

PHYSICS OF MOLECULES

Conference materials

UDC 535.37

DOI: <https://doi.org/10.18721/JPM.153.364>

Photoluminescence from lead halide perovskite superlattices

P. A. Tonkaev ¹✉, E. V. Grechaninova ¹, A. P. Pushkarev ¹, S. V. Makarov ¹

¹ ITMO University, St. Petersburg, Russia

✉ pavel.tonkaev@metalab.ifmo.ru

Abstract. Lead halide perovskites are a new class of materials with promising optoelectronic properties. Bulk halide perovskites have been applied as solar cells, light-emitting diodes, photodetectors, and nanolasers. Colloidal lead halide perovskite nanocrystals have shown high quantum efficiency of photoluminescence. Moreover, perovskite nanocrystals can be assembled in an ordered 3D array or superlattice to demonstrate superfluorescence emission. In this work, we synthesized CsPbBr₃ superlattices with the linear size of several micrometers and studied their photoluminescence properties at room temperature and 6 K. We demonstrated that the photoluminescence spectra of perovskite nanocrystals are preserved in superlattices at both temperatures. We also found a small spectral shift, which we attribute to a more uniform size distribution of nanocrystals in the superlattice.

Keywords: halide perovskites, nanocrystals, superlattice, photoluminescence, Mie resonance, Purcell effect

Funding: This work was performed with financial support of the Russian Science Foundation (project No. 22-22-20077).

Citation: Tonkaev P. A., Grechaninova E. V., Pushkarev A. P., Makarov S. V., Photoluminescence from lead halide perovskite superlattices. St. Petersburg State Polytechnical University Journal. Physics and Mathematics, 15 (3.3) (2022) 326–329. DOI: <https://doi.org/10.18721/JPM.153.364>

This is an open access article under the CC BY-NC 4.0 license (<https://creativecommons.org/licenses/by-nc/4.0/>)

Материалы конференции

УДК 535.37

DOI: <https://doi.org/10.18721/JPM.153.364>

Фотолюминесценция сверхрешеток свинцово-галогенидного перовскита

П. А. Тонкаев ¹✉, Е. В. Гречанинова ¹, А. П. Пушкарёв ¹, С. В. Макаров ¹

¹ Университет ИТМО, Санкт-Петербург, Россия

✉ pavel.tonkaev@metalab.ifmo.ru

Аннотация. В работе были синтезированы сверхрешетки CsPbBr₃ с линейным размером в несколько микрометров, их фотолюминесцентные свойства были исследованы при комнатной температуре и 6 К. Было показано, что спектры фотолюминесценции нанокристаллов перовскита сохраняются в сверхрешетках при обеих температурах.

Ключевые слова: галогенидные перовскиты, нанокристаллы, сверхрешетки, фотолюминесценция, резонансы Ми, эффект Парселла

Финансирование: Исследование выполнено за счет гранта Российского научного фонда № 22-22-20077.

Ссылка при цитировании: Тонкаев П. А., Гречанинова Е. В., Пушкарёв А. П., Макаров С. В. Фотолюминесценция сверхрешеток свинцово-галогенидного перовскита // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 3.3. С. 326–329. DOI: <https://doi.org/10.18721/JPM.153.364>



Статья открытого доступа, распространяемая по лицензии CC BY-NC 4.0 (<https://creativecommons.org/licenses/by-nc/4.0/>)

Introduction

Lead halide perovskites are a class of new materials with outstanding properties and low-cost fabrication methods that have been applied in the field of photovoltaics [1], light-emitting diodes [2], and photodetectors [3]. Moreover, due to relatively high refractive index, perovskite nanostructures support Mie resonances in the optical and near-infrared ranges which enhance photoluminescence [4], increase nonlinear absorption [5], and lower the lasing threshold [6]. Meanwhile, lead halide perovskite nanocrystals with quantum confinement have high photoluminescence quantum yield [7]. Furthermore, perovskite nanocrystals can assemble in the ordered 3D arrays or superlattices. These structures allow additional control of emission properties and provide the opportunity to develop new effective optical nanosources. Herein, we aim to study the photoluminescence of unordered perovskite nanocrystals and single CsPbBr₃ superlattices with linear dimensions of several micrometers at room temperature and 6 K.

Materials and Methods

The CsPbBr₃ perovskite nanocrystals were obtained by the hot injection method. The resulting nanocrystals were separated by centrifugation and dispersed in toluene to obtain a colloidal solution. Superlattices were formed from these colloidal nanocrystals. The CsPbBr₃ superlattices were fabricated on a silicon substrate. The transverse dimensions of individual superlattices ranged from 1 μm to 10 μm, while some of them agglomerated to form clusters of superlattices, and some remained spatially isolated, which made it possible to measure photoluminescence for individual objects.

The photoluminescence spectra of the samples were measured using a pump provided by a femtosecond laser with the wavelength of 400 nm for the temperature of 6 K and 350 nm for room temperature. The 150 fs pulses with a repetition rate of 100 kHz were focused onto the sample surface at normal incidence by a 50x microscope objective. The emission was collected in transmission for room temperature and in reflection for the cryogenic one.

Results and Discussion

The normalized photoluminescence spectra measured at room temperature are shown on the Fig. 1, *a*. The emission spectrum of unordered perovskite nanocrystals (dash-dotted curve) has a maximum at wavelength of 518 nm, whereas the superlattice assembled from these nanocrystals (a curve with circles) demonstrates a maximum at 517 nm. We attribute this slight difference to the smaller size distribution of perovskite nanocrystals. Meanwhile, the spectral shift between the bulk perovskite film and nanocrystal structures is significant due to quantum confinement. At room temperature, the photoluminescence maximum of the bulk perovskite thin film is approximately at 525 nm (curve with squares). All three spectra have comparable widths at half-height, which are 19.4 nm for the bulk film, 17.6 nm for unordered nanocrystals, and 20 nm for the superlattice. These results demonstrate that superlattices assembled from perovskite nanocrystals preserve quantum confinement and do not transit into the bulk material state.

The photoluminescence spectra obtained from perovskite structures at cryogenic temperature are illustrated in the Fig. 1, *b*. All three structures demonstrate redshift with the decrease of temperature to 6K. Thus, the perovskite superlattice has a photoluminescence maximum at a wavelength of 530 nm, whereas unordered nanocrystals and the bulk perovskite film have their maxima at 532 nm and 538 nm, respectively. All three emission spectra become narrower than they were at room temperature due to reduction of non-radiative losses. The photoluminescence spectra of the film and the superlattice still have comparable widths, which are 2.2 nm and 2.7 nm, respectively. However, for unordered perovskite nanocrystals this value is several times larger and equals to 6.7 nm. This difference between widths correlates with the previous assumption that unordered perovskite nanocrystals have wider size distribution than nanocrystals in the superlattice.

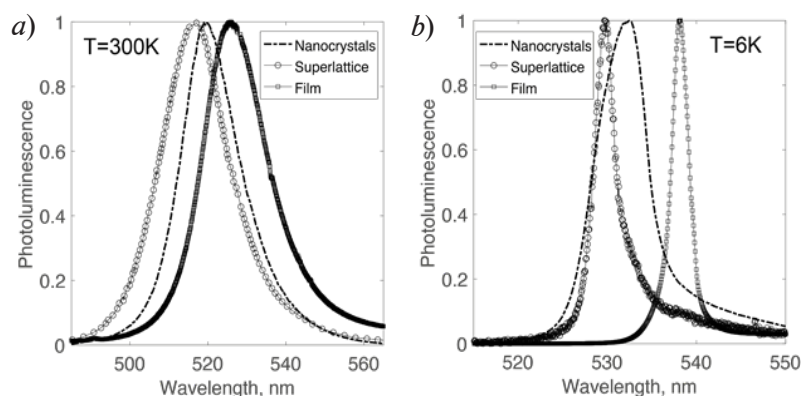


Fig. 1. Photoluminescence spectra from the thin perovskite film, not ordered nanocrystals and the superlattice at room temperature (a) and cryogenic temperature (b)

In addition, we conducted measurements of superlattice photoluminescence via pump power. The results are shown in Fig. 2. The lowest spectrum represents pump power of 4 μW . The next spectra correspond to the gradual increase of the power pump to 140 μW , whereas the top spectrum corresponds to the power of 9 μW returned back after high power. With the pump power increase, the second peak appears gradually at the wavelength of 532 nm. Consider that with switching back to low pump power the position of the second peak is preserved. Thus, the change that has taken place is irreversible. We assume that by laser-induced heating part of perovskite nanocrystals agglomerate to nanocrystals with bigger size and lower quantum confinement, which have longer emission wavelength.

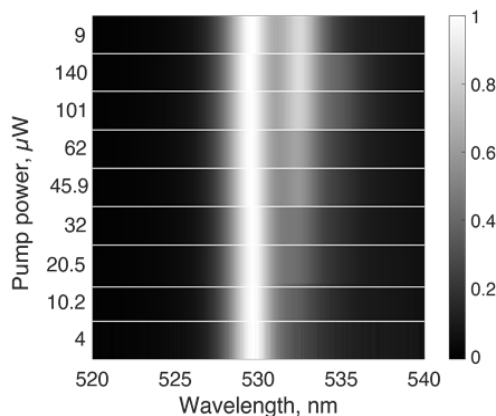


Fig. 2. Photoluminescence spectra from the superlattice at the temperature of 6K for different pump power, which starts from 4 μW , go to 140 μW , and back to 9 μW

Conclusion

The photoluminescence properties of superlattices assembled from CsPbBr_3 nanocrystals at room temperature and 6K were studied. It was demonstrated that photoluminescence spectra of perovskite superlattices are similar to emission spectra of initial colloidal nanocrystals, but have a slight blueshift which we attributed to uniform size distribution of nanocrystals. These structures allow modification of optoelectronic properties of perovskite nanocrystals at 3D level. In addition, perovskite superlattices are promising structures for micro- and nanolasers and photodetectors.

REFERENCES

1. **Snaith H. J.**, Present status and future prospects of perovskite photovoltaics, *Nature Materials*. 17 (5) (2018) 372–376.
2. **Lin K. et al.**, Perovskite light-emitting diodes with external quantum efficiency exceeding 20 per cent. *Nature*. 562 (7726) (2018) 245–248.



3. **Marunchenko A. A. et al.**, Single-Walled Carbon Nanotube Thin Film for Flexible and Highly Responsive Perovskite Photodetector, *Advanced Functional Materials*. 32 (12) (2022) 2109834.
4. **Tiguntseva E. Y., Zograf G. P., Komissarenko F. E., Zuev D. A., Zakhidov A. A., Makarov S. V., Kivshar Y. S.**, Light-emitting halide perovskite nanoantennas, *Nano Letters*. 18 (2) (2018) 1185–1190.
5. **Tiguntseva E. et al.**, Room-temperature lasing from Mie-resonant nonplasmonic nanoparticles, *ACS Nano*. 14 (7) (2020) 8149–8156.
6. **Fan Y. et al.**, Enhanced Multiphoton Processes in Perovskite Metasurfaces, *Nano Letters*. 21 (17) (2021) 7191–7197.
7. **Protesescu L. et al.**, Nanocrystals of cesium lead halide perovskites (CsPbX₃, X= Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut, *Nano Letters*. 15 (6) (2015) 3692–3696.

THE AUTHORS

TONKAEV Pavel A.

pavel.tonkaev@metalab.ifmo.ru
ORCID: 0000-0003-1849-0653

GRECHANINOVA Evgeniia V.

e.grechaninova@metalab.ifmo.ru
ORCID: 0000-0003-4087-8224

PUSHKAREV Anatoly P.

anatoly.pushkarev@metalab.ifmo.ru
ORCID: 0000-0002-1793-6812

MAKAROV Sergey V.

s.makarov@metalab.ifmo.ru
ORCID: 0000-0002-9257-6183

Received 11.07.2022. Approved after reviewing 14.07.2022. Accepted 15.07.2022.