Aligning Transition Dipole Moment toward Light Amplification and Polarized Emission in Hybrid Perovskites

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Orientational manipulation of transition dipole moment (TDM) plays an important role in controlling the polarization of excited states in light emission as well as lasing actions. The present work discovers vertically aligned TDMs in hybrid perovskite films through angle-resolved photoluminescence (PL) measurements, which show enhanced emission through the film edge. With increasing excitation intensity, the edge emission induced by these vertically aligned TDMs becomes dominant and eventually leads to amplified spontaneous emission (ASE) through the edge view. Meanwhile, polarized emission of both PL and electroluminescence (EL) provides further evidence for vertically aligned TDMs. Surprisingly, the degree of polarization (DOP) through the film edge is increased when grain boundary defects are passivated through either stochiometric engineering or self-passivation by mobile ions under working conditions. With increasing DOP, ASE threshold of the perovskite film is reduced owing to enhanced collective behaviors of light-emitting states. This work presents a useful method to manipulate TDMs in organic–inorganic hybrid perovskites.

1. Introduction

Metal halide perovskites have recently demonstrated remarkable electroluminescence (EL) actions with solution processing and spectral tuning properties, as a result of extensive efforts from materials synthesis and device interface engineering.[1–7] With the external quantum efficiency (EQE) quickly increasing to over 20%,[8–11] polarization control becomes important for enriching the applications such as 3D display, magneto-optic disks and coherent detection systems.[12–14] Moreover, realizing polarized light-emitting states will create an opportunity to develop cooperative interaction in excited states toward developing superluminescence.[15] An effective approach for polarization control in light emission is to manipulate transition dipole moment (TDM), which is the electric dipole moment associated with the transition between the excited state and ground state, and the direction gives the polarization of the transition. Along this line, previous reports made use of the interfacial anisotropy between substrate and perovskite film for the alignment of TDMs. For example, De Angelis and co-workers reported the presence of oriented permanent dipoles at the titanium dioxide/perovskite interface, providing a practical strategy to align TDMs.[16] Liu and co-workers further observed controllable anisotropic light emission of photons originating from vertically aligned TDMs at cesium lead bromide/substrate interface.[17,18] An obstacle of this approach is that the electric dipole nature of TDM can be easily influenced by charged defects and mobile ions within organic–inorganic hybrid perovskites, leading to a challenge to achieve optically/electrically polarized light-emitting states.

In the present work, vertical asymmetry is realized in our methylammonium lead tribromide (MAPbBr3) perovskite polycrystalline film prepared by mixed large/small grains in micrometers/nanometers onto poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) substrate. As a consequence, TDMs are vertically aligned, leading to enhanced emission and dominant amplified spontaneous emission (ASE) at high excitation intensity through the edge view. Interestingly, polarized light emission through the edge view is observed by both optical and electrical excitation. The degree of polarization (DOP) can be further increased by passivating grain boundary defects either through electrically driven mobile ions to enable self-passivation or through stochiometric engineering. As such, we demonstrate a new approach to align TDMs in MAPbBr3 perovskite films and provide a unique platform to develop polarized light-emitting states in metal halide perovskites.
2. Results and Discussion

We follow our previous recipe to develop the perovskite (MAPbBr₃) films with mixed large/small grains by using one-step solution processing method onto the PEDOT:PSS substrate. The resulting perovskites show X-ray diffraction (XRD) patterns with featured peak at 14.8° (corresponding to (100) plane) (Figure S1a, Supporting Information) and an optical bandgap of 2.28 eV (Figure S1b, Supporting Information), consistent with previously reported polycrystalline MAPbBr₃ perovskites. This fabrication procedure enables the controlled passivation of large grains through small grains within one perovskite film. Mixed large/small grains are confirmed by scanning electron microscopy (SEM) images in Figure S2a (Supporting Information), which shows that micrometer-size large cubic grains are surrounded by around 100 nm small grains.

We demonstrate charge/energy transfer between large and small grains by performing photophysical characterizations. Photoluminescence (PL) spectrum of the film (in Figure S2b in the Supporting Information) contains the light emission from both large and small grains with different peaks at 516 and 545 nm. However, the EL spectrum only shows the light emission from large grains with the peak wavelength at 544 nm, indicating efficient charge transfer from small grains to large grains. Transient absorption (TA) results (in Figure S2c,d in the Supporting Information) further confirm this efficient transfer, where TA signal at 500 nm (refers to small-grain component) quickly decreases while the signal at 550 nm (refers to large-grain component) increases within 3 ps. Moreover, the PL lifetime of small-grain component (detected at 500 nm) is much shorter than that of large-grain component (detected at 540 nm) in Figure S3 (Supporting Information), consistent with the transfer process from small grains to large grains. It should be noted that, with increasing photoexcitation intensities (excitation direction is switched to 90°z). The ratio of PL intensity from large-grain component becomes dominant (Figure S4, Supporting Information).

To demonstrate the presence of vertical aligned TDMs, we use a home-built setup to measure the angle dependent PL. The dipole radiation theory determines that luminescence outputs at viewing angle of 90° and 0° to the film plane correspond to more contributions from lateral (parallel to film plane) TDMs and vertical (perpendicular to film plane) TDMs, respectively. As such, a distribution of light intensity other than the Lambertian characteristic (perpendicular to film plane) TDMs, respectively.[21] As such, a distribution of light intensity other than the Lambertian surface indicates the presence of aligned TDMs. As illustrated in Figure 1a, the excitation is fixed with the direction perpendicular to the film plane from one side while PL spectra are characterized at different viewing angles (from 0° to 150°) from the other side. With this setup, we measure angle-resolved PL under different excitation intensities (the excitation source is femtosecond pulse laser): 10, 30, and 60 μW (Figure 1b–d). The overall integrated PL intensity in Figure 1e shows an elliptical-like curve with major axis parallel to the film plane and non-negligible emission at the viewing angle of 0°. This is in stark contrast to the widely observed Lambertian distribution with a circular curve and no emission at the viewing angle of 0°. The fact that our films show elliptical feature and nonnegligible edge emission indicates the contributions from the vertically aligned TDMs.

We note that the vertically aligned TDMs can affect the ASE in the samples, where the ASE feature is identified in our previous work with both spectral narrowing and nonlinear increase of PL output.[19] At the high excitation intensity of 60 μW (Figure 1d), ASE is observed with significantly narrowed PL peak (full width at half-maximum (FWHM) of around 5 nm) at 2.29 eV. Interestingly, the dominant ASE emission appears at lower viewing angle (around 40°), different from spontaneous emission in Figure 1b,c with the dominant emission at 90°. It indicates that this collective emission (ASE) may originate from the vertical manipulation of TDMs. To understand the relationship between vertically aligned TDMs and collective emission (ASE), we compare the normalized PL spectra at different viewing angles with excitation intensity of 60 μW in Figure 1f. The ratio between spontaneous emission (broad peak) and ASE (sharp narrow peak) differs with the viewing angle. When the viewing angle is decreased from 90° to 0°, which refers to increasing contributions from vertically aligned TDMs, ASE ratio is growing. Moreover, at 0°, spontaneous emission is fully suppressed with only one narrow ASE peak. This provides a strong evidence that ASE is correlated with vertically aligned TDMs, and is consistent with our previous work which shows that ASE is absent without vertically aligned TDMs in small-grains-only perovskite films.[20]

The fact that TDMs can affect the ASE indicates that collective emission (ASE) may originate from vertically aligned TDMs with coherent interaction. Therefore, we explore the coherent behavior of vertically aligned TDMs by polarization characterization through the film edge. The PL polarization of edge emission (corresponds to vertical TDMs) is measured with the setup schematically shown in Figure 2a. In front of the detector, a linear polarizer together with a 1/2 waveplate are applied to filter the emission with controllable polarization direction, where the angle of the analyzer at 0°/90° refers to the polarization direction parallel/perpendicular to the film plane. It should be pointed out that a relatively high excitation intensity (around 500 mW cm⁻², 450 nm laser diode) is applied, which leads to only one dominate emission peak at around 545 nm (large-grain component). When the polarization direction is 0°, the PL intensity is relatively low (see Figure 2b). When the polarization direction is switched to 90°, around 48% increment on PL intensity is obtained. It indicates that the edge emission is partially linearly polarized with the direction perpendicular to the film plane, which is the same direction as vertically aligned TDMs. Therefore, the vertical inhomogeneity of our film leads to vertically aligned TDMs with coherent interaction. The DOP of 18.6% is obtained by fitting the polarization direction dependent PL intensity curve in Figure S5 (Supporting Information).

Now, we further explore this coherent emission under the electrical operation by characterizing the DOP of EL. The perovskite light emitting diodes (LEDs) were fabricated with the device architecture of indium tin oxide (ITO)/PEDOT:PSS/MAPbBr₃/electron transporting layer (poly(methyl methacrylate) (PMMA) mixed with bathophenanthroline (Bphen))/lithium fluoride (LiF, 0.7 nm)/silver (Ag). Figure S6 (Supporting Information) shows the EL–voltage–current characteristics, which indicates continuously increasing EL intensity and current efficiency at constant bias voltage (Figure S7, Supporting Information).
due to the self-passivation of grain boundary defects during EL operation. Specifically, the self-passivation process is verified by continuously increasing EL efficiency at constant bias and the increase of PL quantum efficiency after the poling of the bias.[19]

In order to normalize the continuously variable EL intensity, we design a dual detection method to characterize the DOP of EL through film edge. As shown in Figure 3a, the light emission is measured simultaneously from perpendicular and parallel directions to device plane. The EL at perpendicular direction is used as the reference signal, labeled as $I_R$, to track time evolution of EL intensity. At the same time, the EL at parallel direction (edge emission), labeled as $I_P$, is monitored through a linear polarizer setting at 0° and 90° degrees relative to film plane, giving the light emission defined as $I_{0°}$ and $I_{90°}$. The polarization degree was calculated by using the formula

$$DOP = \frac{I_{90°} - I_0}{I_{90°} + I_0} \cdot I_R$$

Figure 3b shows the $I/I_R$ measured at two different polarisation directions with the linear polarizer setting at 0° (parallel to
film plane) and 90° (perpendicular to film plane) as a function of time. At a constant bias of 3 V, $I_R$ gradually increases with time from the initial value 1.7 to over 6000 cd m$^{-2}$ within 10 s (as shown in Figure S8 in the Supporting Information). This gradual increase of EL intensity suggests the self-passivation process that the grain boundary defects are slowly passivated during the device operation.[19] Simultaneously, the relative EL output $I_{90}/I_R$ measured at polarization direction of 90° gradually increases and stabilizes after around 10 s, which is of the same timescale as self-passivation process. In contrast, the output $I_0/I_R$ measured at polarization direction of 0° shows negligible change during the EL operation. This phenomenon provides the direct evidence that the EL gradually becomes a linearly polarized output in the direction perpendicular to film.

Figure 2. Characterizations of PL polarization of MAPbBr$_3$ polycrystalline film. a) Experimental setup of PL polarization measurement. b) PL spectra at different polarization directions: 0° (black curve), 30° (red curve), 60° (blue curve), and 90° (magenta curve). Here, 0° refers to the direction parallel to film plane and 90° refers to the direction perpendicular to film plane. The excitation source is a CW laser (450 nm, intensity $\approx$500 mW cm$^{-2}$).

Figure 3. Characterizations of EL polarization of MAPbBr$_3$ polycrystalline film. a) Experimental setup of EL polarization measurement. b) Relative EL output ($I_{90}/I_R$) as a function of time at different polarization directions: 0° (red curve) and 90° (black curve). Here, 0° refers to the direction parallel to film plane and 90° refers to the direction perpendicular to film plane. c) Stabilized relative EL output intensity as a function of polarization direction.
plane, which is the same direction as PL polarization direction. Figure 3c plots the stabilized $I/I_0$ values at varying polarization angles (from 0° to 360°), further verifying the linear polarization with fitting of sine function. The DOP increases to 29.2% after about 10 s during the EL operation in Figure 3b. The similar time dependence between DOP and EL intensity increment indicates that the light-emitting states are gradually polarized under electrical field as the grain boundary defects are slowly passivated.

The connection between the DOP and passivation leads us to believe that defect passivation presents a necessary condition for polarizing light-emitting states in perovskite LEDs. The TDMs are electric dipoles which can be easily influenced by localized electric field of charged defects, leading to a screening effect to the coherent interaction between TDMs. Through reducing the screening effect via neutralizing these charged defects (i.e., defect passivation), coherent interaction can be established and polarized output is expected. Therefore, defect passivation is supposed to increase DOP.

To verify our proposed hypothesis, we further compare EL DOP values of other devices fabricated with intrinsically varied defect densities by changing the amount of excess methylammonium bromide (MABr) in the precursor solution. As shown in Figure 4a, with increasing amount of MABr, PL intensity increases significantly (over 20 times enhancement), indicating the passivation effects of MABr. To exclude the possibility of morphological or structural changes that induce the PL enhancement, we have compared both SEM (Figure S9, Supporting Information) and XRD (Figure S10, Supporting Information) results of two selected perovskite films mixed with large/small grains. No obvious morphological or structural difference is observed, indicating that excess MABr will not alter the morphology or crystal structure and that the PL enhancement originates from the passivation effect of excess MABr. In our experiment, both electrically driven condition and excess MABr can passivate defects, indicating that the defects are most probably bromide vacancies. Under a constant bias, the defects passivation is enabled by the mobile ions,[19] where bromide ions are the most possible origin. The excess MABr can also provide the bromide source for the passivation.

In addition, the PL position from large-grain component (around 544 nm) keeps nearly unchanged while the PL position from small-grain-component is gradually blueshifted from 528 to 515 nm. The increase on PL intensity and blueshift indicate that stoichiometric control of MABr provides a convenient method to essentially decrease the defects on large grains in the mixed large/small grains. Interestingly, by decreasing the defects through increasing the amount of MABr, the DOP of EL output at 3 V is largely increased from 19% to 29.2% in the MAPbBr$_3$ LEDs. The DOP decreases at a significantly over-excessive amount of MABr, probably due to detrimental effects from MABr in this case.

These results confirm that the polarization of light-emitting states is enhanced as the defects are decreased on the large grains in the film containing mixed large/small grains. It provides a unique method to control the polarization of light-emitting states in perovskite LEDs to enhance the device performance. Interestingly, the DOP increase through defect passivation is also beneficial for the reduction of ASE threshold. As reported in our previous work, ASE threshold is largely decreased from 13.6 to 4.4 µW with the MABr: lead acetate trihydrate (Pb(Ac)$_2$·3H$_2$O) ratio increasing from 3 to 4.5. It indicates that polarizing excited states toward coherent interaction will lead to enhanced light amplification.

3. Conclusion

In summary, our MAPbBr$_3$ film mixed with large/small grains on the PEDOT:PSS substrate leads to vertically aligned TDMs toward linearly polarized emission during PL and EL operations. With coherent interaction between TDMs, dominant ASE is observed through the film edge. Moreover, the DOP can be increased by decreasing boundary defects either through electrically driven self-passivation or externally adding MABr. This enhanced DOP is beneficial for coherent interaction between excited states, resulting in reduced ASE threshold. As such, our work presents a unique design toward developing polarized light-emitting states in organic–inorganic hybrid perovskite LEDs.
4. Experimental Section

Materials Processing and Device Fabrication: The ITO substrates were cleaned by ultrasonic treatment with detergent, deionized water, acetone and isopropanol respectively for 20 min in each cycle. Then the cleaned ITO substrates were exposed to UV ozone for 30 min followed by the spin coating of PEDOT:PSS with the thickness of 40 nm. The PEDOT:PSS films coated on ITO substrates were thermally annealed at 150 °C for 0.5 h.

The perovskite (MAPbBr3) films with mixed large/small grains were prepared based on the following procedures. First, two solutions were prepared: i) 0.3552 g PbAc2·3H2O and 0.4704 g MABr were dissolved in 1 mL dimethylformamide (DMF) solution (with molar ratio PbAc2·3H2O:MABr = 1:1.45) for small grains, and ii) 0.5620 g lead bromide (PbBr2) and 0.1796 g MABr were dissolved in 1 mL DMF solution (with molar ratio PbBr2:MABr = 1:1.05) for large grains. Second, these two solutions with volume ratio of 1:4 (more PbBr2 portion) were mixed to prepare mixed large/small grains. The mixed solution was spin-coated onto PEDOT:PSS layers in nitrogen atmosphere at the rate of 3000 rpm to form MAPbBr3 films with mixed large/small grains, then annealed for 30 min at 60 °C. To compare the effects of MABr amount (fils in Figure 4), the molar concentration of PbAc2·3H2O was fixed while the amount of MABr was changed in precursor (i) intentionally. The following fabrication procedures were the same.

The electron transport layer was spin cast at the rate of 8 krpm for 60 s with two mixed chloroform solution of Bphen (20 mg mL⁻¹) and PMMA (20 mg mL⁻¹) with volume ratio of 1:2. Then LiF and Ag were thermally deposited under vacuum with the thicknesses of 0.7 and 80 nm, respectively. The perovskite light-emitting devices were prepared with the architecture of ITO/PEDOT:PSS/MAPbBr3/Bphen:PMMA/ LiF(0.7 nm)/Ag. The fabricated perovskite light-emitting devices were encapsulated by UV curable epoxy for experimental measurements.

Characterizations and Measurements: The angle-dependent PL intensity was characterized by angular resolved measurement setup (IdeoOptic, RI) with the excitation source of 400 nm femtosecond laser (with the spot size of around 500 μm in diameter) and collection by fiber coupled spectrometer (IdeoOptic, PC2000 pro). XRD patterns were characterized by an X-ray diffractometer (Pananalytical X’Pert Pro) with an X-ray tube (Cu Kα, λ = 1.5406Å). The transient and steady-state PL characteristics were measured using a Fluoro Log III spectrometer with lifetime acquisition. The photoexcitation wavelength for PL is 405 nm. The current-voltage characteristics were measured by Keithley 2400. The film morphologies were characterized by SEM (Zeiss sigma 300). The current-voltage characteristics were measured by Keithley 2400. The EL brightness was characterized by power meter (ST86LA).

For PL polarization measurement, a 450 nm laser diode was applied to excite the film through the glass side (as shown in Figure 2a). Along the direction of film edge, a ¾ waveplate (WP/IV0-405, purchased from Thorlabs) was placed with the waveplate plane perpendicular to the perovskite film plane. A linear polarizer (WP50L-VIS, purchased from Thorlabs) was placed in between the ¾ waveplate and photodetector. During the PL polarization measurement, ¾ waveplate was rotated via a motorized rotation mount (KIOCR1/M, purchased from Thorlabs) with a step of 50 and step interval of 10 s for spectrum collection.

Supporting Information

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

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Conflicts of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

Keywords

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[15] D. J. Heinzen, J. E. Thomas, M. S. Feld, Phys. Rev. Lett. 1985, 54, 677.
[16] V. Roiati, E. Mosconi, A. Listorti, S. Colella, G. Gigli, F. De Angelis, Nano Lett. 2014, 14, 2168.
[17] M. J. Jurow, T. Lampe, E. Penzo, J. Kang, M. A. Koc, T. Zechel, Z. Nett, M. Brady, L.-W. Wang, A. P. Alivisatos, S. Cabrini, W. Brütting, Y. Liu, Nano Lett. 2017, 17, 4534.
[18] M. J. Jurow, T. Morgenstern, C. Eisler, J. Kang, E. Penzo, M. Do, M. Engelmayr, W. T. Osowiecki, Y. Bekenstein, C. Tassone, Nano Lett. 2019, 19, 2489.
[19] J. Qin, J. Zhang, Y. Bai, S. Ma, M. Wang, H. Xu, M. Loyd, Y. Zhan, X. Hou, B. Hu, iScience 2019, 19, 378.
[20] Y. Bai, J. Qin, L. Shi, J. Zhang, M. Wang, Y. Zhan, H. Zou, S. Haacke, X. Hou, J. Zi, Adv. Opt. Mater. 2019, 7, 1900345.
[21] W. Brütting, J. Frischeisen, T. D. Schmidt, B. J. Scholz, C. Mayr, Phys. Status Solidi A 2013, 210, 44.
[22] S. W. Liu, J. X. Wang, Y. Divayana, K. Dev, S. T. Tan, H. V. Demir, X. W. Sun, Appl. Phys. Lett. 2013, 102, 26.
[23] J. S. Kim, P. K. Ho, N. C. Greenham, R. H. Friend, J. Appl. Phys. 2000, 88, 1073.