepared in a 10 mL sized vial. The freshly grown MSCs were held right above the vial containing MA solution (without capping) with the natural crystal facade exposed to the MA gas. The treatment was

controlled by the MA exposure time. To examine the surface morphology influenced by MA gas treatment, we performed top-view scanning electron microscopy (SEM). As shown in Figures 1B and S1A,B in the Supporting Information (SI), we cannot observe any grain boundaries in these samples, in line with the single crystalline feature. The MSC with MA gas treatment displays a smoother surface feature with the disappearance of the imperfect spots (in the pristine MSC). On the other hand, there appear visible cracks with an average thickness of ~ 0.6 μm on the surface of MA-treated crystal (6 s), which may be caused by a varied surface tension upon MA treatment or the solvation of MAPbI_3 by MA gas. We further examined these cracks in the actual charge transporting channels of MSC diodes (see SEM in Figure S2, SI). The density of cracks tends to be proportional to the treatment time, for example in the 3 s treated MSCs, these cracks are merely observed. Surprisingly, the surface of MSCs with 9 s treatment seems to be healed, displaying considerably reduced density of cracks. At this moment, the exact reason for the appearance of cracks in the specific morphology is not fully understood. However, as will be discussed below, these cracks are found not to serve as a significant barrier for the lateral charge transport in the MSCs.

The presence of surface traps in perovskites, commonly originating from under-coordinated ions or structural defects can significantly influence the photophysical processes and resulting device behavior. In this perspective, it is informative to examine photoluminescence (PL) properties to assess the surface traps in MSCs. We first examined steady-state PL on MSCs by confocal laser scanning microscopy with the spectra shown in Figure 1C. The PL of untreated MSCs is positioned

at ~ 775 nm, consistent with the result in previous studies.¹⁹ Upon incrementally varying the time for MA treatment, the PL intensity increases, which indicates the enhancement of radiative recombination, possibly due to the decrease in the concentration of surface traps. Moreover, the PL exhibits progressive blue-shifts with increasing MA gas treatment time (see dashed arrow in Figure 1C,D). The maximal blue-shift is ~ 17 nm with 12 s treatment. Figure 1E,F display the PL mapping of untreated and MA-treated (9 s) MSCs (scan size = $16 \mu\text{m} \times 16 \mu\text{m}$). Both samples exhibit a relatively homogenous PL distribution while this result does not necessarily indicate the lack of grain boundaries because of the poorer lateral resolution (~ 400 nm) of the PL mapping with respect to the grain sizes that are generally found to be much smaller in perovskites. Given a large solubility of MAPbI₃ in MA gas,¹⁷ the monocrystalline structure at the surface may be destructed upon over-exposure to MA gas, therefore, treatments beyond the optimal conditions (around 9 s) are beyond the interest of this study.

To shed more light on the surface traps, we examined steady-state PL alongside the PL decay kinetics of MSCs using above-band gap excitation (532 nm). We compared the PL of freshly grown samples with mechanically cleaved MSCs, through which the surface and bulk properties influenced by MA gas treatment are disentangled. Figure 2A,B show two-dimensional images of time-resolved PL spectroscopy registered by a streak camera. In noncleaved MSCs, we observed progressive blue-shifts in PL upon increasing the MA treatment time. The PL in MA-treated MSCs is slightly broadened, especially after 9 s treatment. Here, the PL measurements performed were in the single-photon mode which mainly reflects the surface conditions (due to the large extinction coefficient in MAPbI₃). The broadening PL width seems to be in line with an increased polycrystallinity at the vicinity of the MSC surface after MA gas treatment.¹⁷ To note, the blue-shifts become less pronounced for PL measured on mechanistically cleaved surfaces after MA treatment. The intensity of PL (with MA-treatment) also changes less significantly in comparison to that of the MA-treated MSC without cleavage. Such differences are interpreted by the isolation from the MA surface modification in the bulk region. We further extracted the PL decay kinetics of different MSCs with the results shown in Figure 2C,D. The transients were fitted with the bi-exponential decay model (see results in Figure S3, SI) and the extracted time constants alongside respective coefficients are summarized in Table 1. The main spectroscopic evidence includes: (1) longer-lived PL (for both fast and slower decays) in noncleaved MSCs upon increasing the MA exposure time, indicative of a shrinkage of surface

trapping; (2) reduced impact of MA gas treatment on the decay kinetics of cleaved samples. These results point to an indication that the modifications provided by MA gas treatment primarily occur at the surface region of the MSC while the bulk is less affected, and thus, the elongated PL lifetime mainly results from the surface traps passivation by MA gas treatment.

We attempted to attain the knowledge on the structural impact of MA treatment by X-ray diffractometry (XRD). As shown in Figure S4, SI, the surface of pristine MAPbI₃ should be in the form of single crystal and we cannot observe the peaks arising from the crystallographic planes along other orientations. In contrast, with the application of MA gas treatment, additional XRD peaks that are assigned to other crystallographic planes (with respect to the main lattice structure in MSCs) are observed. The longer the MA gas was treated, the larger number of XRD peaks appeared, which points to more random orientations. These results indicate that MA treatment possibly leads to changing the surface of MSCs to the polycrystalline form and after certain time, the surface is dominated by polycrystalline MAPbI₃.

With the structural changes to polycrystalline form, larger numbers of grain boundaries are likely introduced into the surface area in the perovskite crystal, causing more severe structural defects. This result seems to be counter-intuitive to the observed enhancement of PL properties. To clarify the effect of MA-treatment on surface trapping, we performed X-ray photoelectron spectroscopy (XPS). Figure 3A shows high-

Figure 3. (A) High-resolution (normalized) X-ray photoelectron spectroscopy of core level I 3d and Pb 4f measured on various MSC samples. (B) Adsorption of MA molecules to the (110) surface of MAPbI₃ perovskites attained by density functional theory calculation. Oval highlights the MA molecule used to passivate the perovskite surface.

Table 1. Decay Time Constant and According Percentage of Time-Resolved PL Spectroscopy in Figure 2C,D Obtained through Bi-exponential Fittings

		τ_1 (ns)	τ_2 (ns)
cleaved	w/o MA gas-treated	1.884 (84.9%) ^a	16.33 (15.1%)
	MA-treated, 6 s	3.61 (67.3%)	15.8 (32.7%)
	MA-treated, 9 s	12.08 (43.6%)	41.23 (56.4%)
noncleaved	w/o MA gas-treated	5.93 (74.5%)	39.7 (25.5%)
	MA-treated, 6 s	5.42 (61.1%)	43.6 (38.9%)
	MA-treated, 9 s	9.33 (60.3%)	61.99 (39.7%)

^aValues in parenthesis are the percentage of each decay component.

resolution XPS spectra of the core level Pb 4f and I 3d in MSCs. On the basis of the peak area calculation, we estimated the ratio of I to Pb with the results provided in Table 2. In all cases, the ratio ranges between 2 and 2.5, exhibiting an I-deficient (or Pb-rich) feature at the MSC surface. This agrees with a previous study where Pb-rich surfaces were identified in MSCs.^{20,21} Notably, the I/Pb ratio increases with increasing

Table 2. Percentage Ratio of I 3d to Pb 4f Peaks in X-ray Photoelectron Spectroscopy of MSCs with Various Surface Treatments

	pristine	MA gas (6 s)	MA gas (9 s)
averaged ratio ^a	2.045	2.356	2.533

^aValues are averaged on the XPS measurements at three different locations in each sample.

t_{MA} , indicating a reduction in the nonstoichiometry near the surface area. It is generally known that the presence of under-saturated Pb ions (near the perovskite surface) serves as the main source for electron traps. In the regard, the reduced nonstoichiometry points to the mitigation of surface electron traps. This result fully agrees with the enhanced PL with a longer decay time, due to the suppression on nonradiative recombination.²² To shed more light on the possible chemical pathway for the surface passivation with MA gas treatment, we performed density functional theory (DFT) calculations (see calculation details in the SI). The calculated adsorption energies for different binding sites in MAPbI₃ with MA indicate that the MA molecule tends to be stabilized at the top

site of Pb²⁺ with an adsorption energy of -0.48 eV. On the basis of the DFT results, we schematically illustrate the adsorption of the MA molecule on the (110) plane of MAPbI₃ perovskites (see Figure 3B). We also found that MA displays a tendency to bind to the surface through a N atom with the Pb–N distance of 2.79 Å. On this basis, the improved stoichiometry evidenced by XPS may be interpreted by the stabilization for those under-saturated Pb²⁺ cations (at the surface) with the adsorption of MA, leading to effectively decreasing surface electron trapping.²²

Combining these surface analyses, the modified surface with the passivation for Pb²⁺ can be the main reason for the enhanced PL, despite the associated structural disorder (with likely more grain boundaries) after MA treatments.

Photoresponse in MSC Photodiodes. With the identified impacts of MA treatment on the surface properties, we examined the SNE in MSC planar diodes mediated by MA gas treatment. Concerning the adopted device architecture shown in Figure 4A, the transport direction in MSC diodes is along the natural crystal facade (or <110> plane) defined by the two Au electrodes in parallel. In a previous study, the electrical poling was shown to play a significant role in the diode

Figure 4. (A) Illustrated device structure of MSC planar photodiodes. (B) Dark current density versus voltage (J – V) characteristics of MSC planar diodes without and after MA surface treatment (9 s). Also compared are J – V curves of devices before and after electrical poling. (C) J – V characteristics of nonpoled and poled MSC planar diodes with MA surface treatment measured under continuous wavelength (CW) irradiation. (D) The photocurrent to dark current ratio of various MSC planar diodes in response to CW irradiation. (E) Spectral response of MSC planar diodes under monochromatic irradiation. (F) Comparison of the spectral narrowing on the photoresponsivity of MSC planar diodes without and after MA surface treatment.

Figure 5. Temporal evolution of PL measured on (A) noncleaved and (B) mechanically cleaved MSC samples with various surface treatments examining the photon-cycling effect. (C, D) Diagrammed charge generation processes near the surface (surface charge generation zone) and bulk (bulk charge generation zone) areas inside (C) nontreated and (D) MA gas-treated MSCs. The horizontal lines in (C) with arrows denote the electrical field across the planar device.

behavior of MAPbI₃ polycrystalline films.²³ Here, we found that electrical poling (with applying a pre-direct current (DC) bias of 60 V on the device for 300 s) is necessary to attain stable device operation under irradiation. As a background study, we first compared dark carrier transport in MSCs with the current versus voltage (*I*–*V*) characteristics under various pre-conditions shown in Figure 4B. The device without poling and MA gas treatment displays a pronounced hysteresis with the least current. In contrast to the symmetric *I*–*V* curve in the nonpoled device, strong rectification is observed after poling based on both pristine and MA-treated MSCs. This behavior resembles that in sandwich devices using asymmetric contacts and can be rationalized by the poling-induced electrochemical doping near the contact areas, such that the *V*_{bi} across the device is changed.^{24,25} Of note, the MA-treated diodes display a considerably reduced hysteresis. Given the origins of the occurring hysteresis in perovskites including traps, and/or ion motion etc.,^{26–29} it is likely that the smaller hysteresis benefits from the mitigated surface traps or/and ionic motion in the MA-modified MSC surface with passivated Pb ions. Through the combination of electrical poling and MA treatment, we attained hysteresis-free and strongly rectified diode characteristics. This allows for a photodiode operation based on the planar device structure with symmetric Au electrodes. Hereinafter, we focus on the behavior of photoresponse in the reverse bias regime.

Figure 4C shows *I*–*V* curves of various MSC diodes under continuous wavelength (CW) irradiation. In all devices, enhanced current at reverse bias is observed. We calculated the photocurrent to dark current ratio ($(I_{\text{light}} - I_{\text{dark}})/I_{\text{dark}}$), where *I*_{light} and *I*_{dark} denote the current under illumination and in the dark (see results in Figure 4D). As can be seen, the device in the absence of poling and MA treatment displays the largest photocurrent to the dark current ratio (>10⁴%) under

CW illumination, which can be mainly due to the poorest dark transport. Those with MA-treatment display a reduced ratio under CW irradiation (in the order of 10³%), which will be discussed below, is mainly due to the narrowed spectral response.

Next, we focused on the SNE in MSC devices under various pre-treatments, which is an important metric for NB-PDs. Figure 4E displays the photocurrent of MSC planar diodes under monochromatic illumination under a DC bias of –1 V. The same pre-poling condition was applied to the compared MSC diodes, which assures the reliability of measurements under continuous biasing. As can be seen, the device based on nontreated MSC exhibits a flat photoresponse up to ~800 nm, which is slightly blue-shifted with respect to the absorption cut-off at ~850 nm (see absorption spectra of MSC in Figure S5, SI). The flat spectral response is consistent with the broad absorbance of MSCs. Notably, the spectral shape starkly changes after MA gas treatment and an obvious SNE with peak-like spectral shape is observed. The increased spectral selectivity around 820 nm leads to a suppression on the photoresponse in the range below 750 nm and above 900 nm. Such phenomenon is analogous to the demonstrated SNE in sandwich perovskite photodetectors where the EQE from the above-band gap absorption is strongly suppressed when the perovskite absorber reaches a threshold thickness. Advantageously, the rendered SNE in the MSC planar diodes with MA gas treatment does not rely on the thickness of perovskites. It is important to note that the absorption of MA-treated MSCs maintains a broad feature (Figure S5, SI) with the absorption cut-off nearly unchanged after MA treatment. On the basis of these results, the realization of the SNE should be ascribed to other photophysical origins which will be explored below.

To enable more quantitative assessments on the SNE, we calculated the photoresponsivity (*R*) with the relation, *R* =

$I_{\text{light}}/P_{\text{light}}$ where P_{light} denotes the energy of incident illumination. As shown in Figure 4F, we attained an R of ~ 60 A/W around 820 nm, which could be owing to an efficient charge migration with a long diffusion length in MSCs.¹⁹ Of interest, the maximal R remains unchanged, regardless of the MA modification while the spectral center is slightly red-shifted in the MA-treated device. The sharp photoresponsivity leads to small FWHMs < 40 nm. These values are on a par with the state-of-the-art devices based on halide perovskite photoabsorbers.¹⁴ We further examined the influence of the MA treatment time (t_{MA}) on the spectral shape (see results in Figure S6, SI). In contrast to the evident variation in the PL properties, the SNE is seemingly insensitive to t_{MA} (up to 9 s), revealed by the resembling peak position and FWHM. Upon increasing the t_{MA} to 12 s, the R slightly decreases, which is possibly due to the dissolution of MSCs upon excess exposure to MA gas, inducing a destructive effect on the photoresponse.

To gain further insights into the mechanism behind the enhanced spectral selectivity, we measured temperature (T)-dependent characteristics of photocurrent versus irradiation wavelength with the results shown in Figure S7, SI. In previous studies, the mobility of MSCs was found to be associated with a positive T -coefficient roughly described as $\mu \sim T^\alpha$ (where μ is the carrier mobility and α is the T -coefficient).^{30,31} The positive value of α can indicate an increased $\mu\tau$ product (where τ is the carrier lifetime) with decreasing T (assuming τ is roughly T -independent). On the basis of this, we expect an increased R at lower T due to the increase in carrier mobility that promotes the charge sweepout process. Conformingly, we observe a monotonous enhancement of R with decreasing T down to 250 K (see Figure S7). Within 250–320 K, the spectral shape and FWHMs remain roughly invariable in MA-treated devices. As the width of the photoresponsivity peak is generally correlated to the penetration depth of incident illumination and balanced between the competitive processes of charge recombination and extraction near the surface of MSCs,¹⁵ the nearly invariable spectral selectivity at different T indicates that the thermal energy tends to play an insignificant role in these opto-electrical processes of MSCs, which is beneficial for the device operation within a wide T -window.

Spectral Narrowing Effect in MSCs. So far, our combinatorial analyses evidence that MA treatment leads to suppressed surface traps that are related to the presence of Pb^{2+} ions and associated SRH recombination. Intuitively, these modifications should benefit charge collection, resulting in photocurrents upon irradiation in MSC planar diodes. As shown previously, the mechanism for NB-PDs was proposed to rely on the enhancement of surface recombination to attain a suppressed EQE in the above-band gap regime. In our case, the passivation of Pb^{2+} and the resulting decrease in nonradiative recombination seems to impede the realization of SNE. To promote our understandings, we further compared the temporal evolution of PL in Figure 5A. As shown, the reference MSC displays obvious red-shifts at the first 350 ps. This phenomenon has been interpreted by the photon-cycling effect (PCE) in MSCs that are characteristics with a sharp absorption edge together with a large PL and small Stokes shifts.^{32,33} The origin of the PCE is briefly explained as follows: during exciton migration, high energy excitons that diffuse to the interior region of crystals tend to experience reabsorption by the perovskite. With the elapse of time, low energy emissions become dominant, resulting in the red-shift in PL.

We note that the PCE in MA-treated samples visibly reduces and the PL energy merely changes. This result indicates a weaker effect of photon cycling with reduced exciton diffusion into the interior region of MSCs. As a conformation, we also examined the temporal evolution of PL with the laser beam incident on the cleaved MSC surfaces to mimic the bulk of MSCs. As seen from the results in Figure 5B, the pristine and MA-treated MSCs display resembling red-shift tendencies, which confirms the insignificance of MA modification in the bulk region of crystals. The reduced PCE with MA treatment can suggest that the created excitons may dominantly recombine at the surface area of MSCs in comparison to the situation in pristine MSCs.

Given the induced cracks in MSCs treated by MA, one may speculate that charge transporting barriers may be formed to negatively affect the lateral transport, which in turn affects the photoresponse. To evaluate this possibility, we also compared both dark and photocurrent under CW irradiation of lateral diodes (see results in Figure S8, SI). Surprisingly, the dark current hardly changes with the MA treatment while the photocurrent decreases in the reverse bias and remains unaffected by MA in the forward bias, consistent with the result of the SNE. If these cracks are the main barrier that retards the lateral charge transport, a reduction in both dark current and photocurrent will be expected with the likely “trapping” of charges by these barriers. However, our results in Figure S8 imply that the cracks should not be the main barrier for the lateral transport and the resulting SNE in the devices. However, the role of cracks in the ultimate opto-electronic behaviors cannot be entirely excluded and to some degree these structural defects can still hamper the overall efficiency of charge sweepout in MSC diodes.

The data so far provide a clear picture for the spectral narrowing which is briefly summarized as follows: With the reduced effect of photon-cycling, enlarged amounts of excitons tend to accumulate at the surface area of MSCs. As a result, the surface recombination may be enhanced, which likely causes more severe losses in the photocarriers. Another likely reason may be related to the presence of structural defects related to the cracks at the MSC surface with MA gas treatment, which could also impede the overall efficiency of charge sweepout.

On the basis of this rationalization, we propose the operational mechanisms for MSC devices. In nontreated devices (see Figure 5C), there are two zones that are differentiated in terms of charge generation depth inside the MSCs. The above surface charge generation zone is mainly correlated to charges originating from the above-band gap absorption, given the large extinction coefficient in MAPbI_3 . The bulk charge generation zone corresponds to those carriers created from near-band edge absorption with longer propagation depth. Without MA-treatment, charge collection in both the surface and bulk generation seems to be efficient, leading to the broadband photoresponse in the above-band gap absorption regime, which is achieved without the spectral selectivity. Figure S9 (SI) shows the spectral response of nontreated MSC diodes under different driving biases. The shape of the spectral response merely varies at forward bias and the maintained broad EQE confirms the efficient charge migration and extraction in both surface and bulk areas.

A distinct mechanism is proposed for MA-treated devices, as outlined in Figure 5D. After the MA surface modification, exciton diffusion into the interior region of MSCs seems to be impeded, the resulting accumulation of excitons at the surface

area can lead to strengthening the surface recombination, causing more severe losses in photocarriers in the MSC diode. This agrees with the observed reduction of photocurrent under CW irradiation. We further examined the impact of driving voltage on the SNE. Figure S10 (SI) shows the R of MA-treated diodes at different biases. In the forward bias regime, the photocurrent in the blind region (above-band gap absorption) exceeds that under reverse bias (Figure 4F), leading to losses of the spectral selectivity. This phenomenon agrees with the observed peak widening in sandwich devices at smaller electrical fields, which is possibly due to the decrease in charge separation efficiency.¹⁴ Further enhancement of the SNE and R in MSC planar diodes may be achieved through fine optimization of the crystallization of MSC and device geometry.

CONCLUSIONS

In summary, we demonstrate an efficient surface modification approach utilizing MA gas treatment to attain effective trap passivation for MSCs and tunability of the spectral response in planar diodes. With respect to the broadband photoresponse in pristine MSCs, we achieve a pronounced spectral narrowing with MA gas treatment with FWHMs < 40 nm. Transient PL spectroscopy in conjunction with DFT calculations reveals that the nonradiative surface charge recombination becomes mitigated after MA gas treatment while radiative recombination via bimolecular path tends to increase, which originates from the passivation of Pb ions with the Lewis base of nitrogen in MA. Combining the results of opto-electrical analyses, we propose two distinct mechanisms for planar diodes based on pristine and surface-modified MSCs. The obtained spectral selectivity is explained by the elevation of radiative recombination with an increased mobile carrier density, such that charge collection and eventual EQE from above-band gap absorption are desirably suppressed. Our work enriches the fundamentals of surface chemistry in perovskite materials and provides an interesting opportunity to modulate key performance metrics of perovskite-based photodetection devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b10782.

Computational details, SEM images, time-resolved PL spectroscopy, UV absorption spectroscopy, photoresponsivity measurement of the MSC devices (PDF)

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Notes

The authors declare no competing financial interest.

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