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Laser post-processing of halide perovskites for enhanced photoluminescence and absorbance

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Abstract. Hybrid halide perovskites have emerged as one of the most promising type of materials for thin-film photovoltaic and light-emitting devices. Further boosting their performance is critically important for commercialization. Here we use femtosecond laser for post-processing of organo-metalic perovskite ($MAPbI_3$) films. The high throughput laser approaches include both ablative silicon nanoparticles integration and laser-induced annealing. By using these techniques, we achieve strong enhancement of photoluminescence as well as useful light absorption. As a result, we observed experimentally 10-fold enhancement of absorbance in a perovskite layer with the silicon nanoparticles. Direct laser annealing allows for increasing of photoluminescence over 130%, and increase absorbance over 300% in near-IR range. We believe that the developed approaches pave the way to novel scalable and highly effective designs of perovskite based devices.

1. Introduction

Organic-inorganic perovskites of methylammonium lead trihalides ($MAPbI_3$) family have attracted considerable attention when their conversion efficiency of photovoltaic (PV) devices raised rapidly from 6.5 to 19% in 2012–2015 [1]. Solution-based perovskite solar cells demonstrated efficiencies of more than 16–18% [2]. These impressive performance allowed perovskites to compete with the leading solar materials of the third generation. Advances in film formation and the optimized perovskite PV architectures have led to further conversion efficiency increase up to 22.1% [3]. Moreover, new applications of this hybrid materials have been investigated, including light emitting diodes, optical amplifiers and lasers [4]. However, these high efficiencies were demonstrated on small samples rather than on large-scale devices, required by modern industry. This fact encourages researchers to develop novel approaches for increase of the efficiencies of the realistic perovskite based devices. One of the most simple method is to introduce resonant nanoparticles fabricated by low-cost femtosecond laser ablation in liquids. Also, direct laser gentle heating of a perovskite film can reduce defects concentration and enlarge size of crystallites.

Enhancement of light harvesting in perovskite based solar cells and photodetectors due to metallic nanoparticles (NPs) has been extensively employed during last few years [5]. The perovskite solar cells with the incorporated plasmonic NPs demonstrate improved efficiencies up to 16.3% [6] as low-cost designs. However, parasitic absorption refers to the loss of photocarriers excited and generated photons in the metal particles themselves that decay via non-radiative channels that produce heat [7]. Therefore, increasing of photoluminescence (PL) from hybrid perovskite films by incorporating resonant NPs is still a challenge. In contrast to plasmonic NPs, all-dielectric nanophotonics based on resonant high-index dielectric NPs is a novel paradigm for light enhancement and manipulation at the nanoscale [8,9], as well as for nanothermometry [10]. Indeed, excitation of Mie-type resonances in such NPs results in strong light scattering and near-field enhancement [11], along with low Ohmic losses. The resonant frequency can be controlled by changing the size and shape of the NPs. Silicon NPs are a building block of all-dielectric nanophotonics, being high-index ($n>3.5$) material in visible and IR ranges, whereas its optical losses are almost negligible as compared with small plasmonic NPs [12]. Therefore, silicon based nanoantennas were successfully used for PL enhancement from dyes [13]. Even organometalic perovskites can be considered as a material with high refractive index, which was recently used for fabrication of perovskite-based resonant nanostructures by high-throughput nanoimprint lithography [14], which demonstrate enhanced PL properties.

In this work, we apply femtosecond laser for improving hybrid perovskite optical properties. In particular, we show that silicon nanoparticles (Si NPs) fabricated by laser ablation and incorporated in a perovskite thin film significantly improve light absorption in near-IR range. Further, we directly apply femtosecond laser pulses for heating and improving the perovskite characteristics. Since we use cheap and high throughput methods, we believe that our findings pave the way for low-cost and highly efficient perovskite based optoelectronic devices.

2. Results and discussion

2.1. Laser fabricated silicon nanoparticles within perovskite film

First of all perovskite films were prepared by solvent engineering method. Films thickness was 300-500 nm. Our study perovskite composition contains organic (MA) and inorganic (PbI_3) components. Laser ablation in liquids. In order to create pure colloids of resonant Si NPs, we apply method of laser ablation in liquids. We use femtosecond laser (Avesta Project) providing laser pulses at λ=800 nm with energy up to 2 mJ and pulse duration of 35 fs at the repetition rate of 1 kHz. Laser pulses are focused by lens with 10 cm focal length. Sample is placed before than the focal distance around 10 cm.

For nanoparticles incorporation into the perovskite layer, several steps have to be done. Firstly, laser ablation of single crystalline Si slab in liquid is provided, generating colloids of spherical crystalline Si NPs with a broad size distribution. Toluene is used as the liquid since it is used during our perovskite film formation and doesn't dissolve perovskite. Second step is the deposition of the colloids on a liquid layer of a spin-coated perovskite. After the annealing, the perovskite layer with Si NPs becomes dark and ready for further utilization. As shown in Figure 1b, Si NPs are distributed randomly inside the perovskite. Average size of the Si NPs is about 140 nm. In order to characterize the $MAPbI_3$ perovskite layer with embedded Si NPs, we study its optical properties. According to our reflection/transmission measurements, absorbance increases from near 0 up to 0.3 at 800 nm (Figure 1b). However, PL intensity under 633-nm cw laser photoexcitation is weaker as compared to the similar perovskite without Si NPs (Figure 1a).

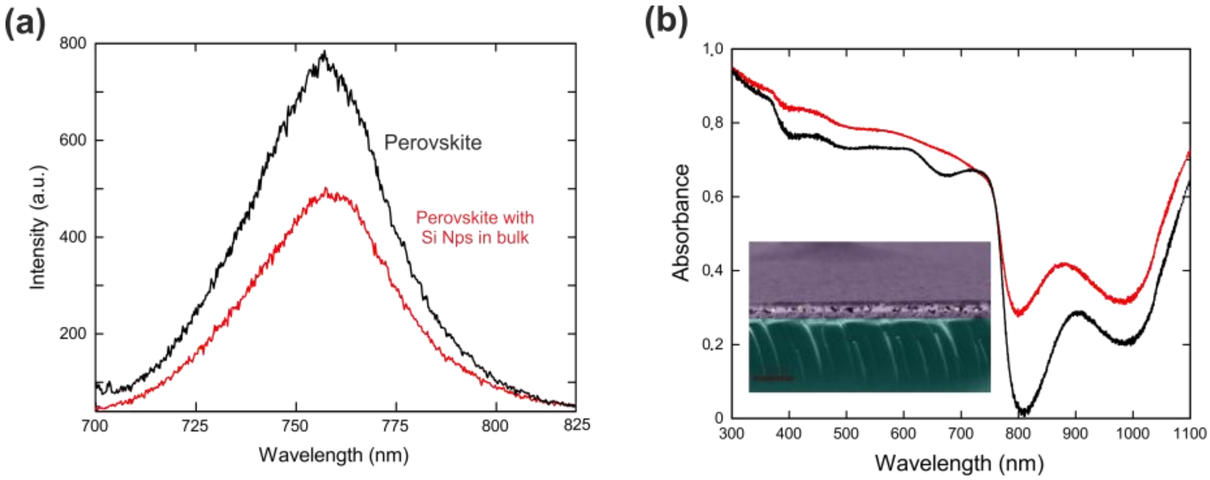

Figure 1 (a, b). (a) Comparison of PL spectra of perovskite film with embedded Si NPs in the bulk (red curve) and without it (black curve). (b) Absorbance spectra for the film with Si NPs (red) and without (black). Inset shows SEM image of perovskite film with Si NPs in the bulk.

2.2. Laser processing on perovskite surface for material modification

Second goal of our research is studying possibility to enhance PL and absorbance properties after the perovskites laser processing. We use Yb^{+3}-doped fiber femtosecond laser with wavelength 1050 nm and pulse width around 300 fs. Film surface was processing at laser fixed average power 35 mW at repetition rate 100 kHz. Different number of laser pulses were applied for the laser processing, resulting in various surface morphologies, as sown in SEM image in Figure 2a.

After laser post-processing of the film, we studied its PL and absorbance spectra. Measurements show different behavior for different post-processing regimes. The regime of irradiation by 1000 pulses has stronger PL spectra than initial plain area (Figure 2b). In absorbance measurements 100 pulses regime shows slight increase from plane area (Figure 2c). The origin of such optical properties modification is in ultrafast and gentle laser annealing of the perovskite film under multipulse femtosecond laser irradiation [15].

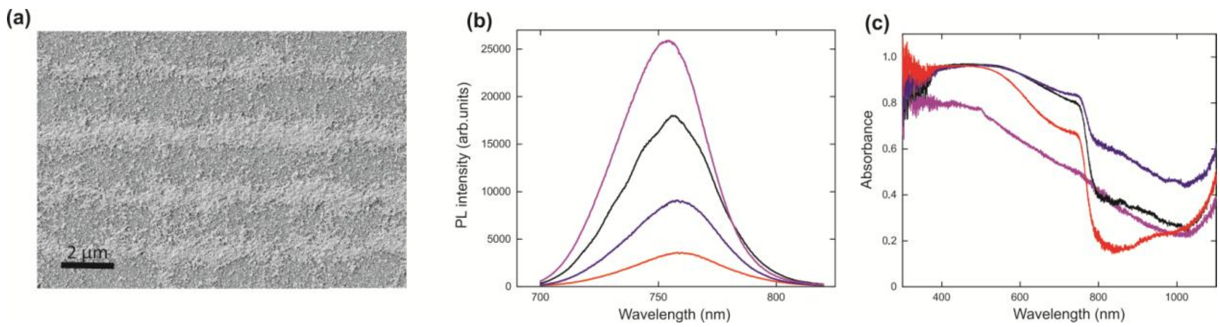

Figure 2 (a, b, c). (a) SEM image of surface after laser-processing (100 pulses). (b) PL spectra for 1 pulse (black), 10 pulses (red), 100 pulses (blue) and 1000 pulses (pink). (c) Absorbance spectra for 1 pulse area (black), 10 pulses (red), 100 pulses (blue) and 1000 pulses (pink).

3. Conclusion

To conclude, we have applied femtosecond laser for postprocessing of organo-metalic perovskite ($MAPbI_3$) films. We have demonstrated high throughput laser approaches, which include both ablative silicon nanoparticles integration into perovskite layer and its laser-induced annealing. By using these techniques, we have achieved 10-fold enhancement of absorbance in a perovskite layer with the silicon nanoparticles. Moreover, direct laser annealing allows for increasing of photoluminescence over 130%, and increase absorbance over 300% in near-IR range. We believe that the developed approaches pave the way to novel scalable and highly effective designs of perovskite based devices.

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