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Designable Layer Edge States in Quasi-2D Perovskites Induced by Femtosecond Pulse Laser

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The low-energy layer edge states (LESS) from quasi 2D hybrid perovskite single crystals have shown great potential because of their nontrivial photoelectrical properties. However, the underlying formation mechanism of the LESSs still remains controversial. Also, the presence or creation of the LESSs is of high randomness due to the lack of proper techniques to manually generate these LESSs. Herein, using a single crystals platform of quasi-2D (BA)$_2$(MA)$_{n-1}$Pb$_{3n}$I$_{3n+1}$ ($n > 1$) perovskites, the femtosecond laser ablation approach to design and write the LESSs with a high spatial resolution is reported. Fundamentally, these LESSs are of smaller bandgap 3D MAPbI$_3$ nanocrystals which are formed by the laser-induced BA escaping from the lattice and thus the lattice shrinkage from quasi-2D to 3D structures. Furthermore, by covering the crystal with tape, an additional high-energy emission state corresponding to the reformation of (BA)$_2$PbI$_4$ ($n = 1$) within the irradiation region is generated. This work presents a simple and efficient protocol to manually write LESSs on single crystals and thus lays the foundation for utilizing these LESSs to further enhance the performance of future photoelectronic devices.

1. Introduction

Quasi-two-dimensional (quasi-2D) perovskites, particularly the Ruddlesden–Popper halide perovskites,[1] have shown great potential for the applications in photoelectronic such as light-emitting diodes (LEDs),[2] solar cells,[3] and photodetectors[4] due to the flexibility in modulating the exciton binding energy and bandgap, high quantum efficiency, and excellent moisture stability.[1b,5] Recently, the low-energy layer edge states (LESSs) have been discovered in these quasi-2D halide perovskites and display attractive photoelectric properties such as long carrier lifetime[6] and high electrical conductivity.[7] LESSs provide a direct pathway for charge dissociation and thus the potential to significantly improve the performance of photoelectronic devices based on quasi-2D perovskites.[8]

In the year of 2017, Blancon et al. firstly reported the LESSs that exhibit a lower-energy photoluminescence (PL) locating at the edge of exfoliated quasi-2D perovskites (BA)$_2$(MA)$_{n-1}$Pb$_{3n}$I$_{3n+1}$ when the quantum well is thick, i.e., $n \geq 3$.[6] They found that LESSs can trap the photogenerated excitons and dissociate them into free carriers with longer lifetime and lower energy. In 2018 Feng et al. revealed that these LESSs can efficiently boost the photocurrent and enhance the photo-response in photodetectors using quasi-2D perovskite single-crystals.[9]
Wang et al. further demonstrated an extraordinary conductive feature along the LESs at room temperature and firstly visualized these states using conductive atomic force microscopy (c-AFM) in 2019.[7] These unexpected properties promote the LESs to be a crucial factor to further improve the device performance of quasi-2D perovskites optoelectronics. In order to understand the formation mechanism of LESs, the intrinsic origin and external influence factors of LESs have been more deeply explored. In 2018, Kepenekian et al. proposed an elastic model, which claimed that the lattice mismatch may induce the formation of LESs.[10] Zhang et al. provided a more profound understanding that the asymmetry in the chemistry of the iodine and Pb atoms at the edge may lead to the LESs.[11] Recently in 2021, Hong et al. demonstrated that the LESs are stabilized by the ferroelectric alignment of organic cations.[12] In addition to these internal factors, Shi et al. revealed that external factors such as moisture level can have an impact on the LESs formation.[13] Zhao et al. reported that the LESs can be modulated by the MAI/BAI solution rinsing process,[14] indicating the LESs are associated with the loss of BA binding ligands. Very recently, Qin et al. observed three-dimensional (3D) MAPbBr3 spontaneously formed in the fresh edges of 2D (BA)n−1PbnI3n single crystal flakes and milling.[15] So far, it is still inconclusive whether intrinsic or extrinsic factor dominates the formation mechanism of LESs in quasi-2D perovskites. Moreover, the generation of LESs is still a random phenomenon occurring in the process of material synthesis or the mechanical exfoliation of the single crystal. Therefore, there lacks a precise control of the LESs formation, let alone the manufacturing or programing of predefined patterns of LESs.

To address these issues, we employ high-power fs pulse laser with a wavelength of 800 nm for the ablation process. Surprisingly, these manually created LESs also exhibit the low-energy emission (760 nm) from edge states has a much longer lifetime at 630 nm in the bulk region is around 1.17 ns. The PL lifetime at the same wavelength (630 nm) in the edge region is 0.82 ns, which is smaller than the bulk region. The low-energy emission (760 nm) from edge states has a much longer lifetime (3.94 ns) and exhibits a relatively slow rising component (~0.42 ns), indicating energy transfer and carrier filling from the higher-energy intrinsic exciton to the low-energy edge states.[5, 14] Similar results are also observed in the n = 4 sample (Figure S2, Supporting Information). The fluorescence lifetime imaging microscopy (FLIM) results further verify the general existence of LESs in the crystal edges in these quasi-2D (BA)n−1PbnI3n perovskites when n ≥ 3 (Figure S3, Supporting Information).

To manually write a pattern of LESs, we employ a high-power fs pulse laser with a wavelength of 800 nm for the ablation process. Surprisingly, these manually created LESs also exhibit the low-energy emission at the laser-induced edge regions in the single crystal samples of quasi-2D perovskites (n ≥ 2). The fs laser pulses possess a pulse width of 200 fs and a repetition rate of 80 MHz. Figure S4 (Supporting Information) shows the correlation between the intensity of low-energy emission emitted from the laser-induced edge and the fs laser fluence upon an identical irradiation time of 50 ms. The low energy PL peak can only be observed when the laser fluence is beyond 11.7 mJ cm−2. The optical images indicate there is a structural damage of the bulk region of quasi-2D perovskite. Figure 2a shows the optical image and low-energy PL (>700 nm) images of the n = 3 perovskite after patterning by fs laser ablation. The PL images are collected upon 395 nm wide-field excitation and the emission signal is selected.
Figure 1. a) Optical images and the crystal structures of quasi-2D single crystals of (BA)$_{2n}$ (MA)$_{n-1}$Pb$_n$I$_{3n+1}$ ($n=1–4$). b) The corresponding single crystal XRD patterns. c) UV–vis–NIR absorption and PL spectra from the bulk (red line) and edge (blue line) regions, respectively. d) Normalized PL decay dynamics of the bulk ($\approx 630$ nm) and the edge ($\approx 630$ and $\approx 760$ nm) regions from the (BA)$_2$ (MA)$_2$Pb$_2$I$_{10}$ ($n=3$) perovskite single crystal.

Figure 2. a) Optical and PL images collected at emission channels of $>700$ nm of (BA)$_{2n}$ (MA)$_{n-1}$Pb$_n$I$_{3n+1}$ ($n=3$) flakes after irradiated with 800 nm fs laser pulses (above) and the corresponding experimental setup scheme (below). b) PL spectra of the 2D perovskite crystal from the bulk and laser-induced edge regions upon 400 nm excitation. c) Normalized PL decay dynamics of the bulk ($\approx 630$ nm) and the laser-induced edge ($\approx 630$ and $\approx 760$ nm) region. d) Time evolution of in situ two-photon excited photoluminescence (TPPL) spectra upon fs pulse laser ablation.
by a 700 nm long-pass (LP) filter before the camera. The corre-
sponding experimental scheme for fs laser ablation and PL imag-
ing is also shown in Figure 2a. We find that the low-energy emis-
sion can be observed at the edges of the laser-irradiated trace.
Figure 2b compares the PL spectra collected at both the bulk
den and laser-induced edge region upon an excitation wavelength
of 400 nm. The original bulk region only has an emission with a
peak at $\approx 630$ nm, while the laser-induced edges exhibit an ad-
ditional low-energy emission (peak A) centered at $\approx 760$ nm and
a high-energy emission (peak B) centered at $\approx 518$ nm, ac-
companied with the original emission at $\approx 630$ nm. The PL spectra
of the lower-energy peak A created by fs laser ablation is simi-
lar to the natural LESs emission. In order to understand the ori-
gin of these peaks, we also quantify the PL lifetime of the LESs
acquired by fs laser ablation (Figure 2c). The PL lifetime of the
lower-energy peak A is 3.92 ns, which is identical to that of nat-
ural LESs created by mechanical exfoliation. In a particular com-
parison with the natural low-energy LESs, the rising component
of peak A is faster here, which indicates a more efficient energy
transfer from the intrinsic exciton to the laser-induced LESs.

The PL lifetime distribution of laser-induced LESs was also confirmed
by the FLIM result, which shows the LESs can only be observed
at the edge region of the laser ablation (Figure S5, Supporting
Information). We speculate these fs laser-induced LESs may be
possibly introduced by the stoichiometric loss of BA component
during the ablation process, as the larger-sized BA spacers pro-
cess a much weaker interaction with the metal halide octahedra
frame. The loss of BA can facilitate the connection of metal halide
octahedra in the out-of-plane direction of the quasi-2D crystal
and consequently lead to the formation of 3D $\text{MAPbI}_3$ nanocrystals
from the laser-induced edge region (Figure S5, Supporting
Information). The SEM images in Figure 4c–f show the different ratio
of Pb and I elements between the bulk and edge regions. The ra-
tio of Pb/I in the bulk position of the sample is about 0.297 which
is consistent with the stoichiometric Pb/I ratio from the original
chemical formula of 2D (BA)$_2$(MA)$_x$Pb$_{11.0}$ (n = 3). In contrast,
the ratio of Pb/I in the edge position of the sample is about 0.313
which is closer to that of 3D $\text{MAPbI}_3$. Furthermore, Raman spec-
tra (Figure S7, Supporting Information) obtained from the laser
induced edge region show two typical bands (113 and 250 cm$^{-1}$)
of 3D $\text{MAPbI}_3$, which are corresponding to the vibration modes
of Pb-I octahedra cage and MA cation, respectively. The varia-
tion of Pb/I ratio, the strong correlation of PL, PL lifetime and
Raman spectra of 3D $\text{MAPbI}_3$ suggest that $\text{MAPbI}_3$ nanocrystals
form at the edges of the laser ablation region and eventually give
rise to the low-energy emission of LESs.

The origin of LESs can be further cross-checked by the compar-
sion study between the fs pulse laser ablation and a continuous
wave (CW) laser ablation. The fs laser with a high peak power in-
tensity can efficiently trigger an electronic heating at a high speed
by two-photon absorption with minimal thermal effect, while
most energy of the CW laser is absorbed by the sample due to the
interband transition and consequently melt the sample.
As shown in Figure S8 (Supporting Information), the 808 nm
CW laser has no laser-ablation effect on the sample, which might be
due to the lower photon energy than the bandgap of quasi-
2D perovskite crystals and thus no absorption. Then we chose a
lower wavelength CW laser of 488 nm (higher energy than the
bandgap of the quasi-2D perovskites to secure the photon absorp-
tion), which is supposed be effectively absorbed by the sample
and cause sufficient melting effect. Figure 5a shows the optical
images of quasi-2D perovskite crystal (n = 3) after ablation with
800 nm fs pulse laser (121 mW as fluence of 48.1 mJ cm$^{-2}$) and
488 nm CW laser (14.5–121 mW), respectively. The middle line
and a Chinese character on the left are drawn by the fs pulse laser,
while three dots on the right are written by CW laser with dif-
f erent powers. According to the PL image shown in Figure 5d,
488 nm CW laser irradiation does not lead to emissive LESs in
the sample, which is consistent to the PL spectra in Figure 5c.
The SEM image in Figure 5b also confirms the melting nature of
the samples irradiated by CW laser and consequently there is no
3D $\text{MAPbI}_3$ nanocrystal formed at the edges. These results sug-
gest that melting without loss of BA molecular cannot lead to the
formation of LESs.
To identify the origin of high-energy emission peak B upon fs laser ablation, two possible species during the decomposition and reorganization process such as PbI$_2$ and (BA)$_2$PbI$_4$ ($n=1$) are prepared for a comparison study. As shown in Figure 5e, the emission peaks of (BA)$_2$PbI$_4$ ($n=1$) and PbI$_2$ single crystal locate at 518 and 525 nm, respectively. The high-energy peak B matches well with the intrinsic emission of the $n=1$ perovskite crystal. Furthermore, Figure 5f shows the PL lifetime dynamics of (BA)$_2$PbI$_4$ ($n=1$), PbI$_2$ single crystal, and quasi-2D perovskite crystal ($n=3$) with fs laser ablation collected at wavelength of 520 nm. The quasi-2D perovskite crystal ($n=2$ and 4) also share the similar PL lifetime of laser induced peak B (Figure S9, Supporting Information). The 520 nm PL lifetime is 0.18 ns which is identical to that of (BA)$_2$PbI$_4$ ($n=1$) but significantly smaller than that of PbI$_2$ single crystals (1.93 ns). This longer lifetime of PbI$_2$ single crystal is also confirmed by the repeating measurement of different PbI$_2$ single crystals in Figure S10 (Supporting Information). The strong correlation between PL spectra and lifetime of (BA)$_2$PbI$_4$ ($n=1$) reveals that the high-emission peak B induced by laser ablation is due to the formation of $n=1$ 2D perovskite crystal rather than PbI$_2$.

In order to understand how the fs laser induced BA component would behave upon the fs laser irradiation (escape to air or reorganize into ordered structures), we prepare the fresh perovskite samples with and without cover tapes for comparison (Figure 6a,b). PL images collected by different emission channel (low-energy peak A and high-energy peak B) are compared to show the variation between the samples either in sealed condition or in open air condition during fs laser ablation. As shown in Figure 6a, when fs laser irradiates the sample with a cover, the high-energy emission (peak B) is mainly observed in the whole region of the laser irradiation. While the low-energy emission (peak A) is only present at the edge regions (periphery of the laser ablated region). As the observed PL intensity of BA$_2$PbI$_4$ ($n=1$) at edge is much lower than that at the laser irradiation region, the majority of the BA$_2$PbI$_4$ is most likely exist on the tapes (Figure S11a, Supporting Information). In contrast, when fs laser irradiates the sample without a cover, the high-energy emission (peak B) even cannot be observed in the whole region of laser irradiation (Figure 6b and Figure S11b, Supporting Information). This comparison experiment reveals that the cover tape provides an enclosed chamber facilitating the re-formation of BA$_2$PbI$_4$ ($n=1$).
Figure 4. a) Optical images of (BA)₂(MA)₂Pb₃I₁₀ \((n = 3)\) single crystal with three dots induced by fs pulse laser ablation. The three dots were created by the identical laser fluence upon irradiation time of 50, 100, and 200 ms, respectively. b) The corresponding PL (>700 nm) image upon 395 nm wide-field excitation. c) The corresponding SEM image. d–f) The respective high-resolution SEM images of these three dots. g,h) EDS analysis of the bulk and the laser-induced edge regions from the \(n = 3\) perovskite single crystal.

Figure 5. a,d) Optical and PL images of (BA)₂(MA)₂Pb₃I₁₀ \((n = 3)\) upon 800 nm fs laser and 488 nm CW laser ablation, respectively. b) SEM images upon 488 nm CW laser ablation. c) PL spectra comparison before and after the CW Laser ablation treatment. e) PL spectra comparison of the PbI₂ single crystal, 2D perovskite crystal \((n = 1)\), and 2D perovskite crystal \((n = 3)\) after fs laser ablation. f) Normalized PL decay dynamics at the wavelength of 520 nm from the samples in panel (e).
2D perovskites. Figure 6c,d illustrates the schematics of the fs laser ablation process in the quasi-2D perovskite crystal at these two conditions. Upon fs laser irradiation, the organic counterparts and inorganic sublattice of quasi-2D perovskites (n > 1) decompose into air due to the photochemical and thermochemical reactions induced by the high peak power of fs pulses in the focal region. Compared to MA molecular, BA spacer has a much weaker interaction with the lead halide sublattice, which is more easily released from the lattice. On the edges of the irradiation spot with lower fluence, BA spacers are partially released and the 3D MAPbI$_3$ nanocrystals are formed by subsequent connection of the octahedra sublattice. In the sealed condition, the enclosed chamber blocks the evaporation of BA into air and thus the high concentration of BA in the enclosed atmosphere facilitates the assembly of the BA$_2$PbI$_4$ (n = 1) perovskites. Hence, an obviously high-energy emission (peak B) is observed. In contrast, in the open-air condition, BA can easily escape to the air and hardly form the BA$_2$PbI$_4$ (n = 1) perovskites. As a result, there is no observation of high-energy emission (peak B) in this condition. While for both cases, as soon as fs laser release the BA from the lattice, the residual MA and inorganic octahedra further shrink the lattice to a 3D structure in their radiation edge, which explains the low-energy emission of LESs in both samples.

3. Conclusion

In summary, we proposed a potential approach of fs laser ablation to write LESs with highly designable capability in quasi-2D (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ (n > 1) single crystals. A series of comparative experiments on optical and morphological properties of the samples before and after fs pulse laser and CW laser ablation have been conducted. The results show that the LESs located at the edges of irradiation trace originate from the formation of the 3D MAPbI$_3$ nanocrystals. These 3D MAPbI$_3$ nanocrystals result from pulse laser induced releasing of BA spacers. Sealing of the irradiated film can facilitate the generation of LESs on the edges and induce additional high-energy states by the formation of (BA)$_2$PbI$_4$ (n = 1) within the irradiation region. So far, most prior LESs from literatures are randomly distributed and remains challenging to pattern or program. This work provides the solution to this, showing that fs laser ablation can be a simple and efficient technique to design and write the emissive LESs with high spatial resolution and high controlling preciseness. This may open more opportunities for developing high-performance quasi-2D perovskite optoelectronics.

4. Experimental Section

Chemicals: Lead(II) oxide (>99.0%), hydroiodic acid (57%), hypophosphorous acid solution (50 wt%), and n-butylamine (99.5%) were obtained from Sigma-Aldrich. Methylammonium iodide (99.5%) was obtained from MACKLIN. All the chemicals were used as received.

Synthesis of Quasi-2D (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ Perovskite Single Crystals: The quasi-2D (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ (n = 1, 2, 3, 4) perovskite single crystals were synthesized according to the previously reported method.[16] 1.126 g lead(II) oxide (2.4 mmol) was firstly dissolved in the mixed solution of 5 mL hydroiodic acid and 850 μL hypophosphorous acid. With heating up to 100 °C, the mixture was continuously stirred until a pale-yellow solution was gained. Meanwhile, in another vial, methylammonium iodide (MAI) and n-butylamine (BA, total ammonium of 5 mmol) in different molar ratios were slowly added into 3 mL hydroiodic acid with an ice bath. Since the transparent solution was obtained, the ammonium precursor was added into the lead solution with stirring at a lifted temperature. Then, the mixture was cooled down at a rate of 0.5 °C/h. Finally, the crystallized crystals were dried at 40 °C in a vacuum oven.

Preparation of Exfoliated Quasi-2D (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ Perovskite Single Crystal Flakes: Scotch tape (3M) was applied to exfoliate quasi-2D perovskite single crystal. Briefly, a piece of the sample was transferred onto the adhesive side of the tape. After folding the tape with a blank position facing the single crystal, the two sides of the tape were separated to exfoliate the single crystals. After repeating this process several times, the adhesive side of tape was pressed on a piece of microscope cover glass (24 × 50, Fisherbrand) and the single crystal flakes could be observed by microscopy (Olympus IX71).
SEM and Raman Measurement: The SEM images along with an EDS analysis were obtained from Carl Zeiss, ZEISS Gemini 500, which has a secondary electron detector and a backscattered electron detector (InLens). The sample was attached to a conducting substrate, and the platinum metal coating was sputtered onto the sample before measurement. The Raman spectra were collected by an inVia Renishaw spectrometer with a 785 nm laser for excitation.

Time-Resolved PL Spectroscopy and Imaging Measurement: Time-resolved PL spectroscopy and imaging measurements were performed by a home-built system, which mainly includes fs pulsed laser, an inverted fluorescence microscope, and a spectrometer integrated with Time-Correlated Single Photon Counting (TCSPC) detection. The excitation laser pulses were generated from a wavelength-tunable femtosecond oscillator (Coherent Chameleon, 200 fs pulse width and a repetition rate of 80 MHz). The excitation laser was introduced into the microscope (Olympus IX71) and focused on the sample via an objective lens (60×). The optical image was taken by two Scientific CMOS cameras (PCO.panda 4.2 & Sony Starvis IMX226). Short-pass filters (for two-photon excitation) or long-pass filters (for one-photon excitation) were placed in the detection path to cut off the excitation laser before measuring. The sample was placed on a 3D nano-translation stage (Physik Instrumente, P-525) for micro-pattern writing.

A precision electronic shutter (Hengyang, GCI-73) was used to control the irradiation exposure time. The ablation position was controlled by the 3D nano-translation stage (Physik Instrumente, P-525) for micro-pattern writing.

Laser Ablation: An 800 nm femtosecond pulsed laser (Coherent Chameleon, 200 fs pulse width and 80 MHz repetition rate) as well as a 488 nm CW laser (CVI Melles Griot) were employed for laser ablation measurement. The ablation occurs when fs laser power was increased beyond 29.3 mW. Both of them were focused onto the sample with a radius of 1–2 μm or even smaller via an objective lens (60× or 100×). A precision electronic shutter (Hengyang, GCI-73) was used to control the irradiation exposure time. The ablation position was controlled by the 3D nano-translation stage (Physik Instrumente, P-525) for micro-pattern writing.

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

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

Keywords
femtosecond pulsed laser, laser ablation, layer edge states, photoluminescence, quasi-2D perovskites

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