Modulation of Broadband Emissions in Two-Dimensional \langle 100\rangle-Oriented Ruddlesden–Popper Hybrid Perovskites

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ABSTRACT: Two-dimensional (2D) Ruddlesden–Popper (RP) perovskites are emerging materials for light-emitting applications. Unfortunately, their desirable narrowband emission coexists with broadband emissions, which limits the color quality and performance of the light source. However, the origin of such broadband emission in \langle 100\rangle-oriented perovskites is still under debate. Here, we experimentally and theoretically demonstrate that unlike \langle 110\rangle-oriented RP perovskites, the broadband emission of the 2D \langle 100\rangle-oriented RP (PEA)_2PbI_4 (PEA = C_6H_5C_2H_4NH_3) perovskites originates from defect-related luminescence centers. We find that the broadband emission of this prototype 2D structure can be largely suppressed by using excess PEAI treatment. Density functional theory (DFT) calculations indicate that iodine (I) vacancies both in the bulk and on the surface are responsible for the broadband emission. We attribute the decreased broadband emission after PEAI treatment to the passivation of both undercoordinated Pb^{2+} ions on the surface and I vacancies in the bulk through I^− ion migration.

Two-dimensional (2D) Ruddlesden–Popper (RP) hybrid perovskites have attracted great attention in the field of optoelectronic devices, especially light-emitting diodes (LEDs), because of their tunable photoluminescence wavelength, high photoluminescence quantum yield (PLQY), and excellent photo- and moisture stability. Conceptually, 2D RP perovskites can be derived by slicing three-dimensional (3D) perovskites along different orientations (i.e., \langle 110\rangle, \langle 100\rangle, and \langle 111\rangle), in which the bulky organic spacers and inorganic layers are periodically arranged. The periodic arrangement of organic spacers and inorganic layers allows large lattice rearrangements in the excited states. In \langle 110\rangle-oriented 2D perovskites, the strong interaction between charge carriers and phonons leads to the formation of self-trapped excitons (STEs) that can radiatively decay with broadband emission. These self-trapped holes [electrons] tend to capture the surrounding electrons [holes] via Coulombic attraction, generating self-trapped excitons (STEs) that can radiatively decay with broadband emission. On the other hand, the origin of the broadband emission in \langle 100\rangle-oriented 2D RP perovskites is still hotly debated. Two mechanisms have recently been proposed to explain the origin of such emission. Similar to the \langle 110\rangle-oriented cases, Smith et...
al. proposed that the photoinduced local deformation of the crystal lattice leads to the formation of STEs in ⟨100⟩ lead bromide perovskites. On the other hand, Zhang et al. showed that the intensity of the broadband emission in (PEA)2PbI4 (PEA = C6H5C2H4NH3) can be tuned by adjusting the concentration of excess iodine during crystal growth. In this case, the authors attributed the broadband emission to iodine interstitials. Park et al. indicated that the broadband emission in the (BA)2PbBr4 (BA = C4H9NH3) crystal may originate from defect-assisted radiative recombination, i.e., organic cation vacancies formed by intercalated water molecules. These contradicting explanations reported in the literature motivated us to decipher the source of the broadband emission. Given the interest in exploiting these materials in light-emitting applications, differentiating between self-trapped exciton emission and intrinsic defect emission will enable the development of synthesis strategies that fully control the material’s luminescence and defect properties.

Here, we experimentally and theoretically explore the optical properties of the prototype ⟨100⟩-oriented 2D RP perovskite (PEA)2PbI4 to reveal the origin of its broadband emission. We demonstrate that the broadband emission in the (PEA)2PbI4 crystals arise from defect-assisted radiative recombination, unlike ⟨110⟩-oriented 2D RP perovskites. By studying crystals grown using different precursors (e.g., PbI2 versus PbO), particularly with excitation power-dependent PL measurements, we identify the defect nature of the broadband luminescence and rule out any substantive role for self-trapped excitons. To clarify the nature of the emissive defect centers, we conducted density functional theory (DFT) calculations on a variety of possible intrinsic defects and found that in-plane iodine vacancies in the bulk and on the surface are the most likely source of the broadband emission. Guided by this insight, we show a postsynthetic treatment strategy based on PEAI that substantially suppresses the broadband emission, as the excess I− ions can effectively passivate these vacancies.
As illustrated in Figure 1a, (PEA)$_2$PbI$_4$ crystals were synthesized via similar approaches but with different precursors of (i) lead oxide (PbO) and ammonium salt (PEAI) and (ii) lead iodide (PbI$_2$) and PEAI. The precursors were dissolved in HI and heated to 100 °C; then, the crystals were grown by gradually cooling the solution to room temperature (see details in Experimental Methods). Optical micrographs and corresponding fluorescence images of the as-synthesized crystals with green and red fluorescence are shown in Figure 1b. The X-ray diffraction (XRD) patterns of the as-grown (PEA)$_2$PbI$_4$ crystals with different precursors show clear (00l) diffraction peaks, l = even number, confirming the layered perovskite structure is aligned along the z-axis (the calculated d spacing is ~1.65 nm). For the 2D layered perovskite, the distortion of the [PbI$_6$]$^{4-}$ octahedra was evaluated by the mean octahedral elongation ($\Delta_{\text{oct}}$) and the octahedral angle variance ($\sigma^2_{\text{oct}}$). The calculated $\Delta_{\text{oct}}$ and $\sigma^2_{\text{oct}}$ of (PEA)$_2$PbI$_4$ are 1.006 and 16, respectively, indicating less octahedral distortion compared to (110)-oriented perovskites, such as (EDBA)$_2$PbCl$_4$ ($\Delta_{\text{oct}}$ = 1.008 and $\sigma^2_{\text{oct}}$ = 260). Thus, based on the distortion of the octahedra, the (100)-oriented (PEA)$_2$PbI$_4$ crystals are categorized as broadband emissive perovskites.

The absorption spectra of the two types of (PEA)$_2$PbI$_4$ crystals show similar features, with an excitonic peak at approximately 533 nm and continuous absorption in the high-energy region (the additional absorption peak around 480 nm for crystals grown with PEAI and PbI$_2$ may originate from the few-layer PbI$_2$ with a calculated band gap of 2.55–2.64 eV). However, the (PEA)$_2$PbI$_4$ crystals grown with PEAI and PbI$_2$ exhibit two distinct emission peaks: a narrowband emission centered at 527 nm and continuous absorption in the high-energy region, while the broadband emission is similar to the white-light emission of (PEA)$_2$PbI$_4$ crystals that is triggered by Sn dopants (the large lattice deformation around the Sn impurities can accommodate the STEs). The different optical features of the (PEA)$_2$PbI$_4$ crystals prepared using different precursors suggest that the intrinsic defects of the (PEA)$_2$PbI$_4$ crystals are controlled by the stoichiometric reaction between the precursors in the HI acid. For instance, when PbO is used, PbO reacts with HI and fully converts to pure PbI$_2$, which further reacts with PEAI. In this case, defect-free (PEA)$_2$PbI$_4$ crystals are formed. However, when PbI$_2$ is used, PbI$_2$ directly reacts with PEAI as well as with HI. This leads to the formation of polyiodide species, e.g., PbI$_{3-n}$ and PbI$_n$, which exhibit the broad emission around 690 nm of the (PEA)$_2$PbI$_4$ single crystal in relation to the excitation power (100–1400 μW).

To understand the origin of the broadband emission in (PEA)$_2$PbI$_4$ crystals, we first performed excitation power-dependent PL measurements. Figure 2a shows the PL spectra of the (PEA)$_2$PbI$_4$ crystals for different excitation powers ranging from 104 to 1319 μW. We can estimate the origin of both emissions from (PEA)$_2$PbI$_4$ crystals using the power-law equation, which is defined as $I_{PL} = nL^k$, where $I_{PL}$ is the integrated PL intensity; $L$ is the excitation power; and $n$ is the emission efficiency. In semiconductor materials, the coefficient k in this equation represents the recombination mechanism: $k = 2$ corresponds to band-to-band recombination; $k = 1–2$ is related to free or bound exciton recombination, and $k < 1$ corresponds to impurity-related recombination. Figure 2b shows the excitation power dependence of the PL intensity for the narrowband and broadband emissions of the (PEA)$_2$PbI$_4$ crystals at room temperature. Similar to previous reports, both emissions show a linear dependence on the excitation power density: the fitted k value for the narrowband emission is 1.28, which is consistent with a free exciton mechanism, while the fitted k value for the broadband emission is 0.96, which can be considered as an indicator of defect-related exciton emission. Note that such defect-induced broadband emission is not saturated in our case because further increasing the excitation power density may damage the crystal surface and create new...
surface defects that contribute to the broadband emission (this will be discussed in detail later).

To decipher the luminescent centers of the defect-induced broadband emission of the (PEA)_2PbI_4 crystal, we performed density functional theory (DFT) calculations of the formation energy of native point defects and corresponding charge transition levels. As illustrated in Figure 3a, we considered two donor defects (out-of-plane and in-plane iodine vacancies, V_{I1} and V_{I2}), two neutral defects (PEAI and PbI_2 vacancies, V_{PEA} and V_{PbI2}), and two acceptor defects (PEA vacancy and iodine antisite, V_{PEA} and I_{II}), as they are expected to be the dominant defects in 2D layered perovskites.30 The computational details can be found in Experimental Methods. As shown in Figure 3b, the overall defect formation energies of neutral defects (V_{PEA} and V_{PbI2}) are much lower than those of the other defects.

However, such neutral defects would not introduce any deep trap state within the valence bandgap (see Figure S1 of the Supporting Information). Under I-rich conditions, the two kinds of V_I defects have larger formation energies than those of the neutral and acceptor defects, especially out-of-plane V_{I1}. As the chemical potential point shifts from I-rich to I-poor conditions, the defect formation energies of I_{II} and V_{PEA} increase (projected density of states and electronic charge densities are shown in Figure S2), and those of V_{I1} and V_{I2} largely decrease. Thus, under I-poor conditions, the donor defects become the dominant defects, with formation energies of 1.08 eV for out-of-plane V_{I1} and 0.84 eV for in-plane V_{I2}.

The charge transition levels of the donor and acceptor defects are shown in Figure 3c. Both out-of-plane and in-plane V_I in (PEA)_2PbI_4 lead to (deep donor) states in the gap with transition levels 1.89 eV for V_{I1} and 1.73 eV for V_{I2} above the valence band maximum (VBM). In contrast, V_{PEA} and I_{II} exhibit shallow transition levels of 0.15 and 0.34 eV above the VBM. Panels d and e of Figure 3 show the projected density of states (PDOS) for (PEA)_2PbI_4 after introducing donor defects. For perfect (PEA)_2PbI_4, the electronic charge densities at the CBM and VBM (mainly composed of I 5p, Pb 6s, and Pb 6p orbitals) of pristine (PEA)_2PbI_4 are delocalized within the inorganic layers (Figure S3). In the case of the (PEA)_2PbI_4 supercell containing V_{I1}, the bandgap of (PEA)_2PbI_4 remains almost unchanged, and the charge densities at both the CBM and VBM retain the delocalized feature. This is different from the PDOS of the (PEA)_2PbI_4 supercell containing V_{I2}, which shows a new intraband state (~0.3 eV below the CBM), as well as a delocalized charge density surrounding the V_{I2} center. Overall, we can conclude that the in-plane I vacancy is a reasonable origin for the broadband emission observed in (PEA)_2PbI_4 crystals because it has lower defect formation energy under I-poor conditions and its charge transition level (1.73 eV) is close to the broadband emission center (1.80 eV).
To support that the broadband emission of ⟨100⟩-oriented 2D RP perovskites originates from the halide vacancies, we further carried out DFT calculations on ⟨100⟩-oriented (BA)$_2$PbBr$_4$, which has a similar PL feature with a narrowband emission at 3.06 eV and a broadband emission centered at 2.25 eV. As shown in Figures S4–S6 of the Supporting Information, in a way similar to the (PEA)$_2$PbI$_4$ case, Br vacancies in (BA)$_2$PbBr$_4$ (which have smaller formation energies (1.74 and 1.33 eV) under Br-poor conditions) can act as radiative recombination centers and have charge transition levels of 2.20 and 1.96 eV consistent with the broadband emission observed experimentally.

In addition to the intrinsic point defects in the bulk of the 2D crystal, I vacancies also form on the surface during the growth of the (PEA)$_2$PbI$_4$ crystal, especially under I-poor conditions. The resulting surface states capture photogenerated charge carriers and trigger radiative decay. We further evaluated the impact of the surface states on the electronic and optical properties of the (PEA)$_2$PbI$_4$ crystal by constructing a slab model terminated with surface iodine vacancies (i.e., a PbI$_2$-rich surface, Figure 4a). Similar to the bulk case with a V$_{II}$ defect, the PDOS of the (PEA)$_2$PbI$_4$ slab shows a midgap state 0.34 eV below the CBM (Figure 4b). The electronic charge density distributions at the CBM and VBM of the (PEA)$_2$PbI$_4$ slab still present a delocalized feature.

Figure 4. (a) Schematic illustration of the surface state and (b) projected density of states (PDOS) and electronic charge densities at the CBM, VBM, and surface state of the (PEA)$_2$PbI$_4$ slab. The calculations were performed at the GGA/PBE level of theory.

Figure 5. (a) PL spectra of the (PEA)$_2$PbI$_4$ crystal with broadband emission before and after PEAI treatment at an excitation wavelength of 473 nm (the insets show the transmission microscopy and corresponding fluorescence images of the (PEA)$_2$PbI$_4$ crystal after PEAI treatment); (b) time-resolved PL decays for the narrowband emission at 527 nm and the broadband emission around 690 nm of the (PEA)$_2$PbI$_4$ single crystal without and with broadband emission before and after PEAI treatment; and schematic illustration of the ion transport mechanisms involving I vacancy hopping between neighboring positions and the corresponding energy profile of the migration path for (c) I$^-$ ion migration within the inorganic plane and (d) I$^-$ ion migration between inorganic layers. The red arrow indicates the ion migration pathway. The calculations were performed at the GGA/PBE level of theory.

To support that the broadband emission of (100)-oriented 2D RP perovskites originates from the halide vacancies, we further carried out DFT calculations on ⟨100⟩-oriented (BA)$_2$PbBr$_4$ which has a similar PL feature with a narrowband emission at 3.06 eV and a broadband emission centered at 2.25 eV. As shown in Figures S4–S6 of the Supporting Information, in a way similar to the (PEA)$_2$PbI$_4$ case, Br vacancies in (BA)$_2$PbBr$_4$ (which have smaller formation energies (1.74 and 1.33 eV) under Br-poor conditions) can act as radiative recombination centers and have charge transition levels of 2.20 and 1.96 eV consistent with the broadband emission observed experimentally.

In addition to the intrinsic point defects in the bulk of the 2D crystal, I vacancies also form on the surface during the growth of the (PEA)$_2$PbI$_4$ crystal, especially under I-poor conditions. The resulting surface states capture photogenerated charge carriers and trigger radiative decay. We further evaluated the impact of the surface states on the electronic and optical properties of the (PEA)$_2$PbI$_4$ crystal by constructing a slab model terminated with surface iodine vacancies (i.e., a PbI$_2$-rich surface, Figure 4a). Similar to the bulk case with a V$_{II}$ defect, the PDOS of the (PEA)$_2$PbI$_4$ slab shows a midgap state 0.34 eV below the CBM (Figure 4b). The electronic charge density distributions at the CBM and VBM of the (PEA)$_2$PbI$_4$ slab still present a delocalized feature.
as in the bulk, while the additional surface charge state shows a delocalized density on the top layers of the slab. In this case, the surface state might represent another radiative channel involved in the broadband emission, as charge carriers can decay via surface defect states located within the bandgap. A similar surface state is observed in the (BA)₂PbBr₅ slab, with an intraband level 0.36 eV below the CBM (Figure S7 of the Supporting Information).

To verify our theoretical results, we treated the (PEA)₂PbI₄ crystals with excess PEAI (i.e., by placing them in PEAI solvent) and found that the broadband emission is largely suppressed (Figure 5a), with a strong decrease in the PL intensity ratio between the broadband and narrowband emissions, compared to the as-grown (PEA)₂PbI₄ crystals. Figure 5b shows the time-resolved PL decays of the two types of (PEA)₂PbI₄ crystal (the excitation fluence is 6.47 μJ/cm²). All the fitting parameters are given in Table S1. The control (PEA)₂PbI₄ crystal without broadband emission has an average PL lifetime of 0.39 ns (τ₁ = 0.32 ns (91.2%) and τ₂ = 1.1 ns (1.9%)), which agrees well with previous reports. However, the (PEA)₂PbI₄ crystals with broadband emission, the average PL lifetimes of the narrowband and broadband emissions are ~5.1 and ~69 ns, respectively. This indicates that the appearance of defect states prolongs the exciton emission lifetime because of reverse electron transfer from defect states to the free excitonic state. After PEAI treatment, the average lifetime of the broadband emission decreases to ~45 ns, but the lifetime of the narrowband emission slightly increases to ~8.2 ns because of the suppression of nonradiative decay (induced by shallow trap states), providing new experimental evidence that PEAI treatment could reduce the defect states of (PEA)₂PbI₄ crystals.

It is worth noting that the as-grown crystals were washed with the antisolvent diethyl ether (DEE) to remove any possible excess acid and dried at 60 °C for both synthesis routes. However, the (PEA)₂PbI₄ crystals prepared with PbO +PEAI (i.e., the control sample) did not show any broadband emission after washing, and the sample prepared with PbI₂+PEAI still had broadband emission. Figure S8 shows PL and TRPL spectra for the control sample as a function of the DEE washing cycle. We find that the PL intensity sequentially decreases and the average TRPL lifetime increases from 0.51 to 0.83 ns with increasing number of cycles (Table S2). The average TRPL lifetime of the control sample after four DEE washes is 1 order of magnitude lower than that of the broadband emitting (PEA)₂PbI₄ crystals. Therefore, we can rule out the idea of extrinsic defect formation due to the antisolvent washing step.

Therefore, the experimental PEAI treatment plays a dual role in passivating the I vacancies of the (PEA)₂PbI₄ crystal. On the one hand, the excess I⁻ ions can remove the surface states by coordinating to Pb²⁺ ions; on the other hand, I vacancies in the bulk can be filled through I⁻ ion migration. To validate this last point, we calculated the migration activation energies for two iodine migration paths, one within the inorganic plane and one between inorganic layers, as illustrated in Figure 5c,d. We find that the lowest activation energy (E_a) for the I⁻ ion is 0.49 eV within the inorganic plane, which is comparable to the calculated E_a for the I⁻ ion of MAPbI₃ (0.36 eV, Figure S9 of the Supporting Information), this suggests active vacancy diffusion of I⁻ ions from the surface to the bulk within inorganic layers in the 2D (PEA)₂PbI₄ crystal, which can significantly reduce the number of defect states. Note that the E_a for I⁻ ions between inorganic layers is much greater (1.76 eV, Figure 5d), pointing to very difficult I⁻ ion migration across layers.

In conclusion, we have synthesized (100)-oriented 2D perovskites without and with broadband emission using the same chemical approach but different reaction precursors. We have found that the broadband emission of the (PEA)₂PbI₄ crystal originates from intrinsic defect states, as confirmed by power-dependent PL and lifetime measurements. It should be emphasized that this behavior is different from the self-trapped exciton-induced broadband emissions in (110)-oriented 2D perovskites. The results of DFT calculations underline that the iodine vacancies both in the bulk and on the surface are responsible for introducing the sub-bandgap states leading to the broadband emission. We have also demonstrated that the broadband emission can be largely suppressed by treatment of excess PEAI, which effectively passivates the I vacancies. By unraveling the origin of the broadband emission in (100)-oriented 2D perovskites, we not only provide a detailed understanding of how to control the optical properties according to the crystal growth conditions but also point the way to the synthesis of highly efficient pristine narrowband emissive 2D perovskite crystals.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.0c01047. Experimental methods, PL spectra of the (PEA)₂PbI₄ crystal after washing, and calculated PDOS and charge densities for (PEA)₂PbI₄ without and with neutral and acceptor defects (PDF)

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