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# Optical Pumped Lasing in Solution Proccessed Perovskite Semiconducting Materials: Self Assembled Microdisk Lasing

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**Abstract**

**Optical pumped lasing has been observed in solution processed perovskite semiconducting materials, $CH_3NH_3PbBr_3$. The self-assembled microcavities have been easily obtained with square or disk shapes and their sizes distribute from 1 to several tens of micrometer. The microcavities show clear multi-mode lasing under the pulsed optical pumping. The mode intervals are well explained by the optical constants with large dispersions of the materials.**

## 1. Introduction

Significant developments have been progressed in the organic semiconductor technology, that takes advantage of the features such as printable, flexible, large area devices and their easy fabrication processes [1]. Solution processes are especially important to realize low cost fabrication and large area devises [2]. Metal halide perovskite type organic photovoltaic devices have showed great progresses and a power conversion efficiency over 10% was achieved with mesoporous layered structures [3]. Perovskite photovoltaic devices with flat layered structures also showed nearly 20% conversion efficiency [4], indicating the promising materials for photovoltaic cells. Perovskite materials with lead halide methylammonium (MA) systems also exhibit laser emissions under the optical pumping [5-8] and LED devices [9, 10]. These facts indicate this material is also strong candidate for current injected organic lasers.

We have developed organic microcavities in order to reduce the lasing threshold under the optical pumping and microcavities are also effective for the current injected lasing [11, 12]. We report here the optical pumped lasing on perovskite microcavities fabricated by using solution process fabrications. The self-assembled microcavities show clear multi-mode lasing.

## 2. Sample Preparations

In the sample preparation, we employed so called one step method for simplicity, described below. Methylammonium Bromide and $PbBr_2$ powders were solved into N,N-dimethylformamide (DMF). The molar weight of $CH_3NH_3Br$ was the same with that of $PbBr_2$ from 5 to 20 mM. The powders were completely dissolved in DMF at RT in the concentrations range. The solutions were casted on the indium tin oxide (ITO) layers sputtered on $Si/SiO_2$ substrates. All of the fabrication processes were carried out in ambient air at RT. Many of $CH_3NH3PbBr_3$, $MAPbBr_3$ microcrystals were formed on the substrate, as shown in Fig. 1. The size of squares and disks distribute from 1 to several tens of micrometer, as shown in Fig. 1. The large crystals tend to be square shapes reflecting cubic structures of $MAPbBr_3$ (P m3m space group) at RT [13]. Thicknesses of the crystals were distributed from 0.1 to 3 micrometer. We chose carefully some microcrystals for the optical pumping experiments. Flat and thin crystals tended to lasing easily, because of having good optical cavities.

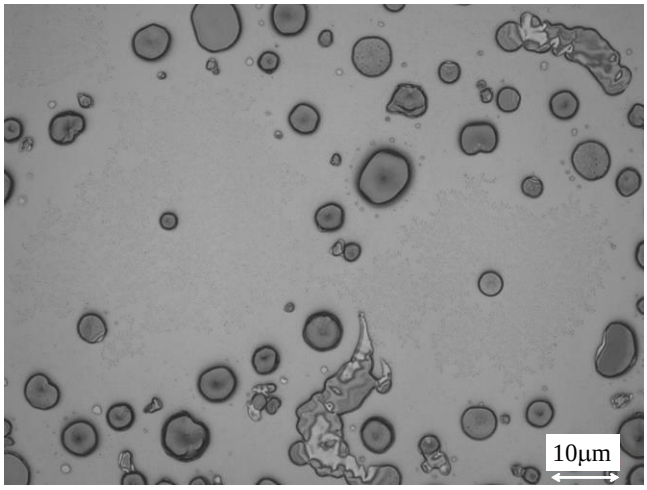


Fig. 1 Microscope image of self-assembled microcrystals of $CH_3NH_3PbBr_3$ casted on ITO layers with the concentration of 5 mM.

## 3. Optical Experiments

We have carried out pulse excitation experiments on the $MAPbBr_3$ microcavities at 397 nm with a pulse width of 200-300 fs and a repetition rate of 1 kHz. All the optical experiments have been conducted at RT in ambient air. Figure 2 show the emission spectra of a $MAPbBr_3$ microdisk. Amplification and lasing were observed around 2.25 eV, which coincided with previous report on the $MAPbBr_3$ material [5, 8]. Microscope luminescence image of lasing crystals are shown in Fig. 3. We found that the bright spots were observed after the lasing threshold at the circumference of the disk cavity, as slightly seen in Fig. 3, indicating whispering gallery mode (WGM) or quasi-WGM lasing. With the increase of the excitation density, the lasing modes shift to high energy side, as shown in Fig. 2.

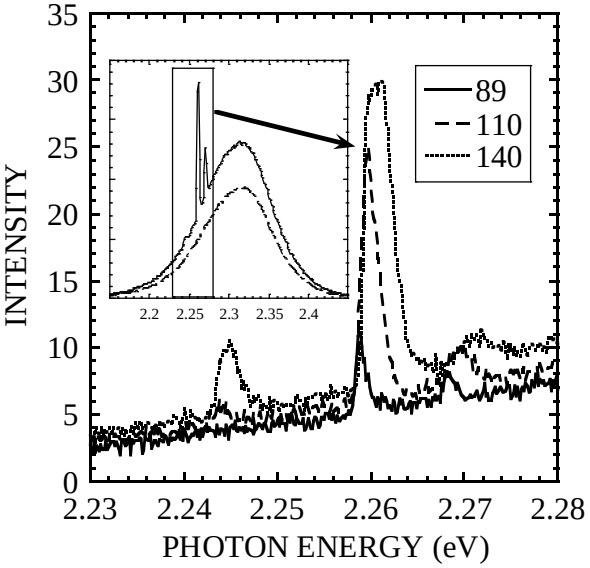


Fig. 2 Lasing spectra of the $CH_3NH_3PbBr_3$ self-assembled microcrystal, as shown in Fig. 3. Whole luminescence spectra are shown in the inset, before (Iex = 56 μJcm$^{-2}$) and after (Iex = 89 μJcm$^{-2}$) the lasing Numbers in the figure indicate the excitation density in the unit of . μJcm$^{-2}$.

As shown in Fig. 2, the mode intervals of both the disk cavity is determined to be 15.8 meV. The lasing mode interval, ΔE is expressed as [14]

$$\Delta E = E_{m+1} - E_m = \frac{hc}{n_{eff} L}, \quad n_{eff} = \left( n + E \frac{dn}{dE}\bigg|_{Em} \right) \qquad (1)$$

where $E_m = mhc/nL$ is the energy of the $m$-th mode, $h$ is the Planck constant, $c$ is the velocity of light in vacuum, $n_{eff}$ is the effective refraction index, $n$ is the refraction index of the gain materials, and $L$ is the resonator length, respectively. In the disk cavity case, $L$ is the circumferential length. Cavity sizes were estimated from Fig. 3 images to be 4.2 μm in diameter in the disk cavity. We can estimate the effective index from eq. (1) to be 5.9 in the disk cavity. The optical constant of perovskite materials has been reported and its refractive index around the band gap is approximately 2.4 [5, 15, 16]. The strong absorption band exists just above the gap, so that the effective refractive index is affected by the absorption dispersion. In this case, the effective refractive index is sometimes over the twice of the pure refractive index Therefore, our observed results of effective refractive index of 5.9 are quite reasonable, because of the strong absorption band. Actually, we have obtained the maximum value of $n_{eff}$=5.8 around the band edge of $MAPbI_3$ materials from the optical constant of Ref. 16 according to the eq. (1) Details be will presented in the conference.

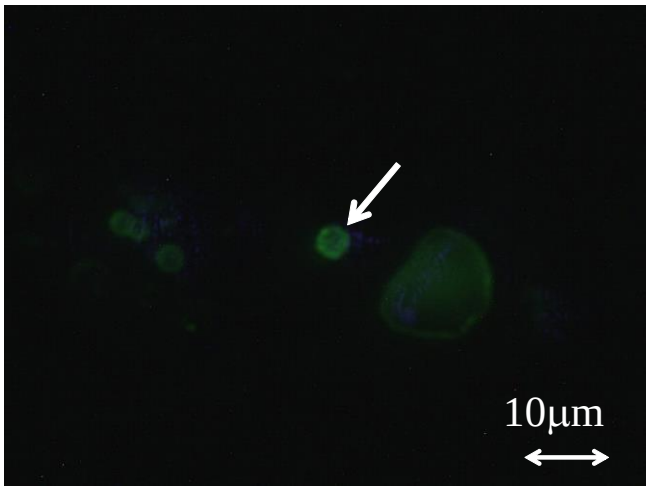


Fig. 3 Luminescence image of the disk cavity whose lasing spectra are shown in Fig. 2.

**References**

[1] J. A. Rogers, T. Someya, Y. Huang, Science **327** (2010) 1603.
[2] A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay and A. Salleo, Chem. Rev. **110** (2010) 3.
[3] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, H. J. Snaith, Science **338** (2012) 643.
[4] H. Zhou, Q. Chen, G. Li, S. Luo, Tze-bing Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, and Y. Yang, Science **345**, (2014) 542.
[5] G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar and T. C. Sum, Nat. Mater. **13** (2014) 476.
[6] F. Deschler, M. Price, S. Pathak, L. E. Klintberg, D.-D Jarausch, R. Higler, S. Hüttner, T. Leijtens, S. D. Stranks, H. J. Snaith, M. Atatüre, R. T. Phillips, and R. H. Friend, J. Phys. Chem. Lett. **5** (2014) 1421.
[7] T. S. Kao, Yu-Hsun Chou, C.-H. Chou, F.-C. Chen, and T.-C. Lu, Appl. Phys. Lett. **105** (2014) 231108.
[8] D. Priante, I. Dursun, M. S. Alias, D. Shi, V. A. Melnikov, T. K. Ng, O. F. Mohammed, O. M. Bakr, and B. S. Ooi, Appl. Phys. Lett. **106** (2015) 081902.
[9] Z.-K. Tan, R.S. Moghaddam, M.L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L.M. Pazos, D. Credgington, F. Hanusch, T. Bein, H.J. Snaith, and R.H. Friend, Nat. Nanotechnol. **9** (2014) 687.
[10] Y.-H. Kim, H. Cho, J.H. Heo, T.-S. Kim, N. Myoung, C.-L. Lee, S.H. Im, and T.-W. Lee, Adv. Mater. **27** (2014) 1248.
[11] F. Sasaki, S. Kobayashi, S. Haraichi, S. Fujiwara, K. Bando, Y. Masumoto, S. Hotta, Adv. Mater. **19** (2007) 3653.
[12] F. Sasaki, M. Mori, S. Haraichi, Y. Ido, Y. Masumoto, and S. Hotta, Org. Electron. **11**, (2010) 1192.
[13] A. Poglitsch and D. Weber, J. Chem. Phys. **87** (1987) 6373.
[14] K. Bando, S. Kumeta, F. Sasaki, and S. Hotta, Jpn. J. Appl. Phys. **50** (2011) 101603.
[15] M. Hirasawa, T. Ishihara, and T. Goto, J. Phys. Soc. Jpn. **63** (1994) 3870.
[16] P. Löper, M. Stuckelberger, B. Niesen, J. Werner, M. Filipič, S.-J. Moon, J.-H. Yum, M. Topič, S. De Wolf, and C. Ballif, J. Phys. Chem. Lett.**6** (2015) 66.