Rapid synthesis and optical properties of CsPbBr$_2$Cl perovskite nanolasers

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Abstract. Nanostructures able to generate laser emission in a broad spectral range of 420-820 nm have become highly demanded objects for nanophotonic and optoelectronic applications such as photonic integrated circuits and ultrasensitive Fabry–Pérot nanosensors. The latter require high quality factors (Q) of stimulated emission which can be achieved in cesium lead halide perovskite nanowires (NWs). In this regard, it is difficult to underestimate the relevance of their rapid and scalable synthesis at ambient conditions. In this work we study optical properties of high-quality CsPbBr$_2$Cl NWs emitting in the 510-520 nm range manufactured by spraying at ambient conditions. The mechanism of NWs formation is based on their ligand-assisted reprecipitation (LARP). Ligands that form bonds with surface Pb atoms and, hence, prevent agglomeration of perovskite crystallites are supposed to be chosen according to the size of the certain perovskite unit cell. This approach allows obtaining numerous separate nanowires with lateral sizes of less than 1 $\mu$m and lengths of 2-50 $\mu$m. When the NWs are pumped with UV pulsed excitation above the lasing threshold ($P \approx 55 \mu$J cm$^{-2}$) they exhibit high-quality stimulated emission with Q-factors at lasing modes up to 5600.

1. Introduction
The rapid progress in nanotechnology and nanoscience revealed metal halide perovskites as promising semiconductors for needs of high-performance photonic designs and optoelectronic devices, such as micro- and nanolasers [1], solar cells [2], and light-emitting diodes (LEDs) [3]. Since the first observation of amplified spontaneous emission (ASE) from solution-processed perovskite thin films [4], room-temperature perovskite lasers having various shapes and sizes have been demonstrated. Significant attention has been paid to lasing nanowires owing to their miniature size, naturally formed Fabry–Pérot (F-P) cavities and highly localized coherent output. In contrast to conventional semiconductor NWs (GaAs/AlGaAs [5], GaN [6] or ZnO [7]) perovskite ones can be produced by simple wet chemical synthesis, show stable excitonic emission at room temperature and possess crystal lattice defect tolerance. Furthermore, broadband tuning (420-820 nm) of the photoluminescence (PL) wavelength in perovskites can be realized via the variation in anionic or cationic stoichiometry. All these advantages allow facile fabrication of perovskite F-P nanolasers exhibiting high quality stimulated emission ($Q = 100000$) above excitation thresholds of 0.2-10 $\mu$J cm$^{-2}$.

The first perovskite NW lasers of APbX$_3$ composition ($A = $ MA - methylammonium, FA - formamidinium; $X = $ Cl, Br, I) was obtained by solution-phase recrystallization [8, 9]. Although they demonstrated high-performance lasing, their long-term operation was limited because of
poor resistance of organic-inorganic perovskites against high temperatures and moisture as well as their high photodegradation rate. From this point of view, the most attractive alternative to MAPbX$_3$ and FAPbX$_3$ NWs is all-inorganic structures based on more stable CsPbX$_3$ materials. For instance, Fu et. al. [10] reported a minor photodamage caused to CsPbBr$_3$ NWs by exposing them to 10$^9$ excitation cycles that is order of magnitude larger than a similar value observed for organic-inorganic counterparts [8, 9].

Besides the aforementioned applications perovskite nanolasers due to their outstanding optical properties are suitable for exploitation as F-P sensors. In particular, CsPbBr$_{3-x}$Cl$_x$ NWs can be sensitive to low concentrations of all types of hydrogen halide vapor HX (X = Cl, Br, I) simultaneously. Exposure of such nanostructures to HX vapor initiates chemical vapor anion exchange (CVAE) [11]. This process leads to the following modification in the NW: the near-surface volume changes its chemical composition and the refractive index. Therefore, a slight surface modification of the NW should cause a minor bathochromic or hypsochromic shift of the lasing modes. To make the spectral shift pronounced the number of the interaction acts between the light confined by the F-P cavity and the modified volume should be as large as possible [12]. That is why high Q-factor (a value proportional to number of internal reflections of the light in the cavity) at lasing mode is crucial for the design of optical sensors able to detect various analytes at ultralow concentrations.

Existing methods of CsPbBr$_{3-x}$Cl$_x$ NWs fabrication such as solution-phase recrystallization [10, 13] or chemical vapor deposition (VD) [14, 15] take long time and require expensive equipment. Recently, we have developed the manufacturing of high-quality CsPbBr$_3$ NWs by simple spraying the perovskite precursors ink at ambient conditions [16]. This approach, in principle, could be extended to the related CsPbBr$_{3-x}$Cl$_x$ structures, however, it turned out that the capping ligands taking part in the ligand-assisted reprecipitation of NWs do not invoke the formation of the desired product. Therefore, another type of the ligands maybe considered for the mixed-halide NWs formation.

Herein we report on optical characteristics of cyan-emitting CsPbBr$_2$Cl nanolasers precipitated from the sprayed perovskite ink droplets consequently treated with ternary water-2-propanol-acetic acid azeotropic (H$_2$O·IPA·AcOH) vapor. Acetic acid ligands ([CH$_3$COO]$^-$) along with alcoholate ones ([CH$_3$)$_2$CHO]$^-$) were found to be yielding separate nanostructures having a large aspect ratio and exhibiting stimulated emission with high Q-factors above low lasing threshold.

2. Results

To produce CsPbBr$_2$Cl NWs lead(II) bromide (PbBr$_2$, 99.999%), cesium chloride (CsCl, 99.99%), dimethyl sulfoxide (DMSO, anhydrus, 99.8%), 2-propanol (IPA, 95%) and acetic acid (AcOH, 70%) were utilized. Perovskite precursors ink was prepared by mixing PbBr$_2$ (110 mg, 0.1 mmol) and CsCl (16.8 mg, 0.1 mmol) in DMSO (1 ml). The mixture was shaken for 30 min in a N$_2$-filled glove box to afford a clear solution. Afterwards, the solution was spray-casted at ambient conditions (room temperature, 30% humidity) onto the hydrophobic glass substrate to give small droplets. Then, the substrate with deposited droplets was enclosed in a preheated Petri dish containing a mixture of 100 µl of IPA · H$_2$O azeotrope and 10 µl of AcOH. Thus, the sample was dried in the ternary azeotropic atmosphere on the hotplate at 50 °C for 5-7 min.

During the drying process the azeotropic vapor condenses over the ink droplet and the intermediate diffusion layer containing all the chemical species is formed. Since 2-propanol does not dissolve PbBr$_2$ it induces the nucleation of the perovskite seeds. Further, anionic ligands generated due to reversible proton transfer between water and protic molecules (IPA or AcOH) bind to surface Pb atoms of the seeds and prevent them from agglomeration. We have established that solely alcoloholate ions are disable to provide sufficient surface passivation of the CsPbBr$_2$Cl crystallites, whereas, the mixture of [(CH$_3$)$_2$CHO]$^-$ and [CH$_3$COO]$^-$ anions are most likely to
supply the appropriate surface screening. We assume the choice of the ligands is specified by
the matching between ligand geometric parameters and sizes of the certain perovskite unit cell.
As a result isolated monocrystalline nanowires are precipitated from the reaction volume.

The optical properties of the obtained NWs were studied using femtosecond pulsed laser
excitation. Fig. 1a demonstrates the evolution of 15.6 µm nanowire photoluminescence
from spontaneous to stimulated emission. Integrated PL intensity versus excitation fluence
relationship (Fig. 1b) revealed the lasing threshold of about 55 µJ/cm$^2$. FWHM (Full Width
at Half Maximum) value remained roughly constant (25 nm) below the $P_{th}$, then abruptly
dropped at the threshold point down to 0.097 nm and slightly increased above it (Fig. 1b).

![Figure 1. (a) Laser generation from 15.6 µm NW. (b) Integrated PL intensity and FWHM
value versus excitation fluence relationship.](image)

Q-factor analysis gave the maximum value at lasing modes up to ca. 5600 (Fig. 2), calculated
as $Q = \lambda/\delta\lambda$, where $\lambda$ is the mode center wavelength and $\delta\lambda$ is the mode width. Furthermore, for
F-P resonators $Q$ is determined from the general equation $Q = -Lk_\parallel/\ln|r_1r_2|$, where $r_1$ and $r_2$
the reflection coefficients at each end facet, $L$ - nanowire length and $k_\parallel$ - wavenumber along the
nanowire axis. According to the latter, the NW 1 (15.6 µm) was expected to show lower $Q$ than
that of longer NW 2 (19.3 µm), however, the opposite trend was observed (Fig. 2), apparently,
owing to the difference in the form of the end facets of the resonant cavities. For instance,
internal reflectivity in NWs with truncated pyramidal end facets can be much higher than in
NWs having rectangular facets.[16] It is worth mentioning that Q-factors for our mixed-halide
nanolasers are more then 5 times higher then the values reported for solution grown CsPbBr$_3$
NWs.[13]

3. Conclusion
In summary we performed a rapid and cost-effective synthesis of cyan-emitting CsPbBr$_2$Cl
nanowires able to serve as optical gain media and Fabry–Pérot cavities. Formation of
separate NWs occurs via ligand-assisted reprecipitation during which the alchoholate and acetate
capping ligands passivate the surface of the perovskite seeds and stave off precipitation of the
polycrystalline sediment. The nanostructures obtained exhibited lasing with Q-factors of 1600-
5258 that are several times higher as compared to the values reported for similar solution grown
NWs. Since the mixed-halide perovskites capable of tuning their optical properties when exposed
to any HX (X = Cl, Br, I) vapor, the achieved high-quality lasing from the NWs is supposed to
be employed for the optical sensing of these analytes at their ultralow concentrations.
Figure 2. Q-factor analysis for the nanowires 1 (15.6 µm) and 2 (19.3 µm) selected to demonstrate lasing. All the spectral lines were fitted with multi-peak Gaussian function.

4. Acknowledgments

Synthesis of the perovskite nanowires was financially supported by Russian Science Foundation (project no. 18-73-00346). Optical characterization of nanowires was supported by Russian Foundation for Basic Researches (project no. 17-03-00621).

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