Semitransparent visualizers of infrared lasers based on perovskite quantum dots

A S Polushkin¹, L E Zelenkov¹, D Khmelevskaia¹, D I Markina¹, A L Rogach² and S V Makarov¹

¹Department of Physics and Engineering, ITMO University, St. Petersburg 197101, Russia
²Department of Materials Science and Engineering, and Centre for Functional Photonics (CFP), City University of Hong Kong, Kowloon, Hong Kong SAR, P. R. China
E-mail: artem.polushkin@metalab.ifmo.ru
s.makarov@metalab.ifmo.ru

Abstract. These days halide perovskite is a very popular material to be applied both in photovoltaics and photonics due to its unique properties and low-cost methods of fabrication. High photoluminescence quantum yield and good nonlinear coefficients of perovskite material allow achieving multiphoton absorption in perovskite. Encapsulation of perovskite quantum dots in polymer matrix enables to prevent interaction with the environment and increase the material lifetime. In this paper, we present a semitransparent visualizer of infrared lasers working on two-photon absorption in halide perovskite nanocrystals encapsulated in the polymer matrix.

1. Introduction

Today high-power infrared lasers are used in many parts of human life, e.g., in medicine, in science, and for cutting and engraving metals. Infrared light is invisible for human eyes; as a result, different laser visualizers are used for visualizing the laser beam path. However, currently available visualizers possess some problems. Several of them work only in a narrow spectral range and are not applicable for any lasers. Other visualizers are "necessary to charge the active region with visible light" which means that they lose brightness of luminescence under the high power laser which makes them not very convenient to be used. Moreover, powerful laser emission can burn and destroy a visualizer. We have decided to develop an infrared laser visualizer that works in a wide spectral range, needs no "charging" and semitransparent which allows it to be used without laser beam path interruption.

After halide perovskite potential for solar cells was demonstrated, they attracted a lot of attention [1]. In addition, perovskite also shows some opportunities for the advanced nanophotonic device design due to its unique optical properties [2, 3]. Halide perovskites possess exciton at room temperature, a high refractive index, great optical gain, and large nonlinear coefficients. Perovskite quantum dots (QDs) synthesized by simple chemical methods can have a quantum yield up to 90% [4]. Furthermore, most laser visualizers are opaque, but active material can be used in a transparent polymer membrane for light up-conversion [5]. However, perovskite material can be damaged by water and oxygen, yet an encapsulation of perovskite QDs in a polymer matrix can protect them from harmful environment [6].

In this work, we synthesize CsPbBr₃ nanocrystals (NCs) encapsulated in polydimethylsiloxane (PDMS) matrix on a glass substrate and use it for infrared light up-conversion.
2. Results and discussion

CsPbBr$_3$ NCs were synthesized according to standard protocol [7, 8]. Perovskite NCs were separated by centrifugation and redispersed in toluene forming colloidal stable solutions. Dow Corning Sylgard 184 was used as an encapsulation matrix. A film curing of the resulting composite on a glass substrate was made by heating.

We have investigated obtained samples on two-photon absorption and photoluminescence (PL). Continuous PL from QDs in the polymer matrix was excited by a 365 nm UV mercury lamp and collected by Axio Imager A2m (Carl Zeiss) microscope with 50x objectives (Carl Zeiss EC Epiplan-NEOFLUAR). An optical fiber spectrometer (Ocean Optics QE Pro) connected with the microscope in a fluorescent regime was used for recording PL spectra. Fig. 1 represents obtained PL spectra and absorption spectra of perovskite NCs in the polymer matrix in the near-IR range. obtained by Shimadzu UV-3600 Plus UV-VIS-NIR Spectrophotometer. Peaks in fig. 1b correspond to the absorption of PDMS. A central wavelength of PL is 512 nm with full width at half maximum (FWHM) 18 nm. Photoluminescence quantum yield of perovskite QDs in PDMS was measured using Labsphere integrated sphere and appeared to be around 12%.

![Figure 1. a) Photoluminescence and b) absorption spectrum of perovskite nanocrystals encapsulated in PDMS matrix](image)

![Figure 2. a) Up-conversion luminescence of perovskite quantum dots in PDMS b) dependence of luminescence integral intensity on pump fluence](image)
Further, we investigated IR to visible light up-conversion. Pharos PH2-SP-20W-2mJ single-unit integrated femtosecond laser system and high power optical parametric amplifier Orpheus-FFor were used for excitation. A Laser beam was focused on the sample by 10x objective (Mitutoyo M Plan APO NIR, NA = 0.26) through the glass substrate and light was collected by 50x objective (Mitutoyo M Plan APO, NA = 0.55). Spectra were obtained by using the imaging spectrograph Andor Kymera 328i with CCD camera Andor iDus. Fig. 2a presents the luminescence spectrum of perovskite QDs in PDMS under the 1000 nm laser with pules duration 150 fs and repetition rate 100 kHz. The peak at 500 nm corresponds to excitation laser go to spectrometer due to no enough filtering. Fig. 2b shows the dependence of PL integral intensity on pump fluency in a log-log scale. A slope in fig. 2b equals two, which corresponds to the quadratic dependence, proving two-photon luminescence.

Moreover, we tested visualization of the infrared laser beam by our samples without any additional focusing. Fig. 3 demonstrates the luminescence under 800, 900, and 1000 nm laser with approximate beam diameter 2 mm. The visualizer is semitransparent and passes more than 50% of light. The sample also luminesces stably with a constant brightness under IR laser excitation and is not damaged by a 4 W laser beam.

In the future, we are planning to reveal the dependence of polymer on up-conversion by comparing samples with different polymers, and to study the dependence of polymer with QDs layer thickness on visualization quality. Creating a non-transparent sample can increase the efficiency of up-conversion by laser beam scattering but lose the semitransparency advantage. Another essential improvement of the visualizers can be the changing CsPbBr$_3$ NCs on CsPbI$_3$ NCs, which have a wider bandgap, that can increase spectral range and efficiency of up-conversion. However, CsPbI$_3$ NCs possess a lower quantum yield and less stability.

3. Conclusion

It has been demonstrated that CsPbBr$_3$ nanocrystals encapsulated in PDMS matrix have photoluminescence on 512 nm with FWHM 18 nm, and support IR to visible light up-conversion. We have also revealed that the dependence of integral intensity on excitation fluence is quadratic. Moreover, perovskite QDs in the polymer matrix can be used as semitransparent infrared laser beam visualizers.
4. Acknowledgments
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