Broadband Antireflection with Halide Perovskite Metasurfaces

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Meta-optics based on optically resonant dielectric nanostructures is a rapidly developing research field with many potential applications. Halide perovskite metasurfaces have emerged recently as a novel platform for meta-optics, and they offer unique opportunities for control of light in optoelectronic devices. Here, the generalized Kerker conditions are employed to overlap electric and magnetic Mie resonances in each meta-atom of MAPbBr$_3$ perovskite metasurface, and broadband suppression of reflection down to 4% is demonstrated. Furthermore, it is revealed that metasurface nanostructuring is also beneficial for the enhancement of photoluminescence. These results may be useful for applications of nanostructured halide perovskites in photovoltaics and semi-transparent multifunctional metadevices where reflection reduction is important for their high efficiency.

1. Introduction

Recently, meta-optics based on halide perovskite nanostructures\cite{1} has attracted a lot of attention due to its numerous applications in structural coloring,\cite{2,3} enhanced luminescence,\cite{4} tunable meta-pixels,\cite{5,6} optical encoding,\cite{7,8} lasing,\cite{9-11} speckle-free imaging,\cite{12} and photovoltaics.\cite{13} Various applications of optoelectronic devices based on perovskites require suppression of reflection to achieve higher transparency in the sub-bandgap spectral range, but parasitic reflection limits the efficiency of photovoltaic devices, smart windows, and active glasses. To reduce reflection, meta-optics employs the so-called Kerker effect and Huygens’ metasurfaces,\cite{14-18} that allow to suppress backscattering from each meta-atom. Such high-transmission metasurface designs were proposed and realized with standard semiconductor metasurfaces for enhancing transparency of thin films in a broadband frequency range\cite{15} and increasing absorption efficiency in active layers of photovoltaic devices,\cite{19} as well as for bending light\cite{20} and creating high-quality holographic images.\cite{21}

In this paper, we propose to employ the Kerker conditions for halide perovskite metasurfaces to achieve broadband suppression of reflection with simultaneous enhancement of photoluminescence properties. We verify our theoretical concept experimentally by nanostructuring MAPbBr$_3$ perovskite thin films creating a periodical lattice of Mie-resonant perovskite nanoparticles. Optical characterization confirms that the optimized geometric parameters of the metasurface correspond to the reduction of reflectivity from 33% down to 4%, while photoluminescence intensity can be increased by at least 15%. Noteworthy, that the material of interest (MAPbBr$_3$) is one of the most prospective for perovskite-based optoelectronics, being applied both for solar cells,\cite{22} and light-emitting devices.\cite{23} Also, optical properties of MAPbBr$_3$ are quite prospective both to create semi-transparent coatings (low losses in half of visible range) and to provide bright green emission, that is, in the most sensitive for human eye spectral range.

2. Results and Discussion

2.1. Theoretical Approach

As was shown previously, the halide perovskite nanoparticles (e.g., those made of MAPbBr$_3$) of various shapes can support excitation of pronounced Mie resonances in visible and near-infrared ranges.\cite{4,24-25} Thus, they should provide interesting physics based on interference between the excited Mie modes, including the Kerker effect.

The Kerker effect was originally predicted by Kerker et al.\cite{26} for spherical particles when dielectric permittivity equals to magnetic permeability. In this case, electric dipole moment, excited in the particle, becomes equal in amplitude and in phase to magnetic dipole moment of this particle (so-called Kerker conditions) (see Figure 1a). Interference between electric and magnetic dipole radiation in this case is destructive in direction of backward scattering and constructive in direction of forward scattering. Thus, in the result, Kerker conditions cause zero scattering in backward direction (see Figure 1b). While materials with electric permittivity equaled with magnetic permeability...
do not exist in nature, Kerker effect still can be observed for interaction of high-index nanostructures with light.[27] This effect is widely used in all-dielectric nanophotonics due to highly transparent features of metasurfaces based on such type of high-index nanostructures.[28] Frequently, high refractive index is treated as a required condition for all-dielectric nanophotonics structures because in case of low refractive index, resonant response of particles is suppressed and interaction with light is rather weak. However, it was shown recently that low contrast between materials of particle and its environment can cause a broadband Kerker effect.[29,30] Interestingly, while in the references above contrast between materials was reduced artificially, halide perovskite has naturally low refractive index which can cause a broadband Kerker effect. It means that metasurface based on perovskite meta-atoms can be non-reflected and almost transparent, besides energy absorbed in the nanoparticle volume. The non-zero absorbance of particle’s material also influences on the scattering properties. In ref. [31], it was shown that increasing of absorbance can destroy directive scattering, even when multipole condition is satisfied.

To optimize metasurface geometry, at first we used approximation of spherical particles which allows us to use fully analytical Mie theory to describe optical response of perovskite nanoparticles.[32] We consider standalone nanoparticle placed in homogeneous environment with refractive index equaling to 1.51, which corresponds to refractive index of glass or polymer. It was shown that for particles with radii up to 100 nm, electric dipole contribution to scattering cross section is predominant for all the visible range (Figure S1, Supporting Information). When radius of nanoparticle is growing further, magnetic dipole contribution is increasing simultaneously with electric quadrupole and magnetic quadrupole contributions. Because of this fact, not original Kerker conditions but generalized Kerker conditions, which includes both dipole and quadrupole contribution, should be considered.[33,34] Let us consider them in details.

The scattered far field of particle of arbitrary shape $E_{\text{sc}}$ is a spherical wave which can be described by following projections in spherical coordinates:

$$E_{\theta} = \frac{e^{ikr}}{-ikr} \cos \varphi \cdot S_1(\cos \theta)$$

$$E_{\varphi} = \frac{e^{ikr}}{ikr} \sin \varphi \cdot S_2(\cos \theta)$$

with the scattering amplitudes $S_1$ and $S_2$:

$$S_1(\cos \theta) = \sum_{n=1}^{\infty} \frac{n+1}{n(n+1)} (a_n \tau_n + b_n \sigma_n)$$

$$S_2(\cos \theta) = \sum_{n=1}^{\infty} \frac{n+1}{n(n+1)} (a_n \sigma_n + b_n \tau_n)$$

Here, $a_n$ ($b_n$) is scattering coefficient of Mie theory, which defines contribution on electric (magnetic) multipole on $n$-th order, and
Figure 2. Analytical and numerical modeling. a) Illustration of generalized Kerker condition satisfaction for a sphere with diameter of 170 nm (see Equation (7)). b) Logarithm of numerically calculated scattering amplitude for the perovskite bullet-type nanoparticle placed into the homogeneous environment as a function of wavelength and observing angle. c) Reflection from a perovskite metasurface on a glass substrate integrated in the spectral range $\lambda = 400–1000$ nm as a function of perovskite nanoparticle height $h$. d) Reflection spectra for metasurface based on spherical (violet line)/bullet-type (green line)/needle-type particles (black line) placed on a glass substrate.

\[ \tau_n = \frac{dP_1^n\left(\cos \theta\right)}{d\theta} \]

\[ \pi_n = \frac{P_1^n\left(\cos \theta\right)}{\sin \theta} \]

(5)

(6)

To obtain suppression of backward scattering, $S_1$ and $S_2$ should be zero when $\theta = 180^\circ$. Taking into account first two Mie coefficients which correspond to dipole and quadrupole contributions, and solving the simple system of linear equations, one can express generalized Kerker condition as follows:

\[ a_1 + \frac{5}{3}b_2 = b_1 + \frac{5}{3}a_2 \]

(7)

Simple optimization using experimental data for perovskite dielectric function shows that diameter of the sphere equaled to 170 nm corresponds to satisfying the generalized Kerker conditions in the vicinity of nanoparticle resonance, and it is expected to satisfy them approximately in all the visible range (see Figure 2a).

2.2. Numerical Simulations

While results for sphere are encouraging, this shape of particle is hardly achievable for manufacturing. Based on used manufacturing methods, bullet-type nanoparticle could be used for experiment (see inset in Figure 2c). We predicted that scattering optical properties of bullet-type nanoparticle are similar to properties of spherical nanoparticle due to similar multipole enhancement.

To verify this prediction, we simulated numerically the scattering pattern of the bullet-type nanoparticle placed in the homogeneous environment with refractive index equaled to 1.51. It corresponds to a case where particle is placed on the glass substrate and covered by the polymer and immersion oil with similar optical density. Figure 2b represents scattering amplitude for considered nanoparticle in specific angle in a wide wavelength range from 400 to 1000 nm. It is clearly seen that in the whole wavelength range energy is scattered predominantly in “zero” angle, which corresponds to the forward direction, so it proves our original concept. Also, it should be noted that for wavelength smaller than 520 nm, scattering in the backward direction increases. It corresponds to the case of absorptive nanoparticle mentioned above. Besides this wavelength range, backscattering is close to zero, so it is reasonable to expect that metasurface based on such nanoparticles possesses small reflectance.
To prove it, we simulate interaction of metasurface based on bullet-type nanoparticles placed on the top of glass substrate with normally incident linearly polarized light and sweep the geometrical parameters of metasurfaces. While the base size of each nanoparticle remained the same, the height and period of metasurface were varied with step size 20 and 25 nm, respectively. Results of simulations, gathered in Figure 2c, show that height of nanoparticle (blue line) equaled to 170 nm and period of metasurface (green line) equaled to 300 nm corresponding to the minimum of integrated reflectance. Smaller nanoparticle heights correspond to the absence of Mie resonances in the considered region, making the reflection from the metasurface closer to that for the unstructured perovskite film. For the larger heights, the number of hot spots inside the nanoparticle volume increases and absorption with reflection grows rapidly.\(^{[31]}\) The optimized period corresponds to the case when near-field interaction between the nanoparticles does not yet modify their Mie resonances considerably, but still far from the appearance of diffraction.

However, these parameters of metasurface could correspond to the just optimal filling factor which could be easily satisfied in the metasurfaces based on the particles of other shape. To show that considered broadband anti-reflectance is not an effect of the special nanoparticle shape or suitable filling factor, we compared results of metasurfaces of different shapes but the same filling factor in Figure 2d. Spherical nanoparticles do not provide the gradient of refractive index between the air and the substrate, but have almost the same properties with the bullet-type nanoparticle due to similar multipole excitation (see Figure S2, Supporting Information), and vice versa, metasurface consisted of long needles with the same filling factor and nanoparticle volume (the height of each needle is 2720 nm, the base side is 42.5 nm, the period is 75 nm; “grid” line in Figure 2d) corresponding to the strong oscillations on reflectance, which cause the increase of the integral reflectance.

To take into account all the parameters of system in an experiment, additional optimization was performed, where a width of a covering polymer layer was added as a parameter of the optimization. This layer can work as additional antireflective coating and could increase antireflective properties too. Performing careful optimization using CST Studio suit software, the following geometry were proposed for fabrication: bullet-type nanoparticles with base side of 170 nm are placed in the nodes of the square lattice with period 300 nm on the glass substrate and covered by the polymer of width 270 nm (i.e., 100 nm above the upper level of nanoparticles). This configuration corresponds to minimal integral reflection \(\int R(\lambda)\, d\lambda\) in the wavelength range 400–1000 nm. Here, \(\lambda\) is a wavelength; \(R(\lambda)\) is reflect coefficient at the \(\lambda\).\(^{[33]}\)

Figure 4c shows simulated reflection spectra for bare perovskite layer and for metasurface. It is worth emphasizing that while reflectance of metasurface is much smaller than reflectance of bare layer in all the visible range, absorption is not reduced dramatically at wavelengths above 520 nm. It is important for effective luminescence of resulted perovskite metasurface.

Noteworthy, since the Mie resonances can be excited in various halide perovskites demonstrating outstanding light-emitting and electronic properties,\(^{[1,4,10,24,25]}\) the demonstrated approach is applicable for a broad range of materials from this family. However, MAPbBr$_3$ is one of the most prospective for various optoelectronic applications from lasers to light-emitting devices and solar cells.

2.3. Experimental Results

Based on the developed design of a broadband antireflective metasurface, we realize it experimentally by employing focused ion beam (FIB) lithography for milling MAPbBr$_3$ thin film of thickness 170 nm. The details of the film synthesis and deposition are given in Experimental Section. Scanning electron microscopy (SEM) images of the fabricated metasurface are shown in Figure 3a,b, revealing the high quality of the design and desired period 400 nm. The bullet-like shape of the nanoparticles in the metasurface originated from the specificity of the FIB milling process, where inhomogeneous ion beam shape smoothes sharp edges of the nanoparticles.\(^{[35]}\)

According to the optical images in reflection (Figure 4a) and transmission (Figure 4b) modes, the fabricated metasurface exhibits pronounced anti-reflective properties. Namely, spectroscopic measurements from the samples confirm the theoretical predictions and reveal reduction of reflectance from 33% down to 4%. The achieved regime antireflection is extremely broadband keeping the 4–6% level over whole visible and part of near-infrared ranges. Remarkably, the slightly increased absorption or scattering in the range \(\lambda = 550–700\, \text{nm}\) (see Figure 4c) in the nanostructured perovskite film does not strongly affect the reflectance and transmittance. In the opposite, the range of \(\lambda = 400–550\, \text{nm}\) corresponds to strong light absorption in the MAPbBr$_3$ perovskite, resulting in big changes after the nanostructuring owing to simple reduction of the lossy material area by more than four times.

On one hand, the removal of considerable part of the film should result in immediate drop of photoluminescence (PL) integral power. On the other hand, according to the simulations, the emission range \(\lambda \approx 520–560\, \text{nm}\) overlaps with ED, MD, and EQ Mie resonances in the nanoparticles (see Figures S1 and S2, Supporting Information). Generally, the coupling of emission in perovskite nanoparticles with such resonances results in the PL enhancement as shown in previous studies\(^{[1,4]}\) because of Purcell effect. However, preliminary tests of PL from the metasurfaces upon irradiation by UV part (\(\lambda = 365\, \text{nm, intensity} \, I \approx 1\, \text{Wcm}^{-2}\)) of a mercury lamp spectrum reveal strong quenching of PL signal. Indeed, because FIB lithography implies material processing by Ga$^+$-ions, which results in defect generation in the perovskite, according to the previous studies.\(^{[35]}\)

In order to overcome this problem, we propose the defect passivation by perovskite exposition in vapors of isopropl alcohol (IPA) outside the glove box. In our experiments, the sample with metasurface is placed in a small Petri dish which is put in a bigger Petri dish and heated on the hot plate at 60 °C for 2 min. Then, 50 µL of the dissolved solution of MABr in IPA with concentration 20 g mL$^{-1}$ (\(V = 0.5\, \text{ml}\)) was dripped onto the bottom of the bigger Petri dish close to the small one, and after that, covered with the preheated lid of the big Petri dish and kept in the mist at 60 °C for 10 min. After that, we observe recovery of the PL intensity. Moreover, the metasurface demonstrates even 15% higher PL signal compared to the neighboring smooth area of the film (Figure 5a). However, taking into account three times less volume
Figure 3. Example of fabricated perovskite metasurface. SEM images of MAPbBr₃ perovskite metasurface from top (a) and 30° side (b) views. Scale bars are 2 µm.

Figure 4. Optical characterization. Experimentally measured spectra of reflectance (a) and transmittance (b) for 170-nm perovskite film (F, blue curve) and metasurface (MS, red curve). Insets show optical images in reflection and transmission, respectively. (c) Photoluminescence spectra from the MAPbBr₃ metasurface and thin film.

of emitting material as compared with the smooth film around, we can conclude that we improved PL yield per volume by more than three times.

According to the previous studies, it is related to the Purcell effect in the resonant perovskite nanoparticles,[1,4] where ED, MD, and EQ are spectrally overlapped around the emission wavelength. Indeed, our simulations of near-field distribution around nanoparticle in each unit cell of the metasurface reveal up to 1.5-fold electric field enhancement (or up to 2.25 times of squared field enhancement) at the emission wavelength (see Figure 5b,c), which is an indication of enhanced Purcell factor according to the reciprocity theorem.[36] Regarding the near-field distribution around the nanoparticle at pump wavelength, we did not observe any significant enhancement because of high losses in UV range (Figure 5d,e).

3. Conclusions

In summary, we have demonstrated that nanostructuring of halide perovskite thin films results in a strong suppression of reflection as well as enhancement of photoluminescent properties. In particular, we have fabricated perovskite metasurfaces with reflection less than 4% and transparency around 90% in a broad spectral range, with photoluminescence signal increased by 15% relative to an unpatterned film of the same thickness. Our design is based on the concept of the generalized Kerker effect realized in individual perovskite nanocuboids forming a periodic lattice. Additional chemical post-processing has allowed for passivating defects in the perovskite film, thus, eliminating the harmful effect of PL quenching after the FIB nanostructuring.

We believe that our approach can be applied to a broad range of perovskite-based light-emitting structures with the refractive index close to that of MAPbBr₃. Thus, a combination of novel strategies for geometrical and chemical optimizations of perovskites paves the way for multifunctional perovskite-based optoelectronic devices with high efficiency and high transparency. More specifically, this concept can be applied for improving light-emitting solar cells,[37,38] when the nanostructured perovskite layer operates as an active semi-transparent layer as well as an additional layer for a solar cell to convert the incident UV light into green photons for improving the device efficiency. Also, perovskite broad-band photodetectors can be substantially...
improved with the proposed antireflective coatings. Finally, the proposed design of anti-reflecting perovskite metasurfaces can be up-scaled by both mechanical nanoimprint and laser printing technologies.

4. Experimental Section

Materials: Lead(II) bromide (PbBr₂, 99.998% trace metal basis, Puratronic, Alfa Aesar), methylammonium bromide (MABr, 99.5% DYESOL), dimethyl sulfoxide (DMSO, anhydrous 99.5%), and diethyl ether (anhydrous, Sigma-Aldrich) were used as received without additional purification.

Preparation of Perovskite Precursor Solutions: MAPbBr₃ solution: PbBr₂ (293.6 mg) and MABr (89.57 mg) were subsequently dissolved in 1 mL of anhydrous DMSO. All the solutions were prepared in a N₂-filled glove box operating at 0.1 ppm of both O₂ and H₂O.

Thin Film Deposition: The glass substrates (18 x 18 mm²) were subsequently ultrasonicated in acetone and 2-propanol for 5 min, respectively, then washed with deionized water, dried with dry air, and finally cleaned with O₂ for 10 min. Perovskite films were spin-coated onto glass substrates by anti-solvent dripping method in the glove box. At first, the glass substrate was fixed on the chuck of the spincoater. Then 100 µL of perovskite ink was dripped into the center of the substrate. The spincoating cycle had the following steps: At the first step, spincoater reached a rotational speed of 1000 rpm for 5 s and kept that speed for 40 s; then it accelerated up to 3000 rpm for 3 s and kept this speed for 40 s. At 32 s of the second cycle, 1 mL of diethyl ether was dripped onto the substrate. The films were annealed on the hot plate at 50 °C for 5 min and then at 100 °C for 10 min.

Metasurface Fabrication: Metasurfaces were milled from the thin perovskite film with the use of focused ion Ga⁺ beam. Structure fabrication was carried out with the system of crossed electron and ion beams implemented in Neon 40 (Carl Zeiss). For the milling process, 10 pA ion current was used, which provided material etching without re-deposition. The result of etching was visualized via scanning with electron beam.

Optical Measurements: Measurements of reflection for thin film and metasurfaces were carried out in an optical microscope (Car Zeiss) with an objective ×100 NA = 0.9 focused and collected white light from a halogen lamp. Transmittance was measured on the same setup but with illumination of the samples from bottom by a condenser lens. The signal spectra were sent to an optical fiber with 600 µm core delivering light to a spectrometer (Ocean Optics, QE Pro). Photoluminescence measurements were carried out on the same setup, but irradiation was done through the objective ×100 NA = 0.9, focusing the UV part (λ = 365 nm, intensity I ≈ 1 W cm⁻²) of the mercury lamp spectrum. All optical measurements were carried out on three metasurfaces with similar parameters and separated by distance 50 µm on one film, revealing the result deviation around 4%. Complex refractive index was measured by ellipsometry in air using an ellipsometer (Woollam M2000) over the wavelength range of 245–1000 nm with a step of 1 nm.

Analytical Modeling and Numerical Simulations: Analytical predictions were made by employing the original Mie calculator implemented in Matlab. Numerical properties of standalone nanoparticles were performed via Comsol Multiphysics. Numerical simulations of metasurface optical properties were performed via CST Microwave Studio due to its high performance in tasks of periodical structure simulations.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

antireflection, halide perovskites, Kerker effect, metasurfaces, nanophotonics
