Anion Exchange Reaction in Halide Perovskite Single Crystals Structured by Laser Pulses

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Abstract. In this work, we carry out chemical processing of halide perovskite (CsPbBr\textsubscript{3}) microplates, where microlenses can be formed on surface by laser ablation by femtosecond laser ablation. Namely, we perform anion exchange reaction and observe spectral tuning of the microplates optical properties. We believe this effect will open new opportunities for tunable and reconfigurable micro-optical devices.

1. Introduction
All-inorganic lead-bromide perovskites (CsPbBr\textsubscript{3}) is a promising class of materials for lasing and micro-optical applications [1-3]. The refractive index of the lead-bromide perovskite is in range $n = 2 - 2.5$, which is large enough to support the various optical resonances in a single nano- or microstructure [4-5], which can enhance local electromagnetic field and provide various spectral changes in scattering and absorption of incident light [6]. At the same time, large-scale and low-cost laser ablation method for fabrication of nano- and microstructures from halide perovskite crystals would enable advanced photonic designs for various applications. Moreover, combining this method with chemical post-processing of the fabricated perovskite microstructure is highly desirable for creation of tunable micro-optical elements and light-sources.

In this work, we demonstrate precise laser ablation and chemical tunability of the CsPbBr\textsubscript{3} microcrystals. The tunability is achieve via the anion exchange reaction, when the perovskite is placed in vapor of HI. We observe strong spectral tuning of photoluminescence (PL) from the perovskite microplates. Since the microplates support high-NA focusing due to microlenses on their surface, the demonstrated ability to tailor morphological, optical, and PL properties of patterned perovskites opens up a novel direction for various applications, including spectrally tunable microlasers and elements of micro-optics (lenses, phase-masks, beam-shape modulators, etc.).

2. Experimental results and Discussions
Synthesis of relatively large (10-microns scale) perovskite microplates require a specially adopted protocol. We used the following materials. Lead(II) bromide (PbBr\textsubscript{2}, 99.999%), cesium bromide (CsBr, 99.999%), dimethyl sulfoxide (DMSO, anhydrous, 99.8%), isopropyl alcohol (IPA, technical grade, 95%) were purchased from commercial suppliers and used as received. For the preparation of perovskite ink solution we used the following procedure. A mixture of metal halide salts PbBr\textsubscript{2} and CsBr was
dissolved in DMSO by stirring at room temperature for 30 min to create a clear solution. Then, the solution was filtered by using a syringe filter with a PTFE membrane. The chemicals were stored and mixed inside a nitrogen-filled glove box with reduced concentration of both O₂ and H₂O level down to 1 ppm. CsPbBr₃ monocrystals deposition. The obtained perovskite solution was used for further deposition at ambient conditions. A glass substrate was placed in the center of a glass Petry dish and heated on the hotplate up to 60 C. A small droplet of the solution was dripped onto the substrate. Immediately after that, IPA-H₂O azeotrope was poured in the dish and, then, it was sealed. The droplet was dried in the presence of the azeotropc vapor for 10 min to give isolated microns-scale CsPbBr₃ single crystals.

Figure 1. (a) Scheme of experimental setup used for fs-laser lithography. Inset: focal-plane intensity profile of various flat-top laser beam used for direct patterning of perovskite microplate.

To fabricate microlens designs, we use direct femtosecond laser multipulse imprinting on a perovskite microcrystal placed on a silica glass substrate with a specially designed laser beam having a donut-shaped lateral intensity profile, optical vortex (OV) beam. The proposed technology is convenient for rapid and high-throughput fabrication of microlaser arrays as well as more complicated designs [7-8]. The microplates were patterned with 180-fs second-harmonic (515 nm) laser pulses generated by a regeneratively amplified Yb:KGW laser system (Pharos, Light Conversion). The laser beam with Gaussian shape lateral intensity profile was focused onto the sample surface with a dry microscope objective (5×, NA = 0.15). We used a single-pulse regime. Incident pulse energy was measured in the sample plane by a calibrated power meter (Nova, Ophir). Samples were arranged onto the PC-driven nanopositioning system (Newport XM series) to provide their precise translation at a movement
accuracy better than 100 nm along all three axes. Some additional details of the experimental setup used for laser lithography are schematically presented in Figure 1.

Figure 2a shows scanning electron microscopy (SEM) image of the fabricated array of microlenses formed on CsPbBr$_3$ microplate surface. It reveals good reproducibility of the fabrication process and absence of ablation debris on the surface. Indeed, halide perovskites have very low thermal conductivity (around 2 times lower than that of glass), which results in reduction of heat-affected zone and, thus, clean material removal. Atomic force microscopy (AFM) image shown in Fig.2b confirms high quality of the formed microaxicons (i.e. microlenses) and reveals their height around 200 nm.

The CsPbBr$_3$ material is completely transparent at the wavelengths larger than 550 nm, and have slight absorption in the range 530-550 nm allowing for light propagation through them [9]. Therefore, we irradiate the CsPbBr$_3$ microcrystal by 532-nm continuous wave laser to test focusing properties of the microlens array. Figure 2c shows far-field distribution of the transmitted light when the microcrystal surface is in imaging plane of the optical microscope, which indicates light defocusing. However, when the imaging plane of the microscope is placed 2 µm above the surface with miclenses (i.e. in their focal plane), we observe appearance of bright spots indicating tight focusing of the light passed through the microcrystal from the bottom.

The characterized CsPbBr$_3$ microplates were subjected to the chemical vapor anion exchange reaction [9] in hydrogen iodine vapor that can be described by the following chemical reaction:

$$y \text{CsPbBr}_3(s) + z \text{HCl}(g) \rightleftharpoons y \text{CsPbBr}_3 \cdot x \text{Cl}_x(s) + (z-xy) \text{HCl}(g) + xy \text{HBr}(g)$$
Figure 3. Photoluminescence images of perovskite microplates before and after anion exchange reaction. Scale bars are 20 µm.

Where HCl is taken in a significant excess as compared to generated HBr. For this reason, in the reaction, despite its reversibility, CsPbBr$_3$-$_x$I$_x$ perovskite is formed. According to the position of the photoluminescence peak, the samples have a composition close to CsPbCl$_3$ [10-11]. The doping was carried out during 8 minutes in HCl acid vapor with concentration around 0.1 mg/cm$^3$. Our spectrometric measurements reveal spectral shift of the microplate PL from 525 nm to 421 nm. In Figure 3, one can see color change of the doped microplate.

3. Conclusion
To summarize, we have demonstrated that halide perovskite microcrystals can be efficiently structured by femtosecond laser pulses to create microlens arrays. This method is clean and does not require any additional post-processing for recovering the perovskite optical properties like in the case of focusing ion beam lithography [12]. We also have checked the ability to chemically tune the optical properties of a perovskite CsPbBr$_3$ microcrystal via anion exchange reaction in HCl vapor. As a next step, we envision further development in the direction of chemical tuning of the microlens focusing properties for transmitted light or for the light emitted from the perovskite microcrystal upon external excitation to make real tunable micro-optical devices.

4. References
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