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Laser deposition of resonant silicon nanoparticles on perovskite for photoluminescence enhancement

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Abstract. Hybrid lead halide perovskite based optoelectronics is a promising area of modern technologies yielding excellent characteristics of light emitting diodes and lasers as well as high efficiencies of photovoltaic devices. However, the efficiency of perovskite based devices hold a potential of further improvement. Here we demonstrate high photoluminescence efficiency of perovskites thin films via deposition of resonant silicon nanoparticles on their surface. The deposited nanoparticles have a number of advances over their plasmonic counterparts, which were applied in previous studies. We show experimentally the increase of photoluminescence of perovskite film with the silicon nanoparticles by 150% as compared to the film without the nanoparticles. The results are supported by numerical calculations. Our results pave the way to high throughput implementation of low loss resonant nanoparticles in order to create highly effective perovskite based optoelectronic devices.

1. Introduction

Interest in the organic-inorganic perovskites of methylammonium lead trihalides (MAPbI$_3$) family increased when their conversion efficiency of photovoltaic (PV) devices raised rapidly from 6.5% to 9.7% and promptly to 19% in 2012-2015 [1]. 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 to 22.1% [2]. Recently, new applications of this hybrid materials have been investigated, including light emitting diodes (LED) and semiconductor optical amplifiers and lasers [3].

The trend toward increasing plasmonic amplification of mesoporous solar cells (MSCs) based on gold or silver can be traced in recent years. Increasing the efficiency of PV by such nanostructures can be conceptually obtained by plasmonic electrodes incorporated into MSCs architecture [4]. MSCs have attractive cost of composite materials, as well as the creation. However, for the visible spectral region in these plasmonic structures the losses are increased. An alternative to plasmonics is a strong magnetic response that can be obtained by the use nanoparticles of dielectric materials. In contrast to plasmon nanoparticles the first resonance of the dielectric nanoparticles is a magnetic dipole that was proved experimentally [5]. High-index dielectric nanoparticles may have an induced magnetic dipole moment and none dissipative losses because of lack of free charges in the medium compare with plasmon nanoparticles. The resonant frequency can be controlled by changing the size and shape of the nanoparticles as well as the ambient conditions [6]. Additionally, the electric and magnetic dipole resonances can be overlapped in spectral range bringing a number of unique optical properties. Namely due to these advantages the dielectric nanostructures can be a good alternative to plasmonic nanostructures. This concept paves the way to all-dielectric oligomer sensors and nanoantennas [7].
dielectric waveguides [8], nonlinear optics [9], all-dielectric Huygens’ metasurfaces [10] and metamaterials [11].

The aim of this work is to apply for the first time resonant silicon nanoparticles to improve optical properties of the hybrid perovskite films. Actually, according to the Mie theory, high-refractive index nanoparticles with low losses support strong local electric field enhancement within perovskite films, while gold plasmonic nanoparticles [12] would additionally strongly absorb useful signal [13]. Moreover, we use cheap and high throughput laser printing method for nanoparticles fabrication and transfer [14] to the surface of the perovskite films.

2. Results

2.1. Perovskite films preparation and characterisation

Thin films of MAPbI₃ perovskites can be obtained by various methods and consist essentially of two basic components: the organic methylammonium and inorganic PbI₃ lead trihalide. There are there common used of perovskite film fabrication: by vacuum deposition, solution processing method and hybrid vapor-solution process [15].

![Figure 1](image1.png)

**Figure 1.** (a) SEM image of perovskite surface without nanoparticles. AFM images of perovskite: (b) 2D and (c) 3D view.

Perovskite films prepared by solution engineering method were investigated by scanning electron microscopy (SEM). The SEM images reveal that the surface consists of non-uniform perovskite grains with an average size from 200 to 250 nm (figure 1a). Also, the film surface was characterized using atomic force microscopy (AFM). AFM method has allowed us to obtain 2D and 3D images of the perovskite surface (figure 1b, c). The AFM images show that in the field of scanning of the perovskite film surface is rather rough and has significant unevenness of the grain surfaces.

2.2. Nanoparticles deposition

To study the possibility of increasing the efficiency of devices based on perovskite (MAPbI₃), the series of experiments have been held on deposition of resonant silicon nanoparticles on the surface of the MAPbI₃ films by the unique technique of laser printing (figure 2a) [14].

![Figure 2](image2.png)

**Figure 2.** (a) Schematics of laser printing of silicon nanoparticles on perovskite surface. (b) SEM
image of a perovskite with silicon nanoparticles. (c) Size distribution of the silicon nanoparticle on the SEM image is shown as a histogram.

In the laser printing method [14] the nanoparticles are fabricated from a smooth surface (in a single-shot regime) in the forward-transfer geometry (figure 2a), when the receiving substrate is placed under the film with a spacing of 50 μm. This geometry has an advantage over the back-transfer geometry owing the possibility of nanoparticle transfer onto a wide variety of substrates, including opaque and structured samples. The silicon nanoparticles are fabricated at laser energies \( E < 2 \text{nJ} \), providing laser fluence \( (F) \) range \( F < 550 \text{ mJ/cm}^2 \). The obtained nanoparticles are almost of a spherical shape and their diameters are usually in the range of 50-200 nm, depending on the laser pulse fluence.

The distribution and sizes of the nanoparticles is studied by SEM (figure 2b). Based on the SEM images, it is seen that the surface perovskite layer is covered by silicon nanoparticles quite arbitrarily. Nanoparticles average size varies from 50 nm to 400 nm. Size distribution of silicon nanoparticles on the surface of the sample present at the histogram (figure 2c). The maximum size of the nanoparticles reach 400 nm in diameter, but it is a small amount as a percentage of the total number.

2.3. Photoluminescence enhancement
Characterization of the photoluminescence (PL) properties of the MAPbI\(_3\) sample was performed using a multifunctional experimental setup (figure 3a). The deposited silicon nanoparticles were observed using a video camera placed in the image plane of our optical layout. The volume of the measured signal is determined by the numerical aperture of collection objective (NA = 0.9) and the confocal pinhole diameter (50 μm) [14].

![Figure 3](image)

Figure 3. (a) A schematic illustration of multifunctional experimental setup for Raman for PL experiments. (b) PL enhancement from perovskite with silicon nanoparticles: maximum signal from perovskite with Si nanoparticles (black line); averaged signal from plain perovskite (red line); averaged signal from perovskite with Si nanoparticles (blue line). (c) Result of numerical calculation of electric fields near a silicon nanoparticle (D = 200 nm). The excitation wavelength is 633 nm.

After depositing the silicon nanoparticles on the surface of the perovskite we studied the PL resulting from such complex nanostructure (Si-MAPbI\(_3\)). PL measurements (figure 3b) show that the PL signal in the area with silicon nanoparticles is stronger than in the area of the sample without nanoparticles. The obtained maximum enhancement in the area with nanoparticles is 150% as compared with the area without them.

Our preliminary calculations by means of CST Microwave Studio show that the silicon nanoparticle allows for near field enhancement in the perovskite film (figure 3C). In particular, we see strong (up to 10 times) increase of E-field around the resonance nanoparticles (D = 200 nm) on the surface of the perovskite. Indeed, this size of the nanoparticle supports excitation of a magnetic dipole resonance at given wavelength providing effective light localization in a subwavelength volume. Such magnetic type Mie mode is more preferable for field enhancement rather than electric one [16].
an electric dipole resonance can be excited for larger nanoparticle, we believe that the contribution of the magnetic one in PL enhancement is dominant according to our size distribution (figure 2c).

3. Conclusion
The obtained experimental results have demonstrated that the proposed concept of resonant silicon nanoparticles deposition on top of a perovskite thin film is valid and the increased photoluminescence quantum efficiency due to near-filed enhancement around nanoparticles in agreement with our calculations. Therefore, this concept is one of the promising directions in the development of highly efficient perovskite optoelectronic devices. In future studies, we plan to incorporate silicon nanoparticles in the bulk of perovskite films in a regular way on the patterned nanostructures such as groves and cylindrical holes created by nanoimprinting, as recently demonstrated in [17, 18].

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