Free-Standing Carbon Nanotube Thin Film for Multifunctional Halide-Perovskite Optoelectronics

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Abstract—Carbon nanotube thin (CNT) films have been extensively studied in optoelectronics for the past two decades. Regarding its chemical inertness they have been successfully integrated with halide-perovskites for next-generation flexible optoelectronics. Following this approach, a few perovskite-based devices have been created, namely solar cells, photodetectors, and light-emitting diodes. However, the synthesis of a high-quality halide-perovskite material directly on carbon nanotube thin films has not been demonstrated. Here, we for the first time show a simple one-step synthesis of CsPbBr₃ microcrystals directly on the substrate-free, free-standing carbon nanotube thin film. We show that the as-synthesized microcrystals show optical lasing at a threshold fluence 140 μ J cm⁻². Our simple approach allows to further study substrate-free perovskite lasers on a carbon nanotube thin film. Furthermore, the proposed design will be perspective for multifunctional optoelectronics, where both CNT film and perovskite crystals may respond various applied stimuli.

Keywords: free-standing carbon nanotube thin film, halide-perovskites, multifunctional optoelectronics

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INTRODUCTION

In optoelectronics devices require efficient interaction of light with matter [1, 2]. Here, compared to bare electronics, the light properties can be additionally manipulated [3, 4]. Moreover, like the electronics need for scaling regarding Moore's law, such devices should operate well at micro- and nano- scale. This not only allows to fit the emerging applications, but as well, to accurately control desirable light properties [5, 6]. The photon absorber as a building block for such devices is needed for optical data transfer (photoluminescence, electroluminescence in presence of applied voltage) and data receiver (photodetection in presence of applied voltage). One of such materials, halide-perovskites, have been extensively studied in photonics applications [7], and are promising in lasing applications [7–11]. Their set of optoelectronic properties such as high absorption coefficient up to 10⁵ cm⁻¹ [12], charge carrier mobility of order 10–100 cm²/V s [13] and carrier diffusion length up to 1 µm [14] have been widely utilized for p-n junction type of devices such as solar cells, photodetectors and light-emitting diodes [15–17]. Still, for halide-perovskite optoelectronics, the usage of metal electrodes affording destructive chemical reactions leads to device degradation [18, 19]. This problem has been currently solved by replacing electrodes to the alternative chemical inert carbon nanomaterial electrodes [20, 21]. Among them CNT films have been popular possession set of properties such as mechanical durability high sheet resistance at 90% transparency which opens them route to the transparent and flexible optoelectronics [21]. Moreover, CNT films can be used in a substratefree design. They provide good optical contrast for the high index semiconducting materials such as GaAs and Si [22]. The placement of the semiconductor particle onto CNT film represents optically sensitive nonvisible device. In addition to optical sensing, CNT film itself can be used as a sensor to the induced electrochemical environment and thus track biological and chemical signals (electrolyte environment, gas sensor) [23].

In this work, we synthesize $CsPbBr_3$ halide-perovskite microcrystals via one-step synthesis approach. The as grown microcrystals demonstrate optical lasing under fluence 140 μJ cm⁻². The provided synthesis

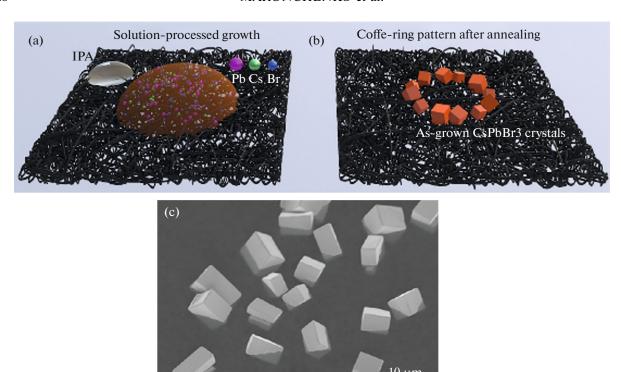


Fig. 1. (a) CsPbBr₃ precursor droplet placed on free-standing CNT film, the growth happens in atmosphere of isopropanol vapor. (b) After annealing, a coffee-ring pattern of CsPbBr₃ cubes is left. (c) SEM image of as-syntehsized CsPbBr₃ microcrystals.

approach will be useful for multifunctional optoelectronics tracking set of optotelectronic stimuli.

SYNTHESIS OF $CsPbBr_3$ MICROCRYSTALS ON CNT FILM

We synthesize single-walled carbon nanotube thin film by aerosol chemical vapor deposition method [24] on the nitrocellulose filters. Afterwards, we use dry-transfer technique to obtain free-standing CNT film. For this, holey metal puck was used. Right after, low-temperature alcohol vapor-assisted method is used for perovskite synthesis [10, 21]. At the beginning, perovskite precursor droplet is placed on the free-standing CNT film (Fig. 1a). The film is heated up to 70°C allowing solvent evaporation and formation of CsPbBr₃ microcrystals. After annealing, the characteristic coffee ring appears at the former place of precursor droplet (Fig. 1b). Scanning electron microscopy is performed to show the micrometer-scale sized CsPbBr₃ microcrystals.

The size of the crystals can be in general controlled from nanoscale (hundreds of nanometrs) to microscale (tens of micrometers) by choosing the appropriate synthesis parameters (such as precursor concentration, annealing temperature, volume of isopropanol antisolvent) [10, 21].

OPTICAL LASING FROM CsPbBr₃ MICROCRYSTAL

For the optical pumping we use Light Conversion Pharos femtosecond laser with 200 fs pulse duration at a wavelength 480 nm. The laser is focused on a spot with diameter 20 μm . The pulse repetition frequency is 10 kHz. One of the collected photoluminescence spectra is shown in Fig. 2a. At a fluence 140 μJ cm $^{-2}$ several lasing modes with quality factor over 5000 are revealed. It is worth to mention that such high-quality factors may be achieved due to good optical contrast provided by CNT film. In the Figs. 2b, 2c we show the crystal from which the photoluminescence signal is collected.

CONCLUSIONS

In conclusion, we have provided a simple one-step synthesis approach for the synthesis of CsPbBr₃ perovskite microcrystals on the free-standing CNT film. In particular, we for the first time synthesized CsPbBr₃ microcrystals on the CNT film via solution synthesis approach. The demonstrated optical lasing of CsPbBr₃ microcrystal on CNT film may open the new area of multifunctional optoelectronics where both CNT film and perovskite microcrystals may be further used for multiple device responses.

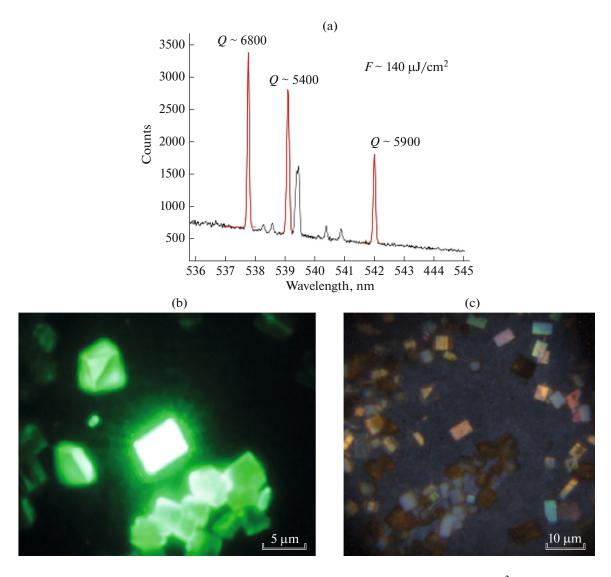


Fig. 2. (a) The optical spectrum shows multimode lasing of CsPbBr₃ microcrystal at a fluence 140 μ J cm⁻². (b, c) Photoluminescence and optical image of the measured CsPbBr₃ microcrystal.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

- 1. Mueller, T., Xia, F., and Avouris, P., *Nat. Photonics*, 2010, vol. 4, p. 297.
- Ren, A., Wang, H., Zhang, W., Wu, J., Wang, Z., Penty, R.V., and White, I.H., *Nat. Electron.*, 2021, vol. 4, no. 8, p. 559.

- 3. Saleh, B.E., and Teich, M.C., Fundamentals of Photonics, New York: Wiley, 2019.
- 4. Sze, S.M., Li, Y., and Ng, K.K., *Physics of Semiconductor Devices*, New York: Wiley, 2021.
- 5. Koenderink, A.F., Alù, A., and Polman, A., *Science*, 2015, vol. 348, p. 516.
- Lee, G.H., Moon, H., Kim, H., Lee, G.H., Kwon, W., Yoo, S., et al., *Nat. Rev. Mater.*, 2020, vol. 5, no. 2, p. 149.
- Makarov, S., Furasova, A., Tiguntseva, E., Hemmetter, A., Berestennikov, A., Pushkarev, A., Zakhidov, A., and Kivshar, Y., *Adv. Opt. Mater.*, 2019, vol. 7, no. 1, 1800784.
- 8. Tiguntseva, E., Koshelev, K., Furasova, A., Tonkaev, P., Mikhailovskii, V., Ushakova, E.V., et al., *ACS Nano*, 2020, vol. 14, no. 7, p. 8149.
- Zhizhchenko, A., Syubaev, S., Berestennikov, A., Yulin, A.V., Porfirev, A., Pushkarev, A., et al., ACS Nano, 2019, vol. 13, no. 4, p. 4140.

- 10. Pushkarev, A.P., Korolev, V.I., Markina, D.I., Komissarenko, F.E., Naujokaitis, A., Drabavicius, A., et al., *ACS Appl. Mater. Interfaces*, 2018, vol. 11, no. 1, p. 1040.
- 11. Liu, A., Guan, G., Chai, X., Feng, N., Lu, M., Bai, X., and Zhang, Y., *Laser Photonics Rev.*, 2022, vol. 16, no. 10, 2200189.
- 12. Green, M. A., Ho-Baillie, A., and Snaith, H.J., *Nat. Photonics*, 2014, vol. 8, no. 7, p. 506.
- 13. Herz, L.M., ACS Energy Lett., 2017, vol. 2, no. 7, p. 1539.
- 14. Stranks, S.D., Eperon, G.E., Grancini, G., Menelaou, C., Alcocer, M.J., Leijtens, T., et al., *Science*, 2013, vol. 342, p. 341.
- Ahmadi, M., Wu, T., and Hu, B., Adv. Mater., 2017, vol. 29, 1605242.
- 16. Park, N.-G., Mater. Today, 2015, vol. 18, p. 65.
- 17. Liu, X.-K., Xu, W., Bai, S., Jin, Y., Wang, J., Friend, R.H., and Gao, F., *Nat. Mater.*, 2021, vol. 20, p. 10.
- 18. Domanski, K., Correa-Baena, J.-P., Mine, N., M. Nazeeruddin, K., Abate, A., Saliba, M., Tress, W., Hag-

- feldt, A., and M. Grätzel, *ACS Nano*, 2016, vol. 10, p. 6306.
- Zhao, L., Kerner, R.A., Xiao, Z., Lin., Y.L., Lee, K.M., Schwartz, J., and Rand, B.P., ACS Energy Lett., 2016, vol. 1, 595.
- 20. Aitola, K. and Domanski, K., Correa-Baena, J.P., Sveinbjörnsson, K., Saliba, M., Abate, A., et al., *Adv. Mater.*, 2017, vol. 29, no. 17, 1606398.
- 21. Marunchenko, A.A., Baranov, M.A., Ushakova, E.V., Ryabov, D.R., Pushkarev, A.P., and Gets, D.S., et al., *Adv. Funct. Mater.*, 2022, vol. 32, no. 12, 2109834.
- Zhigunov, D.M., Shilkin, D.A., Kokareva, N.G., Bessonov, V.O., Dyakov, S.A., and Chermoshentsev, D.A., et al., *Nanotechnology*, 2020, vol. 32, no. 9, 095206.
- 23. Nasibulin, A.G., Kaskela, A., Mustonen, K., Anisimov, A.S., Ruiz, V., and Kivisto, S., et al., *ACS Nano*, 2011, vol. 5, no. 4, p. 3214.
- 24. Tian, Y., Nasibulin, A.G., Aitchison, B., Nikitin, T., Pfaler, J.V., Jiang, H., Zhu, Z., Khriachtchev, L., Brown, D.P., and Kauppinen, E.I., *J. Phys. Chem. C*, 2011, no. 115, p. 7309.