Theoretical study of perovskite nanowires optical response to hydrogen halides vapor exposure

D.I. Markina\textsuperscript{1*}, A.P. Pushkarev\textsuperscript{1}, S.V. Makarov\textsuperscript{1}

\textsuperscript{1}Department of Physics and Engineering, ITMO University, 197101 St. Petersburg, Russia
E-mail: *daria.markina@metalab.ifmo.ru

Abstract. Highly sensitive detection of harmful to the human health and environment hydrogen halide vapors is one of the key problems for the chemical industry. The available electrochemical and optical sensors most often show no selectivity to different hydrogen halides and can be produced via costly high-tech fabrication. In contrast to them, CsPbBr\textsubscript{3} perovskite nanowires (NWs) exhibiting laser generation are capable of selective and precise detecting for HCl and HI. Exposure of a single NW to these analytes results in an anion exchange that modifies the chemical composition of the NW and therefore invokes a small spectral shift of the laser peak. Herein we propose a theoretical model describing such an optical response. Taking into account that the anion exchange occurs at the surface of the NW and initiates the formation of a core-shell structure, we perform numerical estimation of the eigenmode spectral position for different thicknesses of the chlorine- and iodine-rich shell. Calculations reveal that even a 10 nm shell causes a noticeable spectral shift of 0.81 and 0.63 nm for eigenmode in CsPbBr\textsubscript{3}-CsPbCl\textsubscript{3} and CsPbBr\textsubscript{3}-CsPbl\textsubscript{3} core-shell NWs, respectively.

1. Introduction
In recent decades, the chemical industry has been one of the fastest-growing productions. Currently, many branches of the chemical industry utilize hydrogen halides (HX; X = Cl, Br, I) and their by-products as most common chemicals. For instance, HCl is widely used for the production of vinyl chloride, fertilizers, rayon, and various dyes. It is also employed in electroplating, leather tanning, production of textiles and rubber. Furthermore, HCl is a major combustion product of many chlorine-containing materials. As for hydrogen iodide, it is exploited in organic chemistry for converting primary alcohols to alkyl halides. For such reactions, HI has an advantage over other hydrogen halides due to the high nucleophilicity of I\textsuperscript{-} ion. It is also utilized for the decomposition of ethers to produce alcohols and alkyl iodides. Thus, unreactive ethers can be converted into chemically active species required for the synthesis of aliphatic and alkyl aryl ethers. Nevertheless, volatile hydrogen halides are very hazardous substances affecting human health and the environment even in their low concentrations.

Common electrochemical sensors capable of HX vapor detecting possess a number of disadvantages such as a high instrumental error, narrow detection range, and no selectivity to different HX analytes. These disadvantages could be eliminated to some extent for the optical sensors operating by the following principles: i) HX molecule reacts with a detecting molecule and changes its optical properties (e.g. photoluminescence or absorption spectrum) \[1, 2, 3, 4, 5, 6, 7\]; ii) HX vapor changes the refractive index of the surrounding medium (n\textsubscript{SM}) that interacts with an optical mode propagating in a 2D photonic crystal \[8, 9\] or circular...
microcavity resonator [10, 11, 12, 13, 14] (variation of $n_{SM}$ changes the spectral position of the optical mode). However, the technology for producing such optical sensors remains costly. Therefore the development of highly-sensitive and inexpensive photonic designs for selective detection of different hydrogen halides in the wide concentration range is a state-of-art scientific problem since meeting all these requirements is challenging.

In the meanwhile, a new platform for optical sensing of HX vapor could be established with cesium lead halide perovskites ($\text{CsPbX}_3$; $X = \text{Cl, Br, I}$). They exhibit efficient and narrow-band photoluminescence whose spectrum can be tuned across the entire visible range from 420-710 nm by varying the anionic content at the X site and thus obtaining $\text{CsPb(Cl,Br)}_3$ and $\text{CsPb(Br,I)}_3$ mixed-halide structures. Recently, the good opportunity of reaching the latter has been realized via anion exchange between homo-halide perovskite crystals and HX vapor [15, 16]. Furthermore, under certain conditions, all-inorganic lead halide perovskites tend to crystallize in the form of nanowires [17] capable of generating Fabry–Pérot (F-P) laser modes due to reflective end facets, very high optical gain ($\sim 10^4$ cm$^{-1}$ [18]), and high refractive index of the medium ($n = 2-2.5$). Summing up all the above-mentioned properties of perovskites, the idea for the sensing of small concentrations of HX vapor by the small spectral shift of the laser peak is straightforward and attractive. The only roadblock to measuring ultralow analyte concentrations could be an insufficient quality factor of the F-P laser mode ($Q_{\text{las}}$). However, recently, it has been demonstrated that integrating perovskite NWs with low-refractive-index substrates [19, 20] results in a substantial increase in $Q_{\text{las}}$ (up to 7860) owing to the excellent optical contrast between the NW and substrate that provides the laser cavity with improved optical mode confinement.

In this work, we propose a model for optical response of a $\text{CsPbBr}_3$ nanowire laser to HCl and HI vapor exposure. According to the model, anion exchange between the NW and acid vapor produces a core-shell structure with a tribromide core and trichloride or triiodide shell. Since the refractive indices of the core and shell are slightly different the laser mode undergoes a small spectral shift. Numerical simulation shows that the dependence of the TE$_{11}$ eigenmode spectral position on the thickness of the shell has a nonlinear behavior.

2. Results and discussion

To investigate the spectral response of CsPbBr$_3$ nanolaser on HI and HCl vapors presence in the atmosphere, we performed a computer modeling of a core-shell type structure on the low-refractive-index substrate ($n_{\text{substrate}} = 1.15$). The choice of the substrate refractive index is based on the requirement to obtain the highest mode Q-factor, and it corresponds to the effective refractive index of the nanostructured indium tin oxide layer [21]. The core-shell structure of the NW was employed to describe the anion exchange process occurring at the surface of a perovskite crystal. From this point of view, the thickness of the shell is supposed to be proportional to the concentration of acid vapor in the atmosphere to which NW is exposed for a certain period of time. The precise relation between the concentration of the analytes and the thickness of the formed shell can be established experimentally by means of X-ray photoelectron spectroscopy depth profiling and will be reported elsewhere. The cavity volume consisting of the core and shell layer was considered to be $3 \times 0.4 \times 0.4$ µm as the optimal for stimulated emission performance from our previous experiments [20, 17] and not spending significant time cost and computing resources. The shell thickness varied in the 10-50 nm range. To analyze the mode contribution in the lasing regime, material dispersion for different perovskite compositions was acquired from ellipsometry data [15, 22] describing only the real part of a complex refractive index because extinction is supposed to be vanishing in the gain region. The eigenmode spectral position and perovskite refractive indices were estimated near the typical experimental lasing mode wavelength ($530 \pm 5$ nm) of CsPbBr$_3$ NWs. Numerical analysis was performed by full-wave numerical simulations using a finite-element eigenmode-solver in COMSOL software.
Figure 1. (a,b) Normalized electric field spatial distribution of TE$_{11}$ eigenmode in 3×0.4×0.4 μm CsPbBr$_3$ cavity (a) and CsPbBr$_3$-CsPbI$_3$ core-shell cavity of the same size having a 50 nm shell (b). (c) Dependence of the cavity TE$_{11}$ eigenmode spectral position on the thickness of the CsPbI$_3$ shell (top plot) and CsPbCl$_3$ shell (bottom plot).

Figure 1a,b shows TE$_{11}$ mode distribution in the Fabry–Pérot cavity supporting a standing wave pattern by the multiple light reflections from the end facets. We provided the modeling of the core-shell structure and bare CsPbBr$_3$ NW corresponding to zero-thickness of the shell layer. The character of the field distribution in all cases remains very similar.

As it is mentioned above, the eigenmode spectral position depends on the shell thickness and its chemical composition determining the refractive index. Therefore, the eigenmode selected for the numerical simulation undergoes a red shift (Fig. 1c, top plot) in CsPbBr$_3$-CsPbI$_3$ core-shell NW having the refractive index of the shell ($n_I = 2.39$) a bit higher than that of the core ($n_{Br} = 2.3$). By contrast, for CsPbBr$_3$-CsPbCl$_3$ NW, the refractive index of the shell ($n_{Cl} = 2.14$) is a bit lower than that of the core resulting in blue shift of the eigenmode (Fig. 1c, bottom plot). Remarkably, the difference in refractive indices for CsPbBr$_3$ and CsPbCl$_3$ perovskites ($n_{Br–Cl} = 0.16$) is almost two times larger as compared to one for CsPbBr$_3$ and CsPbI$_3$ ($n_{Br–I} = 0.09$). For this reason, CsPbBr$_3$-CsPbCl$_3$ and CsPbBr$_3$-CsPbI$_3$ NWs demonstrate different rates and magnitudes of the spectral shift with increase in the shell thickness (Fig. 1c).

The minimum spectral shifts corresponding to the 10 nm shell were calculated to be 0.81 and 0.63 nm, whereas, the maximum values were equal to 13.41 and 6.84 nm for the 50 nm shell of CsPbCl$_3$ and CsPbI$_3$, respectively. Such spectral changes can be easily detected experimentally by using a spectrometer equipped with a 40 pm spatial resolution diffraction grating.

3. Conclusion
In summary, we proposed a new lead halide perovskite-based platform for the sensing of hazardous hydrogen halides vapor. To describe a working principle of the detection of the analytes by CsPbBr$_3$ perovskite nanowire laser, we introduced a core-shell structure with a
tribromide core and trihalide shell enriched with halogen ions coming from the analyte molecules during the anion exchange between them and perovskite NW. Since the thickness of the shell is supposed to be correlated with the concentration of HX molecules in the atmosphere to which the perovskite NW is exposed, the numerical simulation was conducted for the different thicknesses of the shell (10-50 nm) to address the response of the NW to various concentrations of the analytes. The simulation was aimed to estimate the influence of the shell thickness on the spectral position of the TE$_{11}$ eigenmode in the core-shell Fabry–Pérot NW. It was established that CsPbBr$_3$ NWs exhibit a more pronounced spectral shift in response to exposure to HCl vapor as compared to HI one due to the difference between refractive indices of tribromide and trichloride perovskites is a bit larger than that of between triiodide and tribromide perovskites. Furthermore, even a thin shell of 10 nm thickness has been shown to invoke a noticeable spectral shift, thus making the proposed model applicable for the detection of hydrogen halides vapor at low concentrations.

3.1. Acknowledgments
The work was financially supported by Russian Science Foundation (project no. 20-73-10183).

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