Optical sensing of organic solvents vapor with lead halide perovskite nanowire lasers on one-dimensional polymer nanograting

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Abstract. Timely detection of organic solvent vapors at their low concentrations is an urgent problem of the chemical industry. Various optical applications attempt to solve it, facing the challenges of low sensitivity and costly high-tech production. This work presents the design of the sensitive optical detector based on the CsPbBr\(_3\) perovskite nanowire (NW) laser deposited on a polystyrene (PS) periodic structure responsive to organic solvent presence. Molecules of solvents are effectively absorbed by PS nanograting leading to the reshaping of the last. Enlargement of the PS nanograting acting as a substrate for CsPbBr\(_3\) nanolaser causes a change in the effective refractive index of the medium under perovskite cavity. High-quality lasing modes of the perovskite cavity respond to this change via undergoing the spectral shift. Numerical modeling reveals the sufficient redshift of 0.15 nm in response to the 5 nm increase of PS nanograting ridges. We show that the sensitivity of lasing mode depends on its order which strongly correlates with the field confinement. These results might be useful for further progress in perovskite-based optical gas sensing.

1. Introduction

Lead halide perovskite nano- and microstructures are well known as promising objects for various photonics and optoelectronics applications, operating as nano- and microantennas [1, 2], emitters [3], lasers [4, 5], switchers [6], LEDs [7], solar cells [8, 9], etc. One of the urgent fields for their exploitation is optical sensing based on the change in the refractive index of the surrounding medium. All-inorganic perovskite nano- and microcavities capable of laser generation are perfectly tailored for this purpose. A pronounced spectral shift of extremely narrow emission lines corresponding to the high-quality factor (\(Q\)) lasing modes makes it possible to track the concentration of analyte molecules in the air.

However, very low concentrations of some chemicals hazardous to an ecosystem and human health might be difficult to detect using exclusively perovskite nano- or microcavities. Among these chemicals, there are volatile organic solvents - acetone, toluene, chloroform, and others. Although these solvents are harmful, they act as the most common substances for the production of paints, varnishes, fibers, adhesives, and household chemicals as well as they are widely utilized in the extraction processes and the pharmaceutical industry. The chemical industry cannot refuse the usage of organic solvents and therefore requires sensitive detectors to monitor their in- and outdoor concentration in the air. To the best of our knowledge nor state-of-the-art nanolasers nor well-established thermo-, electrochemical [10, 11], acoustic [12, 13, 14, 15, 16], and
photonic crystal-based sensors [17, 18, 19] cannot address the both cost-effective manufacturing and ultrahigh responsivity.

In the meanwhile, optical properties of perovskite nanowire (NW) lasers can be remarkably improved by integrating them with low-refractive-index nanostructured substrates. For instance, it was shown that CsPbBr$_3$ NW deposited on nanostructured indium tin oxide (NS ITO) thin film exhibits more than 3 times higher Q-factor for lasing modes and 2 times lower laser threshold than that of similar NW on an ordinary ITO substrate [20]. Such a benefit could substantially improve the optical responsivity of a single NW to the change in the refractive index of its surrounding medium caused by the presence of volatile molecules. Further improvement of the responsivity could stem from the ability of a nanostructured substrate to change its geometric parameters and hence an effective refractive index ($n_{eff}$) by absorbing analyte molecules. From this point of view, polymer materials swelling in organic solvents [21, 22, 23] seem to be good candidates for the fabrication of thin nanostructured films employing a nanoimprint lithography method [24]. Thus a device consisting of a perovskite NW laser on a polymer nanograting is supposed to be the most responsive to solvent vapor exposure.

In this work, we report on a theoretical study of the mechanism for sensing of vaporized solvents in the air with CsPbBr$_3$ nanowire lasers on a polystyrene nanograting (PS NG). In our simple model, PS NG absorbs analyte molecules and enlarges its ridges width. Such a change in geometric parameters of PS NG leads to an increase in the effective refractive index of the medium under NW laser and affects spectral position as well as quality factor of lasing modes. It is established that for a NW laser on nanograting with a period of 280 nm, width of ridges of 180 nm, and depth of 110 nm, even a small increase of 5 nm in the ridges width results in a 0.15 nm redshift of a high-order lasing mode. Taking into account the cumulative nature of the swelling process, it is reasonable to suggest the considered photonic design for the manufacturing of a highly responsive device for detection of low concentrated organic solvent vapors.

2. Results and discussion

To perform modeling of a mechanism for highly-responsive optical sensing of organic solvent vapor, we consider a complex device consisting of CsPbBr$_3$ perovskite nanowire laser integrated with a polymer nanograting capable of enlarging its ridges width when absorbing analyte molecules. Polystyrene nanograting was proposed as a substrate due to its transparency in

Figure 1. Schematic illustration of organic solvent vapor detection with CsPbBr$_3$ nanowire laser on polystyrene nanograting capable of enlarging its ridges width by through the absorption of analyte molecules from the air.
the visible range, flexibility, and the most effective absorption of some solvents (e.g. acetone and toluene[21, 22]) manifesting itself in the change of the substrate effective refractive index. Experimental detection of this change should include uniform photoexcitation of NW at normal incidence and collection of the laser emission from its end facets (Figure 1). Experimentally observed lasing modes which undergo a spectral shift in response to the change of $n_{eff}$ of the grating are presented by eigenmodes of the cavity in the perovskite optical gain region.

It is important to note, that it is tempting to use exclusively the swelling ability of the polymers tracking the change in the diffraction pattern (intensity or the spectral position of orders of diffraction etc.) with a change in the NG parameters. However, this approach has several practical disadvantages: the spectral position and intensity of diffraction maxima strongly depend on both the azimuthal orientation of the NG and the angle of the incidence for excitation pulse, which requires extremely high precision and reproducibility of the experimental conditions. Utilization of light-emitting perovskite nanostructures coupled with the grating solves the problem of the high precision since the mode composition of a nanolaser under optical excitation with a constant fluence does not depend on the spatial position and orientation of the NG and the illumination angle. Moreover, the proposed design is supposed to be suitable for cumulative detection of low concentrations of analyte vapors in the atmosphere via their interaction with the PS NG over a long-term period.

The estimation of the substrate effective refractive index change as the result of the increase in NG ridge width caused by solvent absorption can be described as follows:

$$\Delta n = \frac{\Delta x(n_{PS} - n_{SW})}{d}$$

where $\Delta x$ is the linear increase of the NG ridge width, $n_{PS}$ is the refractive index of the NG material (PS), $n_{SM}$ is the refractive index of the surrounding medium (air), and $d$ is the period.

**Figure 2.** (a,c) Eigenmode spectral position (left axis) and its Q-factor (right axis) as a function of the increase of the polystyrene nanograting ridges width for the higher-order TE$_{22}$ (a) and lower-order TE$_{21}$ (c) modes. (b) The dependence for the modes field confinement on the same change of ridges width. (d,e) Distribution of z-component ($E_z$) and normalized $|E|$ electric field for TE$_{22}$ mode in transverse (d) and longitudinal (e) sections of CsPbBr$_3$ NW on the nanograting. (f,g) The same electric field distribution for TE$_{21}$ mode in transverse (f) and longitudinal (g) sections.
of the PS NG.

The numerical simulation was carried out in the COMSOL Multiphysics software package using the finite element method to simulate the eigenmode spectra of $3 \times 0.4 \times 0.4 \ \mu \text{m}$ CsPbBr$_3$ NW on PS NG. The period of the PS NG was taken as 280 nm, width of ridges as 180 nm and the depth was 110 nm considered as optimal for fabrication and, at the same time, small enough to achieve high sensitivity to small changes in linear dimensions.

As a result, it was shown that different modes exhibit different optical responses. One of the highest-Q modes at a wavelength of $\sim 528$ nm (TE$_{22}$, $Q \sim 145$), which corresponds to the optical gain region of CsPbBr$_3$ perovskite, shows an experimentally measurable spectral shift of 0.15 nm with an increase of the ridge width by 5 nm (equal to the refractive index change of 0.02 according to Eq.(1)) and then the shift grows almost linearly with the further ridge width enlargement (Figure 2a). In the case of another high-Q mode ($\sim 535$ nm, $Q \sim 100$), but of a lower order (TE$_{21}$), an almost 6 times smaller spectral shift as compared to that of TE$_{22}$ mode is observed which could be not sufficient for reliable detection with commercially available high-resolution spectrometers (Figure 2c). The difference between magnitudes of spectral shift for TE$_{22}$ and TE$_{21}$ modes can be explained by the careful consideration of the spatial distribution of the field in the cavity (Figure 2 d,e). One can notice that the higher-order mode evanesces in the substrate at a greater distance than the low-order mode, thus becoming more sensitive to the change in effective refractive index of the nanograiting. Such mode leakage into the medium is described in terms of the field confinement that can be estimated as the ratio of the time-averaged total energy inside the NW to the time-average total energy in the entire computational cell. In the case of the lower-order mode, the field in the cavity experiences stronger confinement equal to $\sim 70\%$ which is held almost constant when changing the parameters of the surrounding medium (Figure 2b, red line). Meanwhile, the confinement factor of the field for the higher-order mode has a lower value of $\sim 68\%$ and decreases significantly down to $\sim 65\%$ in response to the PS NG ridges width growth from 0 to 30 nm (Figure 2b, blue line). Since the ratio of energy stored in the cavity to energy leakage is proportional to Q-factor of the mode, the mode showing stronger field confinement (TE$_{21}$) demonstrates lesser Q-factor loss of 4% as compared to a more pronounced decrease of 12% for TE$_{22}$ mode (Figure 2a,c).

3. Conclusion

In summary, we performed theoretical modeling for highly responsive sensing of organic solvent vapors using an original photonic design. The proposed mechanism for analyte detection is applicable to a wide range of solvents and is based on the ability of polystyrene nanograting (PS NG) to efficiently absorb the organic solvent molecules from the vapor phase and indirectly affect the optical response of CsPbBr$_3$ nanolaser coupled with the nanograiting. We demonstrated the numerically estimated redshift of the perovskite NW lasing modes depending on the width of the PS NG ridge in the range of 0-30 nm in longitudinal dimension. A spectral shift sufficient for experimental observation equals to 0.15 nm and corresponds to only 5 nm ridge widening that could be reached by PS NG absorption of very low concentrated vapor for a long-term period of time. The relationship between the order and sensitivity of the lasing modes was revealed by calculating the field confinement in the laser cavity. The higher-order TE$_{22}$ mode shows relatively weak field confinement in the cavity which descends from 68% to 65% with the increase of the width of PS NG ridges from 0 to 30 nm and capable of addressing the high responsivity. On the contrary, the same change in the ridges width invokes only 0.6% loss of the field confinement for the lower-order TE$_{21}$ lasing mode which makes it virtually insensitive to the change in the $n_{eff}$ of the substrate and hence seems to be useless for analyte sensing. We believe that our findings will expedite progress in optical sensing of volatile organic solvents.
3.1. Acknowledgments
This work was supported by RFBR (project no. 20-33-90212).

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