2D Perovskite Micro-optics Enabled by Direct Femtosecond-Laser Projection Lithography

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Abstract. Using direct femtosecond-laser projection lithography in chemically synthesized CsPbBr₃ perovskite microcrystals we demonstrate high-throughput fabrication of advanced binary microscale optical elements for nanofocusing as well as generation of high-order optical vortex beams. The obtained results highlight the CsPbBr₃ microcrystals as a promising material for realization of various complicated 2D micro-optical elements and holograms that can be directly imprinted using non-destructive and practically relevant laser technologies.

1. Introduction

Halide perovskites have recently appeared as a novel class of materials possessing intriguing combination of optical and optoelectronic properties revolutionizing such areas as solar cell technologies and light-emitting devices [1-5]. Inexpensive chemical synthesis was recently adopted to fabricate humidity-robust perovskite 2D microstructures (as microplates and nanowhiskers) promising for various applications ranging from nanoscale coherent light sources for next-generation optical communications to actively tunable micro-optic devices. In particular, realization of various micro-optics based on 2D perovskites hold promise considering ultra-smooth surface of chemically synthesized microcrystals as well as potential ability for in-situ variation of the material optical properties via simple vapor-phase anion exchange reaction. Convenient lithography-based nanofabrication technologies as electron- or ion-beam milling typically cause strong degradation of the perovskite photoluminescence properties being also time- and money-consuming for mass production. Recently, gentle femtosecond (fs)-laser processing appeared as a promising non-destructive approach for perovskite micro- and nanopatterning [6-9]. Additionally, fabrication of Fresnel microlenses was recently demonstrated using direct laser ablation of halide perovskite microplates by tightly focused fs-laser pulses in scanning regime. However, the quality of the obtained elements was far from being perfect, as multi-pulse scanning exposure of the perovskite surface typically leave rather deteriorated ablation layer with a surface roughness that is inconsistent with the quality required for realization of state-of-the-art micro-optical elements and devices.

Here, we reveal the superior potential of single-pulse fs-laser projection lithography for direct imprinting of advanced 2D diffraction-optical elements in chemically synthesized CsPbBr₃ perovskite microcrystals. In particular, we demonstrate fabrication of optical-quality micro-scale Fresnel zone plates (FZP) for generation of tightly focused laser beam, as well as binary spiral micro-axicons and binary fork-shaped gratings (FSGs) allowing generation of vortex beams in reflection mode. The observed ultra-smooth ablation of perovskite microcrystals was explained by ultrafast laser-induced thermalization rate...
as well as extremely low conductivity of the CsPbBr₃ material. The obtained results highlight the CsPbBr₃ microcrystals as a promising material for realization of various complicated 2D micro-optical elements and holograms that can be directly imprinted using non-destructive and practically relevant laser technologies.

2. Material and Methods

Lead (II) bromide (PbBr₂, 99.999 %, Alfa Aesar), cesium bromide (CsBr, 99.999 %, Sigma-Aldrich), dimethyl sulfoxide (DMSO, anhydrous, 99.8%, Alfa Aesar), isopropyl alcohol (IPA, technical grade, 95%, Vecton) were purchased from commercial suppliers and used as received. A mixture of metal halide salts PbBr₂ (33 mg, 0.1 mmol) and CsBr (21 mg, 0.1 mmol) was dissolved in DMSO (1 ml) by stirring at room temperature for 30 min. The solution was filtered by using a 0.45 µm syringe filter with a PTFE membrane. The chemicals were stored and mixed inside a N₂-filled glove box with both O₂ and H₂O level not exceeding 1 ppm. The obtained perovskite solution was utilized at ambient conditions. A glass substrate was placed in the center of tilted (10 deg.) glass Petry dish (80x5 mm²) and preheated on the hotplate up to 60 °C. A small droplet the solution was dripped onto the substrate. Immediately after that, 300 µL of IPA·H₂O azeotrope was poured in the dish and then it was sealed. The droplet was dried in the presence of the azetotropic vapor for 10 min to give isolated high-quality CsPbBr₃ crystals.

As-synthesized CsPbBr₃ microcrystals were further patterned by using second-harmonic (515 nm central wavelength) 200-fs laser pulses coming from the regeneratively amplified Yb:KGW laser system (Figure 1a). The output laser beam having Gaussian lateral intensity profile was first passed through the appropriate amplitude mask to generate the complex intensity pattern (Figure 1b). Then, the generated pattern was transferred with magnification into the focal plane of the dry microscope objective with a numerical aperture (NA) of 0.95 using 4f-optical system. The amplitude masks for beam shaping were fabricated using direct laser writing in a 40 nm-thick Cr films deposited onto a fused silica substrate (CLWS-200). Surface morphology of the laser-processed perovskite microcrystals was analysed using optical and scanning electron microscopy (SEM). The focusing performance of the imprinted perovskite micro-optics was studied by irradiating their surface by 515-nm CW collimated beam while the generated intensity profiles were captured in reflection at the corresponding focal plane using the calibrated CCD-camera.

3. Results and Discussions

We demonstrated the applicability of the fs-laser projection lithography by patterning the CsPbBr₃ microcrystal surface with several practically relevant designs of the binary optical elements: FZPs, spiral micro-axicons and FSGs (Figure 1(b)). Corresponding mm-scale amplitude masks were first produced in the glass-supported Cr films and projected into the focal plane of high-NA lens used for laser structuring. All demonstrated elements were imprinted using single-pulse irradiation of the CsPbBr₃ microcrystals. First, we calculated and optimized amplitude mask for imprinting of the FZP representing a well-known optical element for tight focusing of the incident plane wave into a point at the focal distance \( f \) from the element plane. It should be noted that FZP has a primary focus and an infinite number of secondary focuses. Typical FZPs are a set of alternating transparent and opaque rings (zones) having specific widths and diameters. The n-th ring has an outer radius of

\[
  r_n = \sqrt{n\lambda \left( f + \frac{n\lambda}{4} \right)},
\]

where \( n \) is an integer, \( \lambda \) is a wavelength of the incident laser radiation. The 10-µm diameter FZP imprinted on the surface of CsPbBr₃ microcrystals is shown in Figure 1(c) revealing rather smooth geometry of the produced radial grooves having the typical width between 300 and 500 nm and a depth of about 150 nm. By irradiating the fabricated optical element by CW parallel laser beam (515-nm wavelength) we found tightly focused (1/e-diameter of about 500 nm) laser spot formed few microns above the patterned surface of the CsPbBr₃ microcrystal that confirmed focusing performance of the imprinted FZP.

Further, using similar fabrication technique we produced two types of binary spiral axicons. Such elements allow to convert ordinary Gaussian laser beam into the quasi-non-diffracting optical vortex (OV), special type of laser beams with extended focal depth, donut-shape intensity profile and a helical wavefront [10]. The main parameter of the OV beams is their topological charge (TC) \( m \), a number of
wavefront twists within a wavelength along light propagation axis. Such structure of the OV beam leads to the presence of the orbital angular momentum in such electromagnetic fields equal to $m\hbar$ per photon ($\hbar$ is the reduced Planck's constant). A binary spiral axicon actually contains two vortex conjugated axicons ($\exp(-ikr_jr_m\phi)$ and $\exp(ikr_jr_m\phi)$) and has the following transmission function [11]:

$$T(r, \phi) = \text{sgn} \cos(k\alpha_ir + m\phi),$$

By designing proper geometry of the binary spiral axicon, the OV with the required TC can be generated. In our work, we fabricated two spiral axicons allowing to generate the OV beam with the TC $m=1$ and $3$. The imprinted micro-optical elements are shown in Figure 1(d,e) revealing the applicability of the fs-laser projection lithography to produce more complicated micro-optical elements. Both elements allowed to generate high-quality OV beam with $m=1$ and $3$ at the corresponding focal plane above the CsPbBr$_3$ microcrystal surface. Noteworthy, increase of the TC of the OV beam results in corresponding increase of the donut diameter as it is illustrated by comparing focal-plane intensity patterns of the generated OVs (Figure 1d,e; bottom).

![Figure 1](image)

**Figure 1.** (a) Schematic illustration of the setup for fs-laser projection lithography. (b) Design of the amplitude masks used to generate intensity patterns for laser printing of the FZP, spiral microaxicons and fork-shaped gratings. (c) Top-view SEM images of the CsPbBr$_3$ microcrystal surface imprinted with various micro-optical elements including FZP, binary spiral axicons (b,c) and binary fork-shape grating (d) of the as well as corresponding focal-plane intensity distributions at 515 nm excitation wavelength showing focusing performance of the imprinted 2D perovskite micro-optics.

Finally, we fabricated the FSG that allows to generate OVs with the opposite TCs ($\pm m$) in opposite diffraction orders. Theoretical description of Fresnel and Fraunhofer diffraction of a Gaussian laser beam by the FSGs was presented in [12]. The general transmission function of the FSGs in the polar coordinates is defined as follows:
where $D$ is a period of its rectilinear part, and $t_m$ are the complex (in general case) transmission coefficients. We designed and produced the corresponding amplitude mask for imprinting of the FSG that allows to generate OV beams with the $m=\pm 5$. Noteworthy, the TC is defined by the number of additional grooves that start from the central bifurcation point. The imprinted perovskite fork-shaped grating is demonstrated in Figure 1f. Upon irradiation with plane wave at 515 nm produced optical element generates the two high-order ($m=\pm 5$) OV beams with opposite handedness in the +1 and -1 diffraction orders as well as unconverted Gaussian beam in the main diffraction order.

Excellent performance of the imprinted micro-optics indicates the applicability of the fs-laser projection lithography for direct printing of various functional elements and devices. Here, we demonstrated few common examples of the binary diffraction optical elements that can be produced in the CsPbBr$_3$ microcrystals. However, the developed approach can be easily adopted for fabrication of more complicated elements including binary holograms. The lateral resolution of the fs-laser ablation at 515-nm wavelength of CsPbBr$_3$ can reach 250-300 nm that is generally associated with its extremely low thermal conductivity that is two orders of magnitude lower comparing to those for silicon as well as extremely fast thermalization rate of the material upon laser exposure. CsPbBr$_3$ thermalization processed at sub-picosecond timescales via Auger recombination of photo-excited carriers minimizing the heat-affected zone.

4. Conclusions
To conclude, we highlighted here remarkable performance of direct fs-laser processing for imprinting of high-quality reflection-type binary microscale optical elements – Fresnel zone plates, binary spiral micro-axicons and binary fork-shaped gratings – for laser beam focusing and generation of the vortex beams.

Acknowledgments
The work was supported by Russian Science Foundation 19-19-00177.

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