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# Decoupling excitons behavior of two-dimensional Ruddlesden-Popper PEA<sub>2</sub>PbI<sub>4</sub> nanosheets



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#### ABSTRACT

Two-dimensional (2D) Ruddlesden-Popper hybrid organic-inorganic perovskites are the most promising candidates for highly efficient optoelectronic devices due to their remarkable exciton characteristics, adjustable band structure and long-term environmental stability. However, excitons emission behavior of 2D Ruddlesden-Popper perovskites is still unclear. Here we theoretically-experimentally decoupled the excitons behavior in 2D Ruddlesden-Popper PEA<sub>2</sub>PbI<sub>4</sub> nanosheets. Theoretically, the Elliott theory was used to separate exciton and band edge absorptions of PEA<sub>2</sub>PbI<sub>4</sub> nanosheets and determine an exciton binding energy of about 274 meV. Experimentally, spectral-dependent photoluminescence lifetime and excitation powder density-dependent photoluminescence spectra revealed that a distinct photoluminescence tail emission should be derived from localized excitons and localized excitons with lower emission energy than free excitons. Further, the luminescent component of the free excitons and localized excitons with their corresponding densities of states was theoretically decoupled by line-shape analysis of PEA<sub>2</sub>PbI<sub>4</sub> nanosheets photoluminescence spectra, which is consistent with the experimental results demonstrating the existence of localized excitons. Hence, our work provides understanding on the exciton behavior and luminescence mechanism of 2D Ruddlesden-Popper perovskites, which would benefit the prediction of high-performance excitonic devices based on 2D Ruddlesden-Popper perovskites.

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#### 1. Introduction

Recently, the emerging two-dimensional (2D) Ruddlesden-Popper perovskites have attracted increasing attention in the optoelectronics fields due to their remarkable exciton characteristics, adjustable band structure and long-term environmental stability [1–6]. The general formula for 2D Ruddlesden–Popper layered perovskite is  $R_2A_{n-1}B_nX_{3n+1}$ , where A is small monovalent cation, B is a divalent metal cation, X is halide, R represents large organic cation and n is the quantity of inorganic layers. A monolayer structure is formed when n = 1 and multilayered quasi-2D structures are obtained when n  $\geq$  2. Therefore, the bandgap and electronic band structure of 2D perovskite can be easily tuned by changing the large organic cations or layer number. Furthermore, inserting large organic hydrophobic cation between the inorganic octahedral sheets of

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https://doi.org/10.1016/j.jallcom.2022.168312 0925-8388/© 2022 Published by Elsevier B.V. 2D Ruddlesden-Popper perovskite can effectively suppress moisture intrusion from perovskite crystal lattice to address the notorious stability issue [7–10].

In addition, due to the different dielectric constants of organic chains and inorganic layers, 2D perovskites naturally form multiquantum wells enabling the exciton binding energy of perovskites to exceed hundreds of meV [11,12]. With large quantum confinement and reduced dielectric screening, excitons in 2D perovskites are strongly confined. Excitons are fundamental guasi-particles that form bound electron-hole pairs due to the Coulomb interaction, which modulates the optoelectronic behavior of 2D perovskite [8,13]. Currently, the interdependence of free excitons and selftrapped excitons in the emission process of 2D perovskites is still an open issue. Free excitons can move freely in the crystal space, while the self-trapped excitons (STEs) are localized in the potential well due to local lattice distortion caused by strong electron-phonon interaction [14–16]. STEs are essentially localized excitons, the obvious feature for localized excitons is a broadband emission with a large Stokes shift below the bandgap. Typically, the mutual



Fig. 1. (a) Schematic diagram of the crystal structure of PEA<sub>2</sub>PbI<sub>4</sub>; (b) XRD pattern, (c) SEM image and (d) TEM image of 2D PEA<sub>2</sub>PbI<sub>4</sub> nanosheets.

transformation of free excitons and localized excitons will result in the overlap of the luminescence spectra [17–19]. In this respect, the main issue in the radiative recombination mechanisms understanding relies in the missing of an unambiguous identification of the emitting species (localized excitons vs free excitons). 2D Ruddlesden-Popper perovskites with pronounced exciton emission provide an ideal platform to investigate excitons behavior. Therefore, decoupling the excitons behavior of 2D Ruddlesden-Popper perovskites is critical to understand their intrinsic exciton absorption and luminescence mechanism.

Here we theoretically and experimentally decoupled excitons behavior in 2D Ruddlesden-Popper PEA<sub>2</sub>PbI<sub>4</sub> nanosheets. The intrinsic exciton absorption and luminescence mechanism of PEA<sub>2</sub>PbI<sub>4</sub> nanosheets were investigated by Elliott theory and line-shape analysis. We provide spectroscopic evidence that the photoluminescence (PL) tail emission of PEA<sub>2</sub>PbI<sub>4</sub> nanosheets is dominated by localized excitons with lower emission energy rather than free excitons. The localization effect is also supported by experimental results from spectral dependence of the photoluminescence lifetime. Therefore, this work will provide experimental and theoretical support to understand the exciton behavior in order to use special exciton characteristics of novel 2D perovskite materials for high-performance optoelectronic devices.

### 2. Experiment section

#### 2.1. Materials and chemicals

Lead(II) acetate trihydrate (Pb(Ac)<sub>2</sub>·3 H<sub>2</sub>O, 99.9%, aladdin), oleic acid (OA, 85%, aladdin), 1-octadecene (ODE, 90%, aladdin),

phenylethylamine (PEA, 98%, aladdin), HI (55–58%, aladdin), n-Hexane (99%, aladdin).

#### 2.2. Synthesis of PEA<sub>2</sub>PbI<sub>4</sub> nanosheets

10 mL of ODE, 1 mL of OA, 150  $\mu$ L of PEA, and 0.0758 g of Pb (Ac)<sub>2</sub>·3 H<sub>2</sub>O were loaded in a 100 mL three-necked round-bottom flask. Then, the flask was vacuumed at 100 °C for 20 min. After that, the flask was switched to N<sub>2</sub> and temperature was increased to 140 °C. Finall, 1 mL of HI was quickly injected into the three-necked flask. An ice-water bath was immediately applied to cool the solution after injection. The as-prepared solution was subjected to centrifugation at 6000 rpm for 8 min to discard the supernatant containing unreacted precursor and byproducts. Then, 10 mL of n-hexane was added into the precipitate and centrifuged at 6000 rpm for 8 min. At last, the precipitate was dispersed in 10 mL of n-hexane to form a stable colloidal solution.

#### 2.3. Characterization

Powder x-ray diffraction (XRD) was performed using a Bruker D8 Advance x-ray diffractometer using Cu K $\alpha$  radiation (1.54 Å). Transmission electron microscopy (TEM) study was carried out using a FEI Tecnai G2 F20 field emission transmission electron microscope at an acceleration voltage of 200 kV. The UV absorption spectrum was obtained by UV-2500 (Shimadzu Corporation); the photoluminescence and photoluminescence excitation were investigated at room temperature using FLS980 (Edinburgh Instruments) spectrometer with a 450 W Xenon lamp. Time-resolved PL spectra and excitation power density-dependent PL spectra were also carried out



**Fig. 2.** (a) PL spectrum and absorption spectrum of PEA<sub>2</sub>PbI<sub>4</sub> nanosheets; (b) Absorption spectrum with Elliott theory fitting; (c) band edge absorption curve fitting of PEA<sub>2</sub>PbI<sub>4</sub> and PEA<sub>2</sub>PbBr<sub>4</sub> [31]; (d) exciton binding of semiconductor energy versus bandgap dependence [26].

by an Edinburgh FLS980 fluorescence spectrometer with a timecorrelated single-photon counting (TCSPC) spectrometer and the excitation wavelength was located at 405 nm. Schematic of the optical setup for the PL signal of  $PEA_2PbI_4$  nanosheets were shown in Fig. S1.

#### 3. Results and discussion

The crystal structure of the PEA<sub>2</sub>PbI<sub>4</sub> is shown in Fig. 1a, using PEA as the organic cation yields 2D layered PEA<sub>2</sub>PbI<sub>4</sub>. Layers of the inorganic semiconductor (sheets of corner-sharing PbI<sub>6</sub> octahedra) are sandwiched between layers of insulating PEA counter cations. Fig. 1b shows the XRD pattern of the prepared PEA<sub>2</sub>PbI<sub>4</sub> product by hot injection method. The sample exhibits pronounced peaks at the diffraction angles  $5.28^{\circ}$ ,  $10.69^{\circ}$ ,  $16.24^{\circ}$ ,  $21.74^{\circ}$  and  $27.24^{\circ}$ , which can be indexed to (00/) (/=2, 4, 6, 8, 10) series reflections of PEA<sub>2</sub>PbI<sub>4</sub> indicating high orientation [20]. In addition, the microstructure of the obtained PEA<sub>2</sub>PbI<sub>4</sub> sample was investigated by SEM and TEM. The results in Fig. 1c and d clearly demonstrate the 2D PEA<sub>2</sub>PbI<sub>4</sub> nanosheets were successfully synthesized. Such PEA<sub>2</sub>PbI<sub>4</sub> nanosheets with super quantum confinement effect is conducive to research the exciton behaviors.

The optical properties of the prepared PEA<sub>2</sub>PbI<sub>4</sub> nanosheets are reported in Fig. 2a. A strong excitons absorption peak is well evident at about 2.38 eV (521 nm) and the emission peak is located at about 2.32 eV (534 nm). The exciton and continuum contributions are separated by using the Elliott equation for the Wannier-Mott exciton. To determine the exciton binding energy, the optical absorption of

 $\ensuremath{\mathsf{PEA}}_2\ensuremath{\mathsf{PbI}}_4$  nanosheets was fitted using the Elliott model with the following formula

$$p_E = p_x + \frac{A_C}{2} \left[ erf\left(\frac{(E - E_0) - E_b^x}{\gamma_C}\right) + 1 \right]$$
(1)

$$p_{\chi} = \frac{1}{2\eta} \left[ erf\left(\frac{(E-E_0)}{\gamma_C} - \frac{\gamma}{2\eta}\right) + 1 \right] \exp\left(\frac{\gamma^2}{4\eta^2} - \frac{E-E_0}{\eta}\right)$$
(2)

where  $p_E$  and  $p_x$  are the total absorption line and the exciton absorption line with asymmetric broadening  $\eta$ .  $E_0$  and  $E_b^x$  are the absolute exciton energy and binding energy, respectively.  $\gamma$  is the line width of the absorption peak.  $A_C$  and  $\gamma_C$  are the step height and width of the continuum band edge absorption [21]. The fitting results give exciton binding energy of 274 meV for PEA<sub>2</sub>PbI<sub>4</sub> nanosheets as listed in Table 1, which agrees well with previously reported large exciton binding energy [22,23].

 Table 1

 Fitting parameters in the optical absorption with Elliott theory fitting.

Fitting Parameters	Value
Eo	2.345 ev
$E_{b}^{*}$	274 meV
γ	0.061
Ac	10.04
η	0.11
γς	0.145



**Fig. 3.** (a) PL spectrum of PEA<sub>2</sub>PbI<sub>4</sub> and its single-peak Gaussian fitting; (b) time-resolution spectrum at different emission energies; (c) time-resolved photoluminescence spectrum and its fitting curve; (d) PL lifetime of PEA<sub>2</sub>PbI<sub>4</sub> nanosheets as a function of the emission energy.

In order to describe the impact of excitonic states on the absorption spectrum, the band edge absorption curves of PEA<sub>2</sub>PbBr<sub>4</sub> and PEA<sub>2</sub>PbI<sub>4</sub> are extracted and compared in Fig. 2c. The excitonic behavior in light absorption and recombination process has been studied in detail by our group [24]. These two samples exhibit similar behavior, the reason for this consistency lies in the nature of the electronic structure of halide perovskites. For perovskite semiconductors, the conduction band forms from the antibonding orbitals of the hybridization of the Pb 6p orbitals and the outer p orbitals of the halide (5p for I, 4p for Br). The valence band forms from the antibonding states of Pb 6 s and the same halide p-orbitals [25]. The PL tail for III-V semiconductor materials arise from p and s atomic orbitals. Therefore, the lead-halide perovskite semiconductors exhibit analogous behavior like III-V semiconductor materials. A detailed summary of exciton binding energy and band gap of III-V semiconductor materials and lead-halide perovskite is reported in Fig. 2d. It exhibits linear dependence of binding energy indicating that the lead-halide perovskite system has similar physical properties to III-V semiconductors [26].

Fig. 3a shows the PL spectrum of the PEA<sub>2</sub>PbI<sub>4</sub> nanosheets. It is found that a significant PL tail emission appeared at the long wavelength by single-peak fitting. The PL tail is observed across a large range of perovskite and non-perovskite materials which has several origins such as defects, trap states on charge-carrier recombination and localized excitons [27–30]. Considering that perovskite materials have a soft lattice structure and are susceptible to lattice distortion caused by an external optical field, we consider that the PL tail emission of the 2D PEA<sub>2</sub>PbI<sub>4</sub> nanosheets is caused by localized excitons. To unravel the mechanism of the PL tail emission, we carried out time resolved PL measurements at room temperature. Fig. 3b shows the PL decay curves monitored at different emission energies and we can observe the PL lifetime decreases with increasing emission energy. A typical fitting result of TRPL spectrum is plotted in Fig. 3c, our experimental results yield the decay lifetimes  $\tau 1(3.49 \text{ ns})$ ,  $\tau 2$  (0.54 ns), and  $\tau 3$  (11.3 ns). Then, all the spectra were fitted and the lifetime values decrease with the increase of emission energies, which satisfies the spectral dependence property of the exciton localization [31]. Notably, the PL tail of PEA<sub>2</sub>PbI<sub>4</sub> nanosheets is originated from localization effect.

In order to further probe the recombination mechanism of PEA<sub>2</sub>PbI<sub>4</sub> nanosheets, an excitation powder density-dependent PL measurement was provided and the result is shown in Fig. 4. Series PL spectra of PEA<sub>2</sub>PbI<sub>4</sub> nanosheets were accorded under elevated excitation power density with a 405 nm pulsed laser diodes in Fig. 4a. The shapes of these PL spectra are almost identical in the whole range of excitation power intensity and PL intensities also increases with the enhancement of excitation power intensity. Representative PL intensities as a function of excitation power density (log(I)-log(P)) are shown in Fig. 4b. We fitted the dependencies using a relation of I ~ P<sup>K</sup>, where I is the PL intensity, P is the excitation power law dependence on the excitation power density, with a power-law exponent of 1.04. The 1 < K < 2 implies a dominant recombination mechanism given by free and localized excitons.

There is extended state and localized state in the lattice extension space. The extended state refers to the extension of the electron wave function to the entire lattice space in a perfect crystal, while the localized state means that the electron wave function is localized



Fig. 4. (a) PL spectra recorded with increased excitation power density and (b) Logarithm plot of the PL intensity versus excitation power density.



Fig. 5. (a) Physical model of the recombination of localized excitons; (b) PL spectrum with line-shape analysis; (c) free excitons PL component (PL<sub>FREE X</sub>). (d) localized excitons PL component (PL<sub>LOC X</sub>).

around impurities or defects. The localized excitons originate from the localized state which is a bound state, and the boundary between the localized state and the extended state is the mobility edge. Fig. 5a illustrates the physical model of the recombination of localized excitons. The tail states are represented by the local potential minima in the conduction and/or valence bands. The photogenerated carriers interact with phonons to exchange energy with lattice, then undergo relaxation process and transfer to these potential minima to form localized excitons. Under the action of lowenergy excitation light, the localized state is first filled with electrons, but the stokes shift increases because the emission wavelength of localized excitons is smaller than the bandgap energy.

Using line-shape analysis, single PL components can be decoupled in the PL spectrum. The total PL line-shape analysis uses the following expressions [32]:

$$PL_{TOT}(\hbar\omega) = PL_{FREEEX}(\hbar\omega) + PL_{LOCEX}(\hbar\omega)$$
(3)

$$PL_{TFREEEX}(\hbar\omega) \propto A_{FE}(\hbar\omega)^2 e^{-(\hbar\omega - E_{FE})/\kappa_B T} e^{\frac{-(\hbar\omega - E_{FE})^2}{w_{FE}^2}}$$
(4)

Table 2

Fitting parameters in the PL line-shape analysis.	
Fitting Parameters	Value
E <sub>FE</sub>	2.372 ev
A <sub>FE</sub>	0.063 meV
W <sub>FE</sub>	0.0516
ELOC	2.33 eV
ALOC	0.009
WIOC	0.066

$$PL_{LOCEX}(\hbar\omega) \propto A_{LOC}(\hbar\omega)^2 e^{-(\hbar\omega - E_{LOC})/\kappa_B T} e^{-\frac{(\hbar\omega - E_{LOC})^2}{w_{LOC}^2}}$$

where  $h\omega$  is the photon energy,  $E_{\rm FE}$  ( $E_{\rm LOC}$ ) is the free (localized) exciton resonance energy,  $w_{\rm FF}$  ( $w_{\rm LOC}$ ) is the free (localized) exciton Gaussian broadening, A is the amplitude of PL spectrum, T is the carriers temperature in the Boltzmann statistics,  $(\hbar\omega)^2 e^{-(\hbar\omega - E_X)/\kappa_B T}$  is the Boltzmann statistics, the fitting parameters are shown in Table 2. The localization energy of PEA<sub>2</sub>PbI<sub>4</sub> nanosheets is about 42 meV which emerges from the comparison of free exciton energy (2.372 eV) and localized exciton energy (2.33 eV). The acquired localization energy is higher than the RT thermal energy indicating that the PL tail is generated from the localized excitons. The corresponding single PL components are highlighted for free excitons (EX in the legend) and localized excitons ( $EX_{LOC}$  in the legend) in Fig. 5b. Fig. 5c and d display the luminescent component of the free excitons and localized excitons with their corresponding densities of states. The intensity of absorption spectrum was very low after normalized fitting. In order to facilitate observation, the original data were amplified in multiples, thus obtaining the single-component spectra of free excitons and localized excitons. Because the local excitons are in the energy potential well at the band edge, the luminescence energy is lower. The emission peak and absorption density of free and local excitons also show stokes shift, and the emission spectra also conform to Boltzmann statistical distribution. The above theoretical decoupling results are consistent with the experimental results from spectral dependence of the photoluminescence lifetime, demonstrating that the existence of localized excitons inside the PEA<sub>2</sub>PbI<sub>4</sub> nanosheets leads the PL tail emission.

#### 4. Conclusion

In summary, we have theoretically and experimentally decoupled excitons behavior in 2D Ruddlesden-Popper PEA<sub>2</sub>PbI<sub>4</sub> nanosheets in this study. The excitons and band edge absorptions of PEA<sub>2</sub>PbI<sub>4</sub> nanosheets were separated using Elliott theory fitting and the exciton binding energy of 2D PEA<sub>2</sub>PbI<sub>4</sub> was obtained to be 274 meV. The mechanism of PL tail emission was successfully revealed by localized excitons. The luminescent component of the free excitons and localized excitons with their corresponding densities of states was decoupled by line-shape analysis. Consistent theoretical and experimental results successfully resolve the mechanistic behavior of 2D perovskites. We believe that this work will be of immense benefit to understand the intrinsic excitons absorption and luminescence mechanism for the desirable 2D luminescence materials.

#### **CRediT authorship contribution statement**

Wen Li: Data curation, Writing – original draft preparation. Shiyu Yang, Bolin Guo, and Xuehai Fu: Conceptualization, Methodology. Xiankan Zeng and Cheng Yan: Visualization, Investigation. Jingjing Cao and Qungui Wang: Supervision. Weiqing Yang: Writing – reviewing and editing.

## Data availability

Data will be made available on request.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2022.168312.

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