Upconversion photoluminescence of perovskite nanoparticles encapsulated in porous sub-micron spheres supporting Mie resonances.

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Abstract. Currently, halide perovskites are very perspective materials not only for photovoltaics but also for nanophotonic and especially nonlinear optics. These materials have already demonstrated high two-, three- and many-photon absorption coefficients, strong Kerr nonlinearity, and high-efficient second harmonic generation. Easy and cheap fabrication gives halide perovskites a wide area for scientific research and engineering applications. However, to achieve the stability of perovskites is still a challenging task, which scientific community is working on. In this work, we study a new form of encapsulation of perovskite nanoparticles in sub-micron porous dielectric nanospheres. Due to small pores in such spheres, perovskites are not only protected from external factors, but also are confined in size, which brings several features in the photoluminescence emission. We also show resonant properties of spherical sub-micron particles, which can be used for enhancing upconversion photoluminescence intensity.

1. Introduction
At present, nanomaterials based on halide perovskite draw much attention of the scientific community due to their unique physical properties such as tunable spectra of photoluminescence emission, high photoluminescence quantum yield (PLQY), and defect tolerance [1] [2]. Moreover, halide perovskites are low-cost in production and the fact, that it can be synthesized by different methods, opens a lot of ways for their applications. Recently, perovskite photovoltaic devices have reached high efficiencies, comparable with their existing analogs, for example solar cells, light-emitting diodes, nanolasers, and scintillators. [3] [4] [5] [6] Also, halide perovskites demonstrate strong optically nonlinear properties such as Kerr nonlinearity, second harmonic generation, and strong two-photon absorption with upconversion photoluminescence emission. [7] [8] However, nonlinear characteristics can be not so strong for particular applications, for instance NIR laser visualizer or bioimaging, and they can be enhanced by resonance nanostructures, which can localize or direct light and enlarge nonlinear response [9].

In this work, we investigate CsPbBr3 perovskite as it shows one of the highest two photon absorption coefficients and high PLQY [10] [11]. We use a template-assisted method for synthesis CsPbBr3 perovskite nanoparticles in CaCO3 spheres with submicron sizes, which include Mie-resonances in the visible and near-infrared spectral regions [12]. Perovskite nanoparticles inserted in porous of CaCO3 spheres can be encapsulated from the oxygen and humidity, which cause degradation of the material. In addition, pores in the spheres determine perovskite nanoparticles size, therefore it can be controlled by...
the synthesis process [13]. In our case, the pores size is around 20-30 nm, which has led to the quantum confinement in the formed perovskite nanoparticles and their pronounced excitonic optical response. Despite small sizes of perovskite nanoparticles, the PL intensity from CaCO$_3$ sphere can be high due to a large number of separated perovskite nanoparticles in one sphere. Inserted perovskite nanoparticles can be affected by Mie-resonances of CaCO$_3$ sphere, which can lead to resonant enhancement of two-photon absorption and therefore upconversion photoluminescence intensity.

2. Results and discussion

2.1. Synthesis and characterization of submicron porous spheres

Studying CsPbBr$_3$ nanoparticles embedded in submicron CaCO$_3$ spheres (CsPbBr$_3$@CaCO$_3$) were synthesized by the template-assisted method. First, 615 µL of 1 M water solution of calcium chloride (CaCl$_2$) was mixed into 2.5 mL of water. Then under vigorous stirring 615 µL of 1 M water solution of sodium carbonate (Na$_2$CO$_3$) was spilled into the mixture. The mixture was stirred for 30 seconds at 1000 rpm at room temperature. Synthesized CaCO$_3$ nanospheres were washed up via centrifugation twice and then once washed with dimethyl sulfoxide (DMSO). After this process, CaCO$_3$ nanospheres were resuspended in 2 ml of DMSO. To obtain CsPbBr$_3$ nanoparticles on CaCO$_3$ spheres in the 50 µL of CaCO$_3$ solution 140 µl of DMSO, 30 µl of 0.1 M lead bromide (PbBr$_2$), and 30 µl of 0.1M cesium bromide (CsBr) solutions in DMSO were added. The obtained solution was vigorously mixed (1400 rpm at 1 minute). After this supernatant was carefully discarded, the remaining sediment was transferred on a substrate and dried at 70 C.

Synthesized CsPbBr$_3$@CaCO$_3$ nanoparticles were transferred on ITO substrate and under a mercury lamp they showed high photoluminescence intensity. The image of photoluminescent particles is shown in Fig 1a. Different colors of the particles in the figure are probably associated with the quantum confinement of perovskite nanoparticles and color rendering features of the CCD camera. A scanning electron microscope image of the same particles is shown in Fig 1b. After the reaction we could get only CsPbBr$_3$ perovskite nanoparticles, thus, the photoluminescent wavelength can be attributed only with nanoparticles sizes and quantum confinement. It should be noted, that sizes of CaCO$_3$ nanospheres could not dictate the sizes of nanoparticles, as it is shown in Fig 1a, Fig 1b. In Fig 1c it is shown a single CaCO$_3$ nanosphere, which has a porous surface. As we could not see any perovskite nanoparticles on the surface, we suggested that CsPbBr$_3$ nanoparticles are located between CaCO$_3$ pores, which dictate their sizes. [13]

![Figure 1](https://via.placeholder.com/150)

**Figure 1.** Photoluminescence image (a) and SEM image (b) of studying CsPbBr3@CaCO3 nanoparticles.
2.2. Scattering cross-section spectra and Mie-resonances in sub-micron spheres

SEM images showed high quality spherical particles with submicron sizes, which can have Mie resonances in scattering cross-section spectra and also can be resonators with whispering gallery modes (WGM), which can cause lasing emission from CsPbBr₃ nanoparticles. Scattering cross-section spectra were experimentally measured by the dark-field (DF) spectroscopy, when white light is illuminated on the substrate with nanoparticles under an oblique incidence (67 degrees to the substrate normal) through the infinity-corrected objective (NA = 0.26), and the scattered signal is collected by the second objective from the top of the sample and sent to a spectrometer. To control nanoparticle positioning, CCD camera was used. To measure photoluminescence (PL) spectra of particular nanospheres and check possible lasing emission from the samples at room temperature, femtosecond emission from an optical parameter amplifier was used as an optical pump. Laser emission illumination from the bottom excited photoluminescence in perovskite nanoparticles, which was collected by objective from the top. Laser emission was filtered by long-pass filters, and a pure photoluminescence signal was sent to the CCD and spectrometer. Our setup allowed to conduct both experiments; the scheme of the setup is described in Fig 2 a.

Experimentally measured dark field spectra for different polarizations of incident light (Fig 2 b) showed several peaks at 556 nm and 660 nm on TE polarization and at 705 nm on TM polarization. Taking into account the sizes of the CaCO₃ spheres and previous works, these peaks are presumably associated with Mie resonances. As these resonances appeared lower than PL perovskite emission, such resonances can be used, for example for localization light in the red region, to enhance the two-photon absorption process and, thus, upconversion photoluminescence.

2.3. Photoluminescence of perovskite nanoparticles inserted in sub-micron spheres

Photoluminescence spectra of CsPbBr₃ nanocrystals (NC) in CaCO₃ and bulk CsPbBr₃ single crystal, which was synthesized by the method mentioned above, was obtained under the femtosecond laser radiation at 405 nm and 100 kHz repetition rate. Incident laser fluence was 0.2 µJ/cm², which caused no photodegradation of the material. PL spectrum from CsPbBr₃@CaCO₃ spheres showed a peak at 514.4 nm with a full width at half maximum (FWHM) 24 nm. From bulk CsPbBr₃ the peak was at 529 nm with FWHM 24 nm (Fig 3 c). The blueshift of CsPbBr₃ NC in comparison with the bulk is around 67 meV, it can be associated with the quantum confinement of perovskite NCs. Unfortunately, with increasing pumping power for different CsPbBr₃@CaCO₃ spheres, we did not obtain lasing emission, which could be connected with WGM. This fact can be connected with a low-quality factor for the WGM resonator of porous CaCO₃ spheres because the light in it can be strongly scattered on the pores and quits the sphere without resonating.

![Figure 2](image_url)
3. Conclusion

In summary, in this work, we have synthesized CaCO₃ spheres with submicron sizes with perovskite nanoparticles inside by the template-assisted method to protect perovskite from oxygen and humidity, which cause the degradation. Moreover, our method allows to separately accumulate perovskite nanocrystals in one CaCO₃ sphere, which gives a strong PL signal with an excitonic response and blueshifted photoluminescence due to quantum confinement effect. Synthesized CsPbBr₃@CaCO₃ submicron spheres can have Mie resonances in the red and infrared region, which localize the field inside the particle and cause enhancement of multi-photon absorption and, hence, upconversion photoluminescence. Efficient upconversion photoluminescence in such a system can be further used in infrared visualizations, bioimaging, and others.

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