Encapsulation of Recrystallized Inorganic Perovskite Quantum Dots in Nonwoven Fluoropolymer Fibers

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Abstract. Since emerging Metal Halide Perovskites were attracting elevated attention from scientific and industrial communities. Although, we still yet to see commercial products based on perovskite materials a significant body of work has been already done. Here we present our own method of Metal Halide Perovskites integration into possible industrial applications. Our way of Perovskite Quantum Dots encapsulation in polymer fibers provides exceptional water and ambient stability as well as optimal photoluminescence.

1. Introduction
The promising photoactive materials with a general stoichiometry of ABX\textsubscript{3}, where A = Cs, MA, FA; B = Pb, Sn; X = Cl, Br, I, - Metal Halide Perovskites (MHPs) - captivate the attention of international industrial and scientific community due to their excellent optical and electrophysical properties. For instance, Inorganic Metal Halide Perovskite (IMHP) Quantum Dots (QDs), CsPbBr\textsubscript{3} QDs in particular, were reported to possess not only the tunable with the QDs size photoluminescence (PL) spectra but also the 95\% efficient PL quantum yield\cite{1}. Therefore, a significant body of work has already been done to apply CsPbBr\textsubscript{3} QDs in photovoltaic (solar cells) or/and optoelectronic devices (LEDs, LASERs, LASER beam detectors, etc.)\cite{2-6} Nevertheless, to introduce any flexible device into the civil use market it is of crucial importance to encapsulate CsPbBr\textsubscript{3} QDs to improve their stability and user safety (Pb toxicity concerns).

In this work, we present the synthesis of fluoropolymer nonwoven mats with CsPbBr\textsubscript{3} QDs encapsulated in their fibers, where during the polymer fiber electrospinning, we observe the self-organized IMHP QDs recrystallization. Moreover, the perovskite QDs, encapsulated inside of the polymer fibers demonstrate two-photon absorption nonlinear process in addition to excellent water stability.
2. Experimental section

2.1 Synthesis of perovskite nanoparticles
To obtain monodisperse CsPbBr$_3$ QDs we utilize hot injection method[7], where at 140-200 °C under N$_2$ atmosphere perovskite nanoparticles precipitate from dissolved in 1-octadecene perovskite precursors, Cs-oleate and lead (II) halide (PbBr$_2$). Quantum dots were stabilized by introducing 1:1 mixture of oleylamine and oleic acid into 1-octadecane. The CsPbBr$_3$ QDs nucleation and growth takes mere seconds with resulting size distribution from 4 nm to 15 nm, achievable via reaction temperature varying (140-200 °C). The synthesized QDs were transferred from 1-octadecene to toluene by centrifugation due to the higher stability of nanoparticles in toluene. To be ready for nonwoven mats fabrication QDs/toluene solution was dried resulting in stoichiometrically pure CsPbBr$_3$ material.

2.2 Synthesis of nonwoven mats
Polymer material for nonwoven mats is prepared from 12% (wt) solution of vinylidene fluoride-tetrafluoroethylene copolymer (100-150 KDa, Halopolymer, Russia) in a 1:1 mixture of dimethylformamide (DMF) and butyl acetate (BA). For mats containing perovskite material first CsPbBr$_3$ QDs were dispersed in BA, see Figure 1, a) and b), then combined with DMF, next fluoropolymer was dissolved in perovskite containing solution, see Figure 1, c) and d). A typical procedure involves 12 mL of solvent (BA/DMF 1:1), 3.2 mg of NPs and 1.5 g of fluoropolymer.

A conventional laboratory syringe setup was used to electrospin polymer fibers with needle connected to ground terminal of the power supply (HCP 140-65000, F.u.G. Elektronik GmbH, Germany) and negative (60 kV) terminal being a rectangular (15x20 cm) aluminum plate located at 20 cm distance from the needle tip. The polymer solution was pumped through the needle using the syringe pump at a flow of 10 mL/h for 30 minutes and collected onto the coated paper fixed to the metal electrode surface, see the final sample in Figure 1, e) and f).

Figure 1. Photographs of CsPbBr$_3$ QDs in BA under (a) fluorescent and UV (b) lighting, CsPbBr$_3$ QDs in 1:1 BA/DMF solution under fluorescent (c) and UV (d) lighting. Nonwoven mats without (up) and with (down) recrystallized CsPbBr$_3$ QDs in the daylight (e) and under UV lighting (f).

2.3 Microscopic and optical characterization
The imaging of the insides of the nonwoven mats’ fibers were investigated with Transmission Electron Microscopy (TEM), using JEOL JEM-2100F microscope, with an operating voltage of 200 kV. The CsPbBr$_3$ QDs phase content was studied through powder x-ray diffraction method via measurements of 2D XRD patterns in Kappa Apex II diffractometer (Bruker AXS) using CuK$_\alpha$ (λ = 1.54184 Å) radiation generated by a I$_{\mu}$S microfocus X-ray tube. The X-ray powder diffraction patterns were collected from the CsPbBr$_3$ NPs dispersed in the polymer material, and pure polymer material was used as a reference sample.

The continuous PL characterization of nonwoven mats was performed using Axio Imager A2m (Carl Zeiss) microscope with 50× objectives (Carl Zeiss EC Epiplan-NEOFLUAR), 365 nm UV mercury lap and optical fiber spectrometer (Ocean Optics QE Pro) with detection area spot size 2 μm.
To evaluate the IR to visible light up-conversion we used Pharos PH2-SP-20W-2mJ single-unit integrated femtosecond laser system and high power optical parametric amplifier Orpheus-F with laser excitation wavelength of 900 nm, laser pulses repetition rate 100 kHz, pulse duration 220 fs.

The water stability study was carried out in a following manner: the PL signal was first recorded from several points from the dry nonwoven mat sample, next water was added and PL was measured at several time points within a 4-hour time span. Two series of measurements in a one-week interval were performed with samples being stored in a fridge at 2-4 °C.

3. Results and Discussion

The Figure 2 demonstrates the TEM images of reference sample fibers next to fibers with incapsulated CsPbBr₃ QDs. According to our data the average size of perovskite inclusions in the polymer fibers is around 10 nm. The inset in Figure 2, b) shows the powder XRD data, with clearly identifiable (100), (200), and (211) CsPbBr₃ peaks proving the crystallinity of our recrystallized nanoparticles.

![Figure 2](image1)

Figure 2. TEM images of the electrospun mats without CsPbBr₃ QDs and with them. Inset in a) – TEM image of as-synthesized QDs, scale bar is 100 nm. Inset on b) – X-ray powder diffraction pattern of CsPbBr₃ QDs in nonwoven fibers

It can be seen from the Figure 3, a), that recrystallized QDs (mean QD size 10.5 nm) in fibers demonstrate a slightly wider QDs size distribution as well as a PL signal red-shift when compared to the as-synthesized CSPbBr₃ QDs (mean QD size 9.5 nm) in colloid solution. We showed experimentally that the CsPbBr₃ QDs nonwoven mats demonstrate a visible luminesce coming from the two-photon nonlinear absorption phenomenon, which is essential for the IR LASER light detection, see Figure 3, b).

![Figure 3](image2)

Figure 3. a) Normalized spectra of QDs in Tol and in nonwoven mat; b) Representative spectrum of up-conversion PL signal.
Additionally, we conducted water stability tests of our recrystallized QDs: IMHP QDs in nonwoven mats show only a 40% PL signal intensity drop after a 9-hour immersion test, whereas as-synthesized QDs in colloid solution dissolve immediately when placed into water, see Figure 4.

![Figure 4](image)

**Figure 4.** Fluorescence signal from electrospun mats with NPs, intensity related to the initial maximum value. Two series of measurements on a single sample are shown.

4. Conclusion
To conclude, we report spontaneous CsPbBr₃ QDs recrystallization during the electrospinning process of polymer fibers. From PL spectra ($\lambda_{PL} = 506$nm) deconvolution we calculated that the recrystallized perovskite nanocrystals exhibit mean QD size of 10.5 nm with size distribution range of 5–14 nm, which is proven by TEM imaging. In addition to bright UV light down-conversion, our nonwoven mats display up-conversion at IR fluence 1 mJ/cm$^2$ to 513 nm green light. Water stability test reveals 60% PL intensity retention over 9 h.

Thus, the composite system studied can be considered an encouraging solution for perovskite QDs integration into feasible industrial applications, such as IR LASER light detection, etc.

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