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Two-photon optical properties in individual organic-inorganic perovskite microplates*Qi Wei[‡], Bin Du[‡], Bo Wu, Jia Guo, Mingjie Li, Jianhui Fu, Zhipeng Zhang, Jianwei Yu, Tianyu Hou, Guichuan Xing,^{*} Tze Chien Sum,^{*} Wei Huang^{*}*

((Optional Dedication))

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The rapid developments of halide perovskite solar cells in latest years have surprisingly attracted tremendous research attention.^[1, 2, 3, 4] Owing to the interesting inherent properties of halide perovskites such as low trap-state density, long diffusion length and huge linear absorption coefficient at band edge;^[5, 6, 7, 8] halide perovskites are deemed to be promising light harvesting materials.^[9, 10, 11, 12] In particular, the tunable emission wavelength in whole visible spectrum range through anion exchange process and corresponding high photoluminescence quantum yield (PLQY) for perovskite (especially in all-inorganic perovskite where PLQY up to 90%),^[13, 14, 15] demonstrate halide perovskite also possess tremendous application potentials in light emitting diodes and optical pump lasers.^[16, 17, 18, 19, 20, 21] Since light amplifications in lead halide perovskite thin films were reported, multi-

photon nonlinear optical properties were discovered in lead halide perovskites single crystals and quantum dots.^[22, 23, 24, 25, 26, 27, 28, 29, 30, 31] Amplified spontaneous emission (ASE)/lasing actions was also realized in lead halide perovskite micro-lasers by controlling the cavity structures.^[32, 33, 34, 35] In micro-lasers, the regular cavity is more prone to achieve lower threshold and higher quality lasing due to the optical confinement effect. Regular shape of micro-lasers with various sizes also give rise to various optical confinement abilities, which suggested that lasing actions in perovskite micro-lasers showing size-dependent behavior.^[36, 37, 38, 39]

However, one of the critical issues that remained is how the excitons or free carriers influence the basic optoelectronic as well as lasing properties in perovskite, in actually, has not been detail discussed.^[40] The investigations on exciton binding energy in lead halide perovskite have been carried out in some previous works.^[41, 42] Unlike the excitonic emission in bromide based perovskite QDs with large exciton binding energy (~ 375 meV for MAPbBr₃ QDs),^[43] the relatively weak exciton binding energy (reported to be around 76 meV^[44]) in MAPbBr₃ perovskite film leads to a strong temperature-dependent as well as power-dependent photoluminescence properties. Part of the excitons will be thermally dissociated to free charges, considering that the thermal energy ($k_B T$) is around 26 meV at room temperature. In that case, excitons and free carriers are expected to coexist in this MAPbBr₃ 3D metal-halide perovskites.^[45, 46] In virtue of entirely different behaviors for excitons and free carriers, excitons obey the Bose-Einstein statistics; while free carriers obey the Fermi-Dirac statistics, which complicates the ultrafast dynamic processes and the nonlinear optical properties inside perovskite films. Therefore, to figure out the contributions of exciton versus free carriers to linear and nonlinear optical characteristics inside MAPbBr₃ microstructure is hardly avoidable.^[47]

In this work, we first constructed regular square MAPbBr₃ microplates with sizes from 20 to 90 μm . The temperature and power dependent photoluminescence properties were simultaneously studied by two-photon photoluminescence (TPPL) spectroscopy. Due to deep volume excitation of TPPL spectroscopy, it was regarded as a powerful method to study the intrinsic properties of perovskite. According to the power-dependent initial photoluminescence (PL₀) intensity, PL₀ of MAPbBr₃ microplates show approximately a quadratic dependence on photo-injected carrier density ($n = 2.19$), which suggests that free charges represent the dominant species at room temperature. We also discussed the influence of temperature triggered excitons to free carriers transition imposed on ASE threshold of MAPbBr₃ perovskites. To overcome the reduction of PL intensity induced by thermal-assisted non-radiative recombination at higher temperature, higher excitation energy was required to compensate the loss of optical gain resulted in increment of ASE threshold. In addition, the ASE threshold increases with increasing the size of the MAPbBr₃ microplate, which could be well interpreted with the interplay between the optical confinement, defect density and cavity quantum electrodynamics (QED) effect.

Results and Discussion

Solution process preparation of MAPbBr₃ perovskite films is presented in the Experimental section. The edge dimensions of the crystal investigated by Raman optical microscopy and corresponding images showed in **Figure 1 a**, it is obvious to see the plate-shape like perovskites with lateral sizes range from $\sim 20\ \mu\text{m}$ to $\sim 90\ \mu\text{m}$. And the thickness of film is about 150 nm thick (Figure S1). The $\sim 60\ \mu\text{m}$ size MAPbBr₃ square plates, shown in **Figure 1 b**, was selected to study its own nonlinear optic properties; **Figure 1 c** demonstrates the illumination of the square plates, a strong green emission is observed. A distinct depression was centered at square plates can be observed from Scanning Electron Microscope (SEM) images in **Figure 1 d**. The X-ray diffraction (XRD) pattern of MAPbBr₃ film is given in

Figure 1 e, diffraction peaks of MAPbBr₃ at 14.79° for (100) plane, 30.06° for (200) plane , 45.85° for (300) plane, revealed the characteristics of the perovskite square phase according to the previous work.^[48, 49] The linear absorption spectrum is shown in **Figure 1 f**, a sharp peak at 2.35 eV can be ascribed to the excitonic absorption,^[50] the spectrum is then simulated by Elliott's formula,^[42, 51, 52] where the linear absorption can be described by the continuum and excitonic states' absorption. Two-photon absorption coefficient was calculated from pump probe differential transmission spectra (Figure S2). The detail calculation process for two-photon absorption coefficient is presented in Supporting information. We assumed the intensity of incident light will be reduced by linear and nonlinear procedures when light propagating through the sample, it can be expressed as:

$$\frac{\Delta T}{T} = e^{-\beta I_2 L} - 1 \quad (1)$$

Where I_2 is the intensity of pump, α is the linear absorption coefficient, β is the two-photon absorption coefficient, L is optical distance in sample. Here, CdS film serves as a standard sample, the values of $\Delta T/T$ extracted from the differential transmission spectra are -0.00055 and -0.377 for perovskite and the bulk CdS, respectively. Hence, the perovskite two-photon absorption coefficient $\beta_{\text{perovskite}}$ is estimated to be $\sim 4.06 \times \beta_{\text{CdS bulk}}$, where $\beta_{\text{CdS bulk}}$ is the two-photon absorption coefficient of bulk CdS. We utilized $\beta_{\text{CdS bulk}}$ values of 4.9 cm/GW at 800 nm,^[53] instead of 6.4 cm/GW at 780 nm.^[54] One-photon and two-photon PL spectra are obtained at low pump fluences and excitation at 400nm and 800nm, respectively. The 1PP emission peak appearing at around 536nm indicates the band-edge emission in MAPbBr₃ films, while 2PP emission peak is located at 550 nm with slight red-shift compared to 1PP's. We attribute this red-shift to the reabsorption effects^[55, 56], which are commonly seen in other previous reports,^[19, 57] and is relevant to the large penetration depth of longer wavelength. In short, due to the overlap of the absorption and PL spectra, the initial fluorescence will be

reabsorbed and re-emitted multi-time when excited at longer wavelength^[58]. Pump-fluence-dependent stimulated emission spectra are showed in **Figure 2 b** and **2 d**, as the pump fluence increased, the PL spectrum starts to narrow with the emerging of an ASE peak. The gain-induced ASE peaks have a full width at half-maxima about 7 nm for both 1PP and 2PP excitations. The ASE threshold estimated from figure are 20 $\mu\text{J}/\text{cm}^2$ and 3.3 mJ/cm^2 for 1PP and 2PP ASE, respectively. The 2PP ASE threshold is comparable to the previous report.^[37]

In order to understand the contributions of free charge carriers and excitons to the total PL accurately, the knowledge of the PL dependence on temperature is indispensable. The temperature-dependence PL spectrum is plotted in **Figure 3 a**. What we can learn from the figure is that the emission energy is regarded as fixed as the temperature increases, while the PL intensity decreases significantly. Compared to III-V quantum wells like GaAs where free charge, heavy exciton and light exciton emission coexists and fine structure of PL spectra can be obtained at low temperature, however, in this work no other peaks emerge but only one broaden emission exist from low temperature 80 K to 300 K. The temperature dependence full-width at half-maximum (FWHM) for the perovskites PL line is shown in **Figure 3a**, consequently we use Boson model to describe the lineshape:^[59]

$$\Gamma(T) = \Gamma_0 + \sigma T + \frac{\gamma_{LO}}{e^{\hbar\omega_{LO}/k_B T} - 1} \quad (2)$$

The linewidths of PL spectra have both homogeneous and inhomogeneous components, given respectively by the Lorentzian and the Gaussian linewidths. In the equation, Γ_0 is the inhomogeneous broadening contribution, σ is the exciton-acoustic phonon interaction parameter, γ_{LO} is exciton-optical phonon contribution to the line width broadening. The γ_{LO} extracted from the fitting results is about $\sim 160 \mu\text{eV}/\text{K}$. To corroborate our picture of the nature of emitting states in MAPbBr_3 films, time-resolved photoluminescence (TRPL) has been performed. In **Figure 3 b**, a set of power-dependent TRPL spectra is demonstrated. The

pump energy selected here is much lower than the one-photon ASE threshold to make sure the effect of Auger recombination processes can be totally avoided.

The power-dependent initial photoluminescence intensity (PL_0) was plotted in a log-log representation (see **Figure 3 b**). PL_0 with a fitted line shows approximately a quadratic dependence upon pump fluences ($n = 2.19$), namely $PL_0 \propto \Phi^2 \propto n_{eh}$. This behavior agrees well with Saha-Langmuir model. Thus the emission in MAPbBr₃ films can be explained by nongeminate recombination of the free charges.^[45, 60] With careful inspection of the normalized PL intensity (I_{PL}) as a function of temperature of **Figure 3 d**, the intensity is exponentially reduced in the higher temperature region, and well-fitted by the following equation^[61]:

$$I(T) = \frac{I_0}{1 + Ae^{(-E_b/k_B T)}} \quad (3)$$

Noticed that exciton binding energy (E_b) does not depend on temperature in MAPbBr₃ in the range 80 K - 300 K^[62]. E_b is fitted to be in the range of 37 - 60 meV, which is slightly smaller than the previous report value of 76 meV.^[44] The fitted E_b is in the same order of magnitude as the thermal energy at room temperature ($k_B T = 26$ meV at 300 K). Furthermore, we modelled a simulation of the free charge fraction over the total photoexcitation; it assumed that binding energy E_b is independent of excitation density. The fraction of free charges over the total density of excitation, x (n_F/n), for a 3D semiconductor can be expressed as:^[41, 63]

$$\frac{x^2}{1-x} = \frac{1}{n} \left(\frac{2\pi\mu k_B T}{h^2} \right)^{3/2} e^{\left(\frac{-E_b}{k_B T} \right)} \quad (4)$$

Where n is the total density of excitation; μ is effective reduced mass of the exciton with a value $\mu = 0.13m_e$, m_e being the electron mass.^[44] From the equation, it obvious to know that free carrier become more predominant at higher temperature. In **Figure 3 c**, with binding energy 60 meV, the lower excitation density, the greater the ratio of free charge to excitons; at 20 $\mu J/cm^2$ ($\sim 10^{16} cm^{-3}$) excitation density (1PP ASE threshold), most of electron-hole pairs

are dissociated into free carriers indicates that ASE behaviour is determined by free carrier recombination rather than exciton recombination. While at the higher the density of excitations, the lower the ratio of free charge due to the greater possibility for free electron-hole capture events. Hence, combining with the large γ_{LO} and thermal activation energy, the excitons can be easily dissociated at room temperature^[64]. The interchange between excitons and free charges indicates there is a coexistence of the two species under thermodynamic equilibrium.^[45] At room temperature, the ratio of free charge to exciton is very high, and large concentration of free charges results in high probability of electron-hole capture events which also takes responsibility for the PL quenching. Furthermore, the temperature-dependent TRPL decay transients for MAPbBr₃ (**Supporting Information**), exhibits analogously behaviour. By increasing the temperature from 80K to 300 K, the exponentially reduced effective decay lifetime reflects the non-radiative lifetime,^[65] consistent with the fact that thermal-induced non-radiative recombination of free charge carriers are prominently at higher temperature than radiative lifetime at low temperature region. In the meantime, normalized two-photon ASE threshold carrier concentrations n_c^{th} versus temperature are shown in **Figure 3d** (right axis) with a fitted line^[66], where $n_c^{th} \propto e^{\left(-\frac{E_b}{k_B T}\right)}$. Note that, I_{PL} product n_c^{th} with a value of ~ 0.1 , we can realize that to compensate the loss of PL intensity, higher pump energies are required to accomplish the ASE process where expressed as an increment of ASE threshold. To further understand the temperature dependent behaviour of the MAPbBr₃ film power dependent TRPL was taken at 3.8 K and room temperature (see **Supporting Information**). The effective PL lifetimes were extracted and presented in **Figure 3 e** and **Figure 3 f**, in order to fit the experimental results well, we introduced two type recombination processes for low temperature and room temperature, respectively. At 3.8 K, exciton dynamic model was introduced, the dependence of the PL effective lifetime on injected exciton density can be described as the following equation:^[67]

$$\frac{dn_{\text{EX}}}{dt} = -a_{\text{T}}n_{\text{EX}}n_{\text{T}} - bn_{\text{EX}}^2 - cn_{\text{EX}} \quad (5)$$

$$\frac{dn_{\text{T}}}{dt} = -a_{\text{T}}n_{\text{EX}}n_{\text{T}} \quad (6)$$

Where a_{T} is the trapping rate; b is the exciton auger recombination rate; n_{T} is the exciton density; c is the exciton radiative recombination coefficient. In this model, we assumed that photoluminescence emission mainly come from exciton recombination, with trapping and exciton-exciton Auger recombination are considered to be non-radiative decay channels. The fitting parameters are presented in **Table S1**. The trap density n_{T} is about $3.0 \pm 1.3 \times 10^{16} \text{ cm}^{-3}$, the trapping rate is $1.4 \pm 1.1 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$, and the excitonic recombination rate is $0.18 \pm 0.04 \text{ ns}^{-1}$. In a low pump energy region, excitons are prior to filling the trap states manifested as the increase of the effective PL lifetime. After the trap states are saturated with increased excitation density, more free excitons are generated, therefore leading to an accelerated recombination reaction at a higher energy that manifested as the lifetime decrease.

As aforementioned, the emission was dominated by the recombination of free carriers at room temperature. Hence effective PL lifetime was fitted by a model containing free and trapped carriers.

$$\frac{dn}{dt} = -a_{\text{T}}nn_{\text{T}} - bn^2 \quad (7)$$

$$\frac{dn_{\text{T}}}{dt} = -a_{\text{T}}nn_{\text{T}} \quad (8)$$

Here a_{T} is the charge trapping rate; b is the e-h bimolecular recombination coefficient; n_{T} is free carrier trap density. The fitting parameters are presented in **Table S2**, where n_{T} is about $4.4 \pm 0.9 \times 10^{16} \text{ cm}^{-3}$, trapping rate is $1.0 \pm 0.2 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$ and bimolecular recombination rate is $4.6 \pm 0.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. In consequence, the trap density remained in the same order (10^{16} cm^{-3}) at 3.8 K and room temperature. At both 3.8 K and room temperature, PL lifetime shows the same tendency where the trap states will be filled in preferentially. This indicates that the trap density could hardly influence the PL and ASE properties when varying the temperature.

The fatal thermal-activated auger recombination process is possibly responsible for the rising ASE threshold.

Co-existence of excitons and free charge carriers in MAPbBr₃ were then investigated by the TA spectra. The TA spectra obtained at 14 μ W pump energy are presented in **Figure 4 a**, the shape of the spectrum is independent of delay time. Representative TA spectra contain three main spectral features, photobleach (PB) band and photo-induced absorption (PA1 and PA2) bands. There is a sharp PB band at ~ 2.35 eV corresponding to the pronounced exciton linear absorption peaks, which is also correlated to the neighbouring PA band (PA1 and PA2). PB band at absorption band edge can be ascribed to exciton phase space filling.^[68, 69] Turning to the differential transmission dynamics spectra (in **Figure 4 b**), the decay dynamics of PB, PA1 and PA2 are quite different from each other. This denotes that there exist at least two photogeneration species in the perovskites. The PA2 band on the blue side located at the region of continuum section of absorption, similar to a PA band in MAPbI₃, hence, it's appropriate to give an attribute PA2 band to the bandgap renormalization (BGR) or a charge-carrier absorption,^[52] instead of the exciton population in an exciton dominated emission system.^[23, 70, 71] In addition, in virtue of the absence multi-excitonic emission in PL, rational explanation to PA1 on the red side is ascribed to carrier-induced peak broadenings rather than an excitonic interband transitions in unbundled single walled carbon nanotube.^[72]

Size-Dependent and WG mode lasing

As two-photon ASE was observed at 3.3 mJ/cm², by further pumping at higher excitation intensity, equally spaced lasing modes can be obtained (**Figure 5 a**), which is ascribed to the lasing mode competition. The microplates shaped as tetragonal regular polygonal resonator. Lasing reflected between the four side-faces of square (inset **Figure 5 b**) suggests a good mode confinement in the plane of the micro-platelets. The mode spacing $\Delta\lambda$ is ~ 0.451 nm (**s1**) and ~ 0.508 nm (**s2**) at 550 nm calculated from experiment data in **Figure 5 a**, for 51.82 μ m

and 47.45 μm lateral sizes, respectively. The lasing spectra present a decreasing modes number with the reduction of the lateral size. According to previous report^[38], the lasing can be assigned to a whispering gallery mode:

$$\Delta\lambda = \frac{\lambda^2}{n_{\text{ref}} d} \quad (9)$$

Here, λ is the central wavelength of the narrowed emission peak, d is the effective cavity length, n_{ref} is the refraction index of MAPbBr₃. The n_{ref} with value of 2.378 at energy 2.34 eV is in accordance to a previous work.^[73] The cavity length d can be found to be about $4 \times \sqrt{2} \times l$, indicating a twice round trip of light transport inside the micro cavity. The WGM lasers usually demonstrates high quality factor Q and low laser threshold power due to the total internal reflection at the cavity boundary. The quality factor Q is derived from the equation $Q \sim \lambda / \Delta\lambda_{\text{FWHM}}$, where $\Delta\lambda_{\text{FWHM}}$ is full-width at half-maximum of the lasing peak. λ can be considered as a constant, the $\Delta\lambda_{\text{FWHM}}$ is calculated about 0.25 nm of **s1**, and 0.23 nm of **s2**. We can see that the larger number of modes is, the smaller the spectral distance between two adjacent modes, namely, in a certain spectral range the number of modes increases with increasing the cavity size.^[74, 75] This is in agreement with the requirement for a WGM microlaser where the diameter is proportional to the product of wavelength and mode number.^[76] Therefore, the Q -factor has a linear relationship with the edge length. The individual Q factor is about to 2300 (**s2**) and 2190 (**s1**), respectively.

Nano- or micro- lasers typically operate with WGM lasing and regular polygonal resonators (plates, hexagonal, cylinder or sphere).^[52, 77] For an ideal cavity in micro- or nano- crystals, ASE/lasing characteristics are determined mainly by the Q factor^[78] and confinement factor (Γ).^[79] In this kind of nano- or microcrystals, none of surface defects exists and the affection of surface trap density on lasing can be totally ignored. In most nano- micro- lasers, optical confinement demonstrates a size-dependent behavior; the reduction in optical mode confinement with decreased size (450 - 950 nm) results in much less overlap with the gain

medium.^[80] At a certain diameter, the cavity losses outweigh the optical gain and lasing will not occur.^[80] As discussed above, the WGM-type resonance generally supports wider mode spacing due to a smaller resonator volume. The better overlaps between the WGMs and the active region reflect as a larger number of lasing modes. By reduced the cavity length, the single mode lasing can be achieved easily.^[81] In consequence, decreasing the size of either polygonal crystals or nanowires, can result in the increase of lasing threshold. For instance, in F-P mode nanowire lasing for the longer wire ($L > 8 \text{ } \mu\text{m}$), the lasing threshold decreases gradually with reducing length, owing to the decrease of the waveguide loss.

However, in fact, the formation of defects inside micro- or nano- crystals are hardly to avoid during samples preparation. The surface to volume ratio in nano- and micrometer objects strongly depends on the size.^[82] Even in the size of quantum dot scale, surface trap states would dominate photoluminescence dynamics. In larger-sized crystals (hundreds nanometers to hundreds micrometers), surface trap states are not so predominant to affect the recombination processes. In that case, the lasing threshold is influenced only by confinement factor and quality factor. Towards nanocrystals or quantum dots, a relatively high ratio of surface area to volume of surface states, is detrimental for the photoluminescence properties, and presents a weaker optical confinement in subwavelength nanocrystals, the ASE/lasing threshold is therefore proportional to the length of the cavity. This tendency of ASE/lasing threshold versus to cavity lateral size was usually observed in one-photon excitation system. It's worth noting that a complete picture of nano- or microcrystals could be obtained by a two-photon excitation due to the large penetration depth and more homogeneous excitation rather than single-photon excitation. While pumped at two-photon wavelength, ASE or lasing properties usually exhibit unambiguous difference compared to that of one-photon excitation. Hong-Bo Su et al demonstrated the 2PP ASE threshold in perovskite cubic microcrystals, there shows nearly one order of magnitude reduction than that of the 1PP ASE.^[39] The reduction of the threshold was due to a much more perfect internal perovskite lattices excited

by 800 nm lasers (2PP excitation). As Murat Olutas et al reported that 2PP ASE/lasing threshold shows an opposite trend with that of 1PP in nanocrystals.^[33] They suggested that increasing the lateral size of the nanocrystals is important for boosting the nonlinear optical response. Therefore, larger size of nanocrystals gives better response in terms of optical gain threshold despite of the increased overall nonradiative decay channels in the ensemble. The 2PP threshold shows decreasing trend as the lateral size reduces.

Moreover, another important factor for nano- or microcavity laser is the cavity-mode separation (corresponding inversely to the number of lasing modes), which arises by cavity quantum electrodynamics (QED) effect.^[83] The roundtrip time of light is much shorter than the phase coherence time of a dipole, which results in resonant enhancement of the electromagnetic field by multiple reflection in the cavity. Even there are some differences between light confinement abilities among various kinds of polygonal cavity. Somehow, in the multimode cavity, cavity-QED shows the stimulated emission enhancement as well as spontaneous emission enhancement is proportional to the cavity mode separation and inversely proportional to the mode volume.^[84] In the case of multimode cavity lasing, due to the cavity-QED effect, small size of cavity reduces the number of confined modes and increases the mode separation, leading to a reduction of lasing threshold. Eventually, the lasing threshold is almost proportional to the length of cavity.^[85]

Recently, a few perovskite microlasers were developed and lasing action shows size-dependent behaviors.^[36, 37, 38, 39] In this work, we choose two-photon excitation to investigate the relationship between lasing thresholds and lateral size of cavity. The 2PP threshold of each individual micro laser demonstrates a size-dependent characteristic, as present in **Figure 5 b**. In this work, 2PP lasing threshold exhibits opposite trends when varying lateral size compared to other works. It's worth noting that in the range of size from 20 to 90 μ m, surface trap states are not the predominant factor and the trap density mechanism that scarcely affects the recombination processes in this work. Hence, we suppose that cavity-QED effect could be

responsible for the size dependent lasing thresholds. Consequently, the larger cavity length is, the larger number of modes can be observed, the larger of mode separation and higher excitation intensity should be imposed on the microcrystals. By a simple linear fitting, it indicates the tendency of threshold versus lateral size conforms to a linear increase and with a fitted slope ~ 0.01876 . Hence, at the same temperature, excluding the contribution of excitons dissociation and trap states, the excess energy is required to support the fierce lasing mode competition in a larger square plate.

Conclusions

In summary, we have discussed the intrinsic optical properties of micro-sized MAPbBr₃ perovskite plates under two-photon excitation. From the analysis of time-resolved PL, the free charges represent the dominant population up to the excitation density of 10^{16} cm^{-3} . The attenuation of photoluminescence intensity and rise in ASE thresholds are predominantly from the non-radiative channels of charge carriers at room temperature. We also reveal that narrowed PL spectra can be developed at high pump energies with both 400 nm and 800 nm excitation wavelengths. Furthermore, inspired by the excellent nonlinear optical properties, whispering gallery mode lasing and size-dependent 2PP stimulated emission behaviors in MAPbBr₃ were investigated subsequently. The investigation on the interplay between free carriers and PL/ASE/lasing actions here could provide a deeper understanding of the relevant photophysics of MAPbBr₃ perovskites.

Experimental Section

Preparation of MAPbBr₃ film: The precursor solution made by mixing MABr and PbBr₂ with a 1.2:1 molar ratios in DMF, then the 10 wt% stoichiometric precursor solutions was drop-cast onto the substrates. Micrometer-sized MAPbBr₃ plates were obtained after annealing the substrates at 110°C.

Optical Measurements: For femtosecond optical spectroscopy, the laser source was a Coherent Legend regenerative amplifier (150 fs, 1 kHz, 800 nm) seeded by a Coherent Vitesse oscillator (100 fs, 80 MHz). 800 nm wavelength laser pulses were from the regenerative amplifier's output while 400 nm wavelength laser pulses were obtained with a BBO doubling crystal. The emission from the samples was collected at a backscattering angle of 150° by a pair of lenses and into an optical fiber that is coupled to a spectrometer (Acton, Spectra Pro 2500i) to be detected by a charge coupled device (Princeton Instruments, Pixis 400B). TRPL was collected using an Optronis Optoscope streak camera system which has an ultimate temporal resolution of 6 ps. The transient absorption spectroscopy was performed using a home-built white light pump–probe setup described previously.

Supporting Information

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

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Figure 1. a) Raman image of cubic perovskites plates, inset scale bar is 100 μm . b) is the individual perovskite plates with size 60mm; c) is the corresponding illumination Raman image, inset scale bar is 50 μm ; d) is the Scanning Electron Microscope (SEM) images of a selected plate, and the square plate has a concave surface, inset scale bar is 50 μm ; e) The XRD patterns of Si substrate (red solid line) and MAPbBr₃ perovskites (black solid line), inset is the enlarged XRD picture of MAPbBr₃ film, the diffraction peaks of MAPbBr₃ at 14.79° for (100) plane, 30.06° for (200) plane, 45.85° for (300) plane, revealed the characteristics of the perovskite square phase; f) is the normalized absorption spectral (black scatters) of the MAPbBr₃ perovskite film, the absorption of MAPbBr₃ perovskite film was described and

simulated well by Elliott's model, the red line is the fitting line combined with excitonic (blue solid line) and continuum (green-dash line) components.

Figure 2. a) Normalized one-photon pumped (1PP) and two-photon pumped (2PP) photoluminescence spectra, excited at 400nm and 800nm respectively, two-photon pumped PL emission peak with slight red-shift compared to 1PP's, where attributed to a reabsorption effects; c) Output intensity as function of pump fluences, ASE threshold for 1PP and 2PP is $20 \mu\text{J}/\text{cm}^2$ and $3.3 \text{ mJ}/\text{cm}^2$, respectively; b, d) is the evolution of 1PP and 2PP spontaneous emission versus different pump fluences.

Figure 3. a) is the selected temperature-dependent two-photon photoluminescence spectrum (left panel) from 80 to 300 K, at right panel of a) is the full width at half maximum (FWHM) as a function of temperature, with a fitting equation, red solid line is a fitted line. b) Time-

resolved photoluminescence (TRPL) for MAPbBr₃ films (left), power-dependent initial photoluminescence intensity (PL₀) was fitted, where $PL_0 \propto \Phi^n$, Φ is the incident fluences of lasing, n was estimated to be 2.179. c) Simulation of the free charge fraction over the total excitation density (n_F/n) at thermal equilibrium ($T = 300$ K) according to equation (4), with an exciton reduced mass $\mu = 0.13m_e$ and the estimated binding energy of 60meV; d) Integral PL intensity versus increasing temperature (left side axis, blue solid circle scatters is experiments part, blue line is a fitted part); the injection carrier concentrations of corresponding ASE threshold related to temperature (right side axis, red solid circle); the value of IPL product n_c^{th} denotes as open pentagram. e, f) is the effective PL lifetime versus carrier concentration at 3.8 K and room temperature, respectively, the solid line is the fitting line, fitting of MAPbBr₃ at RT based on recombination model of free and trapped carriers, only one type of trap introduced, carriers either recombination via bimolecular or via trap states; while fitting of MAPbBr₃ at 3.8K based on recombination model of exciton radiative, trapping and exciton-exciton Auger type.

Figure 4. a) Differential transmission spectra pumped at 14uW with varying delay time. b) Normalized differential transmission dynamics of PA1 (2.14eV, green hollow triangle), PB (2.35eV, red hollow circle) and PA2 (2.49eV, blue hollow cubic), solid line with is the fitting line.

Figure 5. a) Lasing competition in narrowed stimulated emission peaks for 47.45 μm and 51.82 μm cubic plates, inset images are the corresponding Raman images, the benchmark is 50 μm. b) ASE thresholds versus lateral size (20-90 μm), fitted by a linear line (red line)

Dominant Free carrier emission in MAPbBr₃ perovskite micro-sized plates is confirmed by power dependent Time-resolved photoluminescence (TRPL). The influence of temperature triggered excitons disassociation and thermal-assisted nonradiative recombination imposed on two-photon ASE threshold of perovskite have been discussed. Moreover, optical confinement, trap density and cavity quantum electrodynamics (QED) effect resulted in a size-dependent lasing actions in MAPbBr₃ perovskite micro-sized plates.

Keyword

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Two-photon optical properties in individual organic-inorganic perovskite microplates

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Supporting Information

Two-photon optical properties in individual organic-inorganic perovskite microplates

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Calculation of two photon absorption coefficients:

In the first place, we assumed that the intensity of incident light reduced when light propagating through the sample, the intensity is absorbed by linear and nonlinear procedures, expressed as:

$$\frac{dI}{dz} = -\alpha I_1 - \beta I_1^2 - \beta I_1 I_2 = -\alpha I_1 - \beta I_1 I_2 \quad (1)$$

$$I(z) = I_0 \exp^{-(\alpha + \beta I_2)L} \quad (2)$$

Where I_1 is the intensity of probe, I_2 is the intensity of pump, α is linear absorption coefficient, β is two-photon absorption coefficient, L is optical distance in sample. The first term in the right of equation is linear absorption for probe beam; the second term is two-photon absorption for probe beam; the third term is two-photon absorption induced by probe beam and pump beam. For the energy of probe is much smaller than pump's, thus the term of βI_1^2 can be neglected:

$$\frac{\Delta T}{T} = \frac{I_{\text{pump+probe}}(z) - I_{\text{probe}}(z)}{I_{\text{probe}}(z)} = \frac{I_0 \exp^{-(\alpha + \beta I_2)L} - I_0 \exp^{-\alpha L}}{I_0 \exp^{-\alpha L}} = e^{-\beta I_2 L} - 1 \quad (3)$$

Power-dependent Photoluminescence Lifetime:

At 3.8 K, exciton dynamical model was introduced, the dependence of the PL effective lifetime on injected exciton density can be described as the following equation:[Ref]

$$\frac{dn_{\text{EX}}}{dt} = -a_{\text{T}} n_{\text{EX}} n_{\text{T}} - b n_{\text{EX}}^2 - c n_{\text{EX}} \quad (4)$$

$$\frac{dn_{\text{T}}}{dt} = -a_{\text{T}} n_{\text{EX}} n_{\text{T}} \quad (5)$$

Where a_{T} is trapping rate; b is exciton auger recombination rate; n_{T} is the trap density; c : exciton radiative recombination rate. In this model, we assumed that photoluminescence emission mainly come from exciton recombination, trapping and exciton-exciton Auger radiative are also taken into account. The fitting parameters are presented in **Table S1**, n_{T} is about $3.0 \pm 1.3 \times 10^{16} \text{ cm}^{-3}$, trapping rate is $1.4 \pm 1.1 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$, excitonic recombination rate is $0.18 \pm 0.04 \text{ ns}^{-1}$; in a low pump energy region, the excitons are prior to filling the trap states denoted as the increasing of effective PL

lifetime; after the trap states saturated with increasing the excitation density, more excitons are generated, therefore leading to an accelerated recombination reaction at a high energy, denoted as the lifetime decreasing.

As aforementioned, the emission was dominated by the recombination of free carriers at room temperature. Hence effective PL lifetime was fitted by a model containing free and trapped carriers.

$$\frac{dn}{dt} = -a_T n n_T - b n^2 \quad (6)$$

$$\frac{dn_T}{dt} = -a_T n n_T \quad (7)$$

Here a_T is trapping rate; b is bimolecular recombination rate; n_T is trap density. The fitting parameters are presented in **Table S2**, n_T is about $4.4 \pm 0.9 \times 10^{16} \text{ cm}^{-3}$, trapping rate is $1.0 \pm 0.2 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$, bimolecular recombination rate is $4.6 \pm 0.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, the trap density remain in the same order magnitude compared with the trap density at 3.8 K. In consequently, either at 3.8 K or room temperature, PL lifetime shows the same tendency.

Figure S1. The thickness of MAPbBr₃ perovskite film, the thick of film is about 150 nm.

Figure S2. Pump probe differential transmission spectra of MAPbBr₃ films and CdS bulks, respectively. The calculation of Two-photon absorption coefficients of MAPbBr₃ was mentioned in manuscript.

Figure S3. Temperature-dependent decay curves of MAPbBr₃ films (left), the effective lifetime versus temperature (right).

Figure S4. Power-dependent decay curves of MAPbBr₃ films the effective lifetime versus temperature 3.8 K (a and b) and room temperature (c and d), respectively.

Table1. Fitting parameters of power dependent PL lifetime at 3.8 K with a exciton model

3.8 K	Trap Density (cm^{-3})	Trapping Rate ($\text{cm}^3 \text{ s}^{-1}$)	Exciton Radiative Rate (ns^{-1})	Auger Rec Rate ($\text{cm}^3 \text{ s}^{-1}$)
	$3.0 \pm 1.3 \times 10^{16}$	$1.4 \pm 1.1 \times 10^{-8}$	0.18 ± 0.04	$5.1 \pm 1.5 \times 10^{-9}$

Table2. Fitting parameters of power dependent PL lifetime at 3.8 K with free carrier model

R.T	Trap Density (cm^{-3})	Trapping Rate ($\text{cm}^3 \text{ s}^{-1}$)	Bimolecular Rec Rate ($\text{cm}^3 \text{ s}^{-1}$)
	$4.4 \pm 0.9 \times 10^{16}$	$1.0 \pm 0.2 \times 10^{-8}$	$4.6 \pm 0.5 \times 10^{-9}$