

Up-Conversion Films and Polymer Matrices with CsPbBr₃ Perovskite Micro and Nanostructures

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Received September 20, 2022; revised October 14, 2022; accepted October 20, 2022

Abstract—Up-conversion is a process that can be used for infrared laser visualization. Lead halide perovskite has a fine opportunity to be employed for up-conversion. Halide perovskite has not only good photovoltaic and optoelectronic properties but also good photonic properties. Simple chemical fabrication methods and unique properties make perovskites cheap and attractive materials for different applications. In this article, we show different perovskite structures that possess up-conversion of near-infrared laser emission to visible green light.

Keywords: halide perovskites, up-conversion, nanocrystals, nonlinear optics, IR visualization

DOI: 10.3103/S1062873822700642

INTRODUCTION

Lead halide perovskites attract a lot of attention in the science world after they show good opportunities for solar cell and light-emitting diode fabrication [1, 2]. Nevertheless, perovskite shows good photonic properties, such as a high refractive index, big optical gain, excitonic states at room temperature, and great nonlinear coefficients [3]. Also, simple chemical methods of fabrication and bandgap engineering make perovskite a very good semiconductor material for different applications, like lasers, scintillators, and sensors [4–7].

Visualization of infrared laser emission, invisible to the human eye, can be very useful for any laser beam manipulation in optical laboratories all over the world and other places using infrared lasers. Up-conversion of near-infrared light to visible can be achieved in perovskites through two-photon absorption.

All-inorganic CsPbBr₃ perovskite has bright green luminescence and is much more stable compared to hybrid perovskite like CH₃NH₃PbBr₃ [8]. It was shown that CsPbBr₃ nanocrystals (NCs) can have a photoluminescence quantum yield (PLQY) more than 90% [9]. However, not only perovskite NCs can have bright luminescence [6].

In this work, we demonstrate up-conversion in perovskite films made of different CsPbBr₃ structures with various methods of fabrication. The thick polycrystalline film, film made of perovskite NCs and film of perovskite nanosheets (NSs) are compared. We show the potential for using obtained films as near-infrared laser beam visualizers.

SYNTHESIS

All sample was made on the glass substrate. Before film deposition substrates were consistently washed in an ultrasonic bath with soapy water, deionized water, acetone, and isopropanol. Then isopropanol remains were removed from the glass surface by air gun.

The solution for the polycrystalline film was made in a glovebox with an N₂ atmosphere. 0.4 M (mol/L) CsPbBr₃ solution in DMSO was created by mixing CsBr and PbBr₂ salts. On a clean glass substrate after oxygen plasma treatment, CsPbBr₃ films were spin-coated in 120 s at 1500 rpm inside the glovebox. Annealing of films was made in two steps, at first films were vacuum dried for 1 min, then annealed on the hot plate at 50°C for 5 min. Further, two films were connected surface to surface and were pressed on the Harry Gestigkeit PZ 28-3TD high-temperature titanium hotplate by 250 g weight. Films were heated up to 500°C in 15 min, then taken out from the hot plate. Thus, a thick film was formed on the top glass. The thickness of the obtained film was 500–1000 nm.

CsPbBr₃ nanosheets were fabricated by ligand-assisted reprecipitation method [6]. Typically, the Cs precursor and PbBr₂ precursor were prepared separately, and the reaction was initiated by injecting the latter into the former in a molar ratio of 4 : 1. First, the Cs precursor solution was prepared by dissolving 32 mg of cesium acetate in 1 mL of 1-propanol in a 20 mL vial under stirring in the air at room temperature, followed by the addition of 6 mL of hexane and 2 mL of 1-propanol. Second, PbBr₂ precursor solution was prepared by dissolving 245 mg of PbBr₂ into a

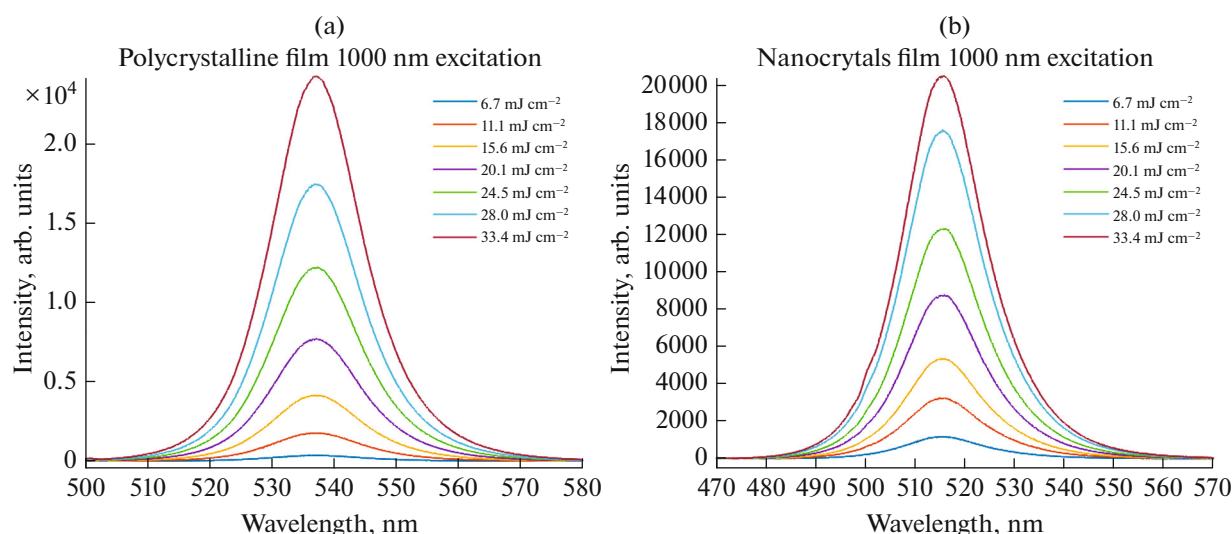


Fig. 1. Spectra of two-photon photoluminescence of (a) CsPbBr₃ polycrystalline film, and (b) film consisting of CsPbBr₃ nanocrystals under 1000 nm laser excitation at different fluence.

mixture solution of 0.45 mL of 1-propanol, 0.45 mL of octanoic acid, and 0.45 mL of octylamine at 90°C in the air under vigorous stirring. Third, the hot PbBr₂ precursor was injected into Cs precursor swiftly under vigorous stirring at room temperature. The system turned green immediately, and the reaction was completed in 2 min. The CsPbBr₃ NSs were isolated by centrifugation at 12 000 rpm. Then NSs were washed from organic remains by toluene with acetone and centrifugation again at 12 000 rpm. Further, perovskite nanosheets were dispersed into 2 mL of toluene and spin-coated (1500 rpm for 2 min) on a clean, not plasma-treated glass substrate. The thickness of the obtained film was approximately 500 nm.

CsPbBr₃ NCs were synthesized following Protesescu et al. [9]. Cs₂CO₃ (0.407 g) was loaded into a 100 mL 2-neck flask along with octadecene (20 mL) and oleic acid (1.25 mL), dried for 1 h at 120°C, and then heated under N₂ to 150°C. 1-octadecene (15 mL) and PbBr₂ (0.207 g) were loaded into a 25 mL 3-neck flask and dried under vacuum for 1 h at 120°C. Oleylamine (1.5 mL) and oleic acid (1.5 mL) were injected at 120°C under N₂. After complete dissolution of a PbBr₂ salt, the temperature was raised to 180°C and Cs oleate solution (1.5 mL, prepared as described above) was quickly injected and, 5 s later, the reaction mixture was cooled by the ice-water bath. The crude solution was cooled down with a water bath, and perovskite NCs were separated by centrifugation (12 000 rpm for 10 min) and redispersed in toluene forming colloidal stable solutions. Separation and redispersion were repeated twice. Obtained CsPbBr₃ NCs were spin-coated at 1500 rpm for 2 min on a clean oxygen plasma-treated glass substrate. The thickness of the obtained film was around 500 nm.

Besides, the CsPbBr₃ nanocrystals—polydimethylsiloxane (PDMS) composite film was fabricated. To prepare composite films toluene solution of perovskite NCs with 3 mg/mL concentration was used. Dow Corning Sylgard 184 was used as an encapsulation matrix. A solution of nanocrystals was added to a mixture of components A and B of Sylgard 184 in a ratio of 5 : 1, respectively. The resulting mixture was homogenized manually. Film curing of the resulting composite on the clean glass substrate was carried out at 80°C for 60 min.

OPTICAL MEASUREMENTS

Pharos PH2-SP-10W-2mJ single-unit integrated femtosecond 1030 nm laser system with high-power optical parametric amplifier Orpheus-F for wavelength shifting were used to investigate two-photon luminescence in obtained perovskite films. Spectra of two-photon photoluminescence (PL) were obtained by Andor Kymera 328i spectrometer with CCD camera Andor iDus. An infrared laser was focused on samples from behind by ×10 objective (Mitutoyo M Plan APO NIR, NA = 0.26), and the signal was collected by ×50 objective (Mitutoyo M Plan APO, NA = 0.55). Figure 1 shows spectra of two-photon luminescence of polycrystalline film (a) and film consisting of NCs (b). The central wavelength of PL of the polycrystalline film was 537 nm with full width at half maximum (FWHM) 17 nm, for the film made of NCs was 515 nm with FWHM 20 nm. Excitation has a 1000 nm wavelength with a 100 kHz repetition rate of 150 femtoseconds pulses. The dependence of the maximum intensity of PL on excitation fluence was estimated from obtained spectra. Figure 2 shows this dependence in

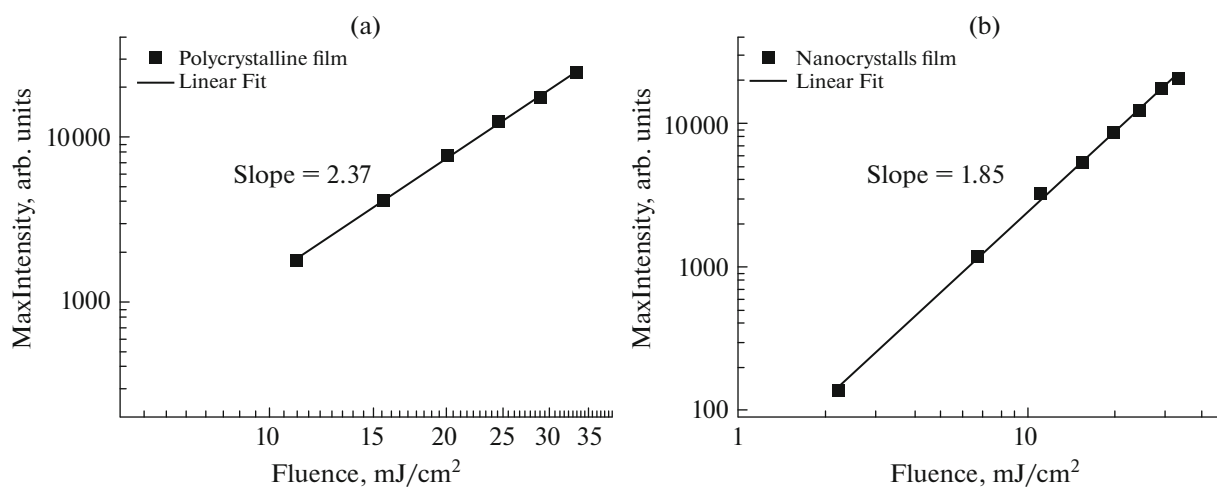


Fig. 2. Dependence of maximum intensity on excitation fluence in log-log scale with a linear fit for (a) CsPbBr₃ polycrystalline film, and (b) film consisting of CsPbBr₃ nanocrystals.

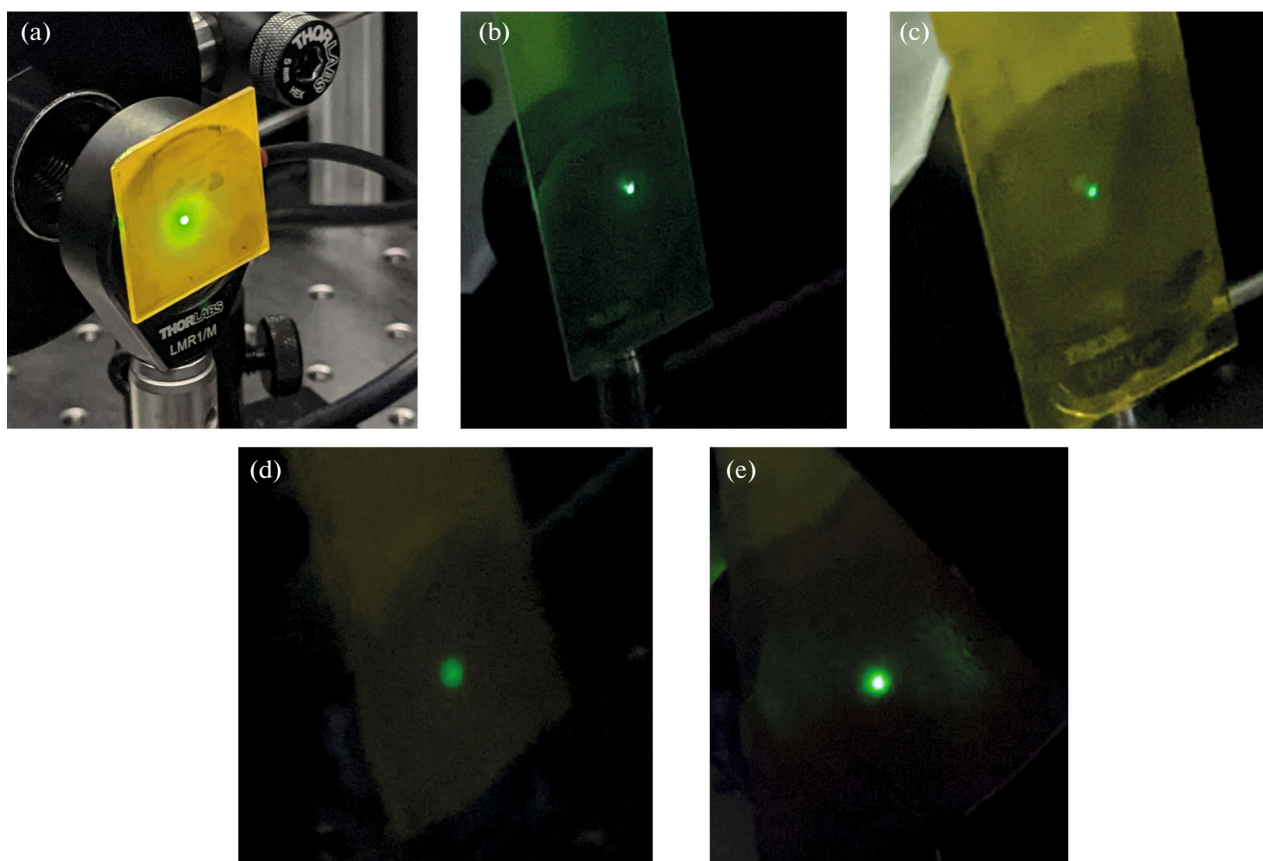


Fig. 3. Up-conversion of non focused 1000 nm laser by (a) CsPbBr₃ polycrystalline film, (b) film consisting of CsPbBr₃ nanosheets, (c) film consisting of CsPbBr₃ nanocrystals on glass, (d) film consisting of CsPbBr₃ nanocrystals in PDMS matrix on glass, and (e) on scattering substrate.

the log-log scale, the slope for the polycrystalline film is 2.37, and for NCs film is 1.85.

Besides, the up-conversion of films was investigated without focusing a laser beam at a different wavelength from 800 to 1000 nm. The diameter of the

laser beam was 2 mm. Figure 3 shows up-conversion in different films without excitation focusing at 1000 nm. The efficiency of up-conversion by different films was compared by estimating the minimal power of 800 nm laser excitation then up-conversion can be noticed by

Table 1. Comparison of 800 nm laser beam visualization by different CsPbBr₃ films. Minimal power of laser excitation at which the eye can notice up-conversion in the film

Film	Polycrystalline film	NSs film	NCs film	NCs with PDMS film on glass	NCs with PDMS on DVD
Minimal power, mW	0.5	12	5	5	2

the eye without any focusing. Table 1 shows the results of the comparison. Also, the influence of substrate was studied. CsPbBr₃ NCs in the PDMS matrix were deposited on a scattering substrate (DVD with metalization). Turn out that up-conversion can be noticed by the eye better on scattering substrate due to a bigger area of laser-matter interaction.

CONCLUSIONS

Halide perovskite shows itself as good material for up-conversion of near-infrared laser in the range 800–1000 nm. Different CsPbBr₃ perovskite films were compared, and the polycrystalline film turns out to have the best performance. The central wavelength of two-photon photoluminescence was 536 nm with FWHM 17 nm. The slope of intensity on excitation fluence dependence in the log-log scale was 2.36.

FUNDING

This work was supported by the Russian Science Foundation (project no. 21-73-20189).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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