Perovskite nanoparticles and films: photoluminescent properties and lighting stability

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Abstract. In this paper, we obtained nanoparticles based on ABX₃ type of metal halide perovskites at room temperature. The development of technological processes allowed us to synthesize the studied nanoparticles with room temperatures. Perovskite materials problem is degradations in moist environment, by light and unsteadiness to differential temperature. We studied perovskite degradation phenomena from light exposure. And were select the optimal layers for perovskite solar cell stability.

1. Introduction
Perovskite structure materials of the type AMX₃ (A = Cs, CH₃NH₃, CH₃CH₂NH₃, (NH₂)₂CH; M = Sn, Pb; X = Cl, Br, I,) are promising for solar energy. They have optimal parameters using in photovoltaics, such as band gap energy, high mobility of charge carriers and their long lifetime. Currently, the organo-inorganic perovskites solar cell (PSC) efficiency has reached a certified value of 25.2%, it exceeds the obtained values cadmium telluride (CdTe) and indium gallium selenide (CIGS) solar cells (SC) [1]. However, such materials are unstable under the influence of a humid environment, in the presence of oxygen, high temperatures and light radiation [2-3]. One of the solutions of this problem and improvement the properties of solar cells are using of mixed perovskite layers and stabilization of the layers by other materials, including perovskite nanoparticles (NPs). At present, perovskite NPs are especially popular in photovoltaics. They have a high photoluminescence quantum yield and their optical properties depending on NPs size and composition [4].

In this work, we developed a modified method for the NPs synthesis at room temperature and NPs films with mixed perovskite layers, their optical properties and degradation under illumination have been studied. Particle sizes vary between 20-200 nm, depending on the synthesis conditions. The optical properties of NPs and films were studied by optical spectroscopy. The films morphology was obtained by scanning electron microscope. It was experimentally found that during the synthesis of NPs, the dimensions of which are 200 nm, have a layered structure, and cubic shapes have NPs with a size of 20 nm [5]. Perovskite and NP layers was applied on substrates by various methods. After exposure to sunlight simulator, the photoluminescence (PL) intensity decreased significant. We repeatedly irradiated substrates with different NP perovskite layers. Based on the PL intensity dependences were selected the most optimal substrates and layers. The film degradation phenomenon from lighting can be associated with various mechanisms of ion mass transfer.

2. Synthesis and methods
2.1. Materials
All synthesis and isolation of colloidal perovskite NPs operations were carried out according to the modified methods at room temperature in an argon atmosphere and in air using absolute solvents [5–6]. Starting reagents: CsI (99.9%, “Aldrich”), Cs₂CO₃, PbI₂ (99.999%, “Sigma-Aldrich”), PbBr₂ (99.999%, “Sigma-Aldrich”), N,N-dimethylformamide (DMF, 99%, “Aldrich”), oleic acid (OA, 97.4%, Ruskhim), oleylamine (OAm, 98%, Sigma-Aldrich), octadecene (ODE, 90%, Alfa Aesar), toluene (Khimm), n-hexane (Khimm) were used without further purification. Dispersion was carried out using an ultrasonic (ultrasound) homogenizer SONOPULS HD 3100, BANDELIN, using a power of 10-30, 60 W and two nozzles d = 3 and 13 mm, for t = 10 and 30 minutes. Microphotographs were taken using a Titan 80-300 transmission electron microscope (FEI, USA). The research sample was prepared by dissolving a colloidal solution in ethyl alcohol in a ratio of 1:10, after which it was applied to a copper mesh with a carbon film of the Lacey type. The film morphology image were obtained by Carl Zeiss NVision 40 scanning electron microscope. Photoluminescence spectra were recorded at room temperature on a Perkin Elmer LS-55 single-beam luminescent spectrometer (resolution 0.5 nm) in the wavelength range from 500 nm to 750 nm at an excitation light wavelength of 486 nm, the slit sizes were 10 nm. The study was carried out using a single-position cell holder for liquid samples.

![Perovskite NPs](image)

**Figure 1.** Perovskite NPs different composition.

2.2. Methods.

2.2.1. Inert solvent synthesis
**Synthesis of CsPbI₃ colloidal NPs.** A mixture of 0.36 g (0.4 mmol) of CsI 0.2 g (0.4 mmol) of PbI₂ and 10 ml of DMF was heated to boiling to form a yellow clear solution A. 0.1 ml of OA and 0.1 ml of OAm were separately mixed and pumped out at 12 mbar for 20 minutes, after which 2 ml of solution A were added to the mixture. The resulting yellow solution was added dropwise to 10 ml of toluene stirring with a magnetic agitator at a speed of 1000 rpm within 5 minutes.

2.2.2. Stabilizing solvent synthesis.
**Synthesis of CsPbI₃.** A mixture of 0.03 g (0.1 mmol) of Cs₂CO₃, 0.14 g (0.3 mmol) of PbI₂, 0.5 ml of OA and 0.5 ml of OAm was dispersed in 10 ml of ODE using a probe d = 13 mm, ultrasound power 10 W, for 10 minutes, with the formation of a suspension A dark brown color. The resulting suspension was centrifuged at 9000 rpm for 10 minutes. The precipitate was dispersed in 5 ml of n-hexane using a probe d = 3 mm, with a power of ultrasound of 10 W, for 10 min, with the formation of a suspension B.
of a bright red color. To obtain a solution with small NPs, suspension B was additionally centrifuged at 2000 rpm for 10 minutes.

**Synthesis of CsPbBr$_3$.** A mixture of 0.03 g (0.1 mmol) of Cs$_2$CO$_3$, 0.11 g (0.3 mmol) of PbBr$_2$, 0.5 ml of OA and 0.5 ml of OAm was dispersed in 10 ml of ODE using a d = 13 mm probe with a power of 10 W for 10 minutes to form a suspension A bright yellow color. The resulting suspension was centrifuged at 9000 rpm for 10 minutes. The precipitate was dispersed in 5 ml of n-hexane using a probe d = 3 mm, with a power of ultrasound of 10 W, for 10 min, with the formation of a suspension B of yellow-green color. To obtain a solution with small NPs, suspension B was additionally centrifuged at 2000 rpm for 10 minutes to form a green suspension.

![Figure 2](image)

**Figure 2.** Perovskite NP synthesis at room temperature: (a) inert solvent synthesis, (b) stabilizing solvent synthesis.

2.2.3. **Technique for applying CsPbI$_3$ and CsPbBr$_3$ NPs films.** We were chosen four materials as substrates composition: silicon (Si), optical glass (K-8), conductive glass (FTO), and MAPbI$_3$ bulk perovskite. This substrates choice was due to various physicochemical properties materials. The perovskite films were prepared by drop-wise deposition: 50 μl NPs suspension were dropped onto a prepared substrate, dark glass covered, without access to sunlight, and the solvent was completely evaporated. The substrates were preliminarily purified in several stages using various solvents: we were placed substrates in potassium dichromate for 10 min, then were treated with distilled water, acetone, and again with water.

3. **Results and discussion**
**Figure 3.** (a) CsPbI$_3$ NPs layered structure, (b) NPs CsPbI$_3$ TEM-image by bright field mode.

As can be seen from TEM-image (Fig. 3, a) the NP forms layered structures consisting of several nanometer strips interconnected by intermolecular (Van-der-Waals) forces. Similar forms were previously observed in the study of inorganic perovskite materials with mixed anions [6, 7]. CsPbI$_3$ NPs by inert solvent synthesis studied by the TEM bright field mode, which indicated strip NPs that up to 200 nm and a thickness of about 40–50 nm (Fig. 3, b). The size of this strip is relatively large, and this does not allow it to be considered two-dimensional, and it more closely matches the 3D size.

**Figure 4.** (a) NPs CsPbI$_3$ TEM-image, (b) NPs CsPbBr$_3$ TEM-image.

CsPbI$_3$ and CsPbBr$_3$ NPs have smaller sizes various 10-20 nm. NPs shape changes depending on the anion composition in the nanoparticles: for CsPbI$_3$ NPs are of a characteristic cubic shape, CsPbBr$_3$ have the hexagon shape. Similar forms were observed earlier in the study of inorganic perovskite materials. Such NPs, as a rule, have bright photoluminescence and are most promising for use in solar energy [7].
**Figure 5.** Normalized PL spectra ($\lambda_{ex} = 486$ nm) of CsPbI$_3$ NPs: 1 – layer structure, 2 – cubic shape.

The quantum-size effect manifests itself in the spectrum of electronic waves, which leads to a change in the wavelength of light emission, which corresponds to the recombination energy of an electron-hole pair [8, 9]. Thus, by PL spectra analysing, one can make qualitative conclusions about the sizes of nanoparticles and their shapes, as well as reveal correlations with TEM data. As can be seen from fig. 5 (1), the PL spectrum is complex and is a superposition of four emission bands. This similar complex PL spectra were observed in [10, 7], in which the perovskite NPs of the composition CsPbI$_3$ and $0.025C_5 \cdot 2CO_3: 0.3PbI_3$, was studied a geometric strip shape. The several bands presence in the spectrum consists of several NPs similar layers to those shown in Fig. 3, a. In this case, with an increase layer number, were observed a shift to the spectrum red region. Accordingly, we assume that for synthesized NPs, according to the literature, the observed bands have a layer number from 18 to 4, that is, emission centres lie in the range from 641 nm to 690 nm. Fig 5 (2) present the PL spectrum of NPs by stabilizing solvent synthesis at 680 nm. The previous spectra were observed early in the NP composition and 20 nm size, which corresponds to our microscope data. According to literature data, such nanoparticles are 0D dimensional objects and are promising composite materials in photovoltaic. Fig 6. present two photoluminescence spectra of NP different compositions. The CsPbBr$_3$ NP emission band corresponds to 520 nm, for CsPbI$_3$ NPs, as cited above 680 nm [3, 4]. NP size by stabilizing solvent synthesis are smaller than NP size by inert solvent synthesis, which is confirmed by TEM-images and PL spectra. Thus, it was found that the emission band number and composition depend from NP size and composition.

**Figure 6.** Normalized PL spectra ($\lambda_{ex} = 350$ nm) of perovskite NP sols: 1 – CsPbBr$_3$, 2 – CsPbI$_3$. 
Figure 7. SEM-image: (a) CsPbI$_3$ film by silicon substrate, (b) CsPbBr$_3$ film by FTO substrate.

We chose four materials as substrates: silicon (Si), optical glass (K-8), conductive glass (FTO) and bulk perovskite MAPbI$_3$ (MAPI). Films were made by drop- and spin-coating. Microphotographs taken for CsPbI$_3$ film by silicon substrate and CsPbBr$_3$ film by FTO substrate. We observed different NP behaviour on substrates. The foundation PL spectra, the most successful composite materials obtained using substrates FTO and MAPI and CsPbI$_3$ NPs, and for CsPbBr$_3$ NPs the most favourable substrates were K8 and MAPI. However, it was not possible to fix the surface composite morphology based on these materials. As can be seen from the SEM-image (Fig.7, a), the NPs spontaneously concentrate on the crystalline central silicon substrates. This agglomeration of particles is confirmed by the PL spectra; we observe the PL peak shift to the short-wavelength region (Fig. 8). According to published data, a change in NP emission band position can be associated with NP size changes. In contrast to CsPbI$_3$ films, the CsPbBr$_3$ films are uniformly distributed over the substrate surface (Fig.7, b). The NP agglomeration on substrates absence is confirmed by the PL results: the emission band does not change position (Fig. 9) [4]. Perovskite NP films also exhibit bright luminescence; however, the emission band shifts to the short-wavelength region, which can be explained by particle agglomeration on the surface. The second emission band $\lambda_{em} = 680$ nm is present in MAPI+NPs CsPbBr$_3$ film, which is not typical of the PL spectrum of particles. This phenomenon can be associated with ion exchange between bulk perovskite and particles.
**Figure 8.** Normalized PL spectra ($\lambda_{\text{ex}} = 350$ nm) of perovskite CsPbI$_3$ NP films by different substrate: 1 – Si, 2 – K-8, 3 – FTO, 4 – MAPI.

![Normalized PL spectra of CsPbI$_3$ NP films](image)

**Figure 9.** Normalized PL spectra ($\lambda_{\text{ex}} = 270$ nm) of perovskite CsPbBr$_3$ NP films by different substrate: 1 – Si, 2 – K-8, 3 – FTO, 4 – MAPI.

![Normalized PL spectra of CsPbBr$_3$ NP films](image)

**Figure 10.** (a) PL spectra ($\lambda_{\text{ex}} = 350$ nm) of perovskite CsPbI$_3$ NP films by different substrate: 1 – Si, 2 – K-8, 3 – FTO, 4 – MAPI, * – film PL spectra after exposure to sunlight (1 h), (b) PL peak ($\lambda_{\text{em max}} = 680$ nm) dependence on the time of irradiation CsPbI$_3$ NP films: 1 – Si, 2 – K-8, 3 – FTO, 4 – MAPI.
We investigated the degradation of films from exposure to light. After exposure to sunlight simulator, the photoluminescence (PL) intensity decreased significantly. Studies have shown that when exposed to sunlight for 1 hour, the films completely degrade (Fig. 10 (a), 11 (a)). Upon repeated irradiation of the films, we observed a decrease in the PL intensity. Figures 10 (b) and 11 (b) show the kinetic dependences of film PL intensity on multiple irradiation. Depending on the NP and substrate composition, it is observed different degradation mechanisms. We attribute this to various mechanisms of the particle binding to the substrate surface, as well as substrate roughness and wettability. We associate film degradation phenomenon from lighting with various mechanisms of ion mass transfer. In various sources there are references to the degradation of bulk perovskite when illuminated in a humid atmosphere and an atmosphere enriched with oxygen [11, 12].

4. Conclusion
We have modified a method for NP CsPbBr$_3$ and CsPbI$_3$ synthesis. The luminescent properties, NP shapes and sizes depend on the conditions of the synthesis, which is confirmed by the literature data. NPs films were formed on different substrates. Perovskite NP films also exhibit bright luminescence; however, the emission band shifts to the short-wavelength region, which can be explained by particle agglomeration on the surface. The film degradation was studied under the illumination influence by a simulator of sunlight and UV light. It was shown that NP films are not stable under the irradiation influence and their degradation depends on the substrate types. We associate film degradation phenomenon from lighting with various mechanisms of ion mass transfer.

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