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Enhancing the stability of perovskite nanocrystals in polyacrylate composites

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In this research, were investigated the incorporation of perovskite nanocrystals into polymers to enhance the optical properties and stability of the nanocrystals for further practical applications (e.g., energy harvesting, luminescent and scintillation detectors, and imaging instruments). These results demonstrate different options for improving the stability and photoluminescence of perovskite nanocrystals of various compositions by incorporating them into polymer systems to prevent their degradation and reduce the impact of different ambient conditions.

Keywords: perovskite, nanocrystals, polymer, composites, stability, photoluminescence.

Підвищення стабільності нанокристалів перовськітів в поліакрилатних композиційних матеріалах. *Т. Скрипник, І. Беспалова, Л. Бозель, О. Сорокін*

Роботу присвячено методу введення нанокристалів перовськітів в поліакрилат за для покращення оптичних властивостей і структурної стабільності нанокристалів, що важливо для практичного застосування (наприклад, у пристроях збору енергії, люмінесцентні та сцинтиляційні детектори, прилади візуалізації, тощо). Отримані результати демонструють покращення стабільності структури та збереження інтенсивності фотолюмінесценції нанокристалів перовськітів у складі поліакриланих композиційних матеріалів, які запобігають їх деградації та значно зменшують вплив навколишнього середовища.

1. Introduction

An all-inorganic metal halide perovskite nanocrystals ((PeNCs)) with a general formula ABX_3, where A is a monovalent cation, B is a divalent metal cation, and X is a halide, could be used in a wide area of research due to the variety of their applications in photovoltaics, optoelectronics, and scintillation physics. Perovskite nanocrystals are novel representatives of semiconductor nanocrystals, whose optical properties originated from an excitonic nature. Hence, their luminescence depends on different factors, like the electronic structure and hybridization of orbitals, defect levels, electron transportation and trapping, energy transfer at high concentrations, size effects, and so on [1-4]

Great attention is paid to lead halide with general formula PeNCs, which are also known as quantum dots due to their high photoluminescence quantum yield and strong tolerance to the surfaces and defects of materials [5]. These materials can be obtained in both colloidal solution and powder forms and possess features such as the quantum confinement effect. This effect means that by varying the proportions between precursors, it is possible to tune the band gap, resulting in coverage of the entire visible spectral range. [1]. The shape and size of PeNCs can be controlled by adding ligands and varying their proportions [3]. However, a disadvantage of PeNCs is their chemical instability, which limits practical applications. These materials are sensitive to external conditions such as moisture, temperature, and light. [2]. To overcome this issue encapsulation of these materials can be used [3], for example, the PeNCs can be combined with different classes of polymers, silica [4, 6]. To improve the stability of NCs were incorporated them into polymer cross-linked systems such as polydimethylsiloxane (PDMS), polyurethane (PU), polymethyl methacrylate (PMMA) [1-3, 8 - 14]. PMMA, PDMS, and PU are employed in numerous composites, but their polymers require long curing times at elevated temperature, which is a reason for the degradation of NCs. In this research, polyacrylate was employed due to its better chemical stability and the possibility of processing the composites through different routes. Furthermore, UV irradiation is used for curing polyacrylate. While UV irradiation can be harmful to NCs, it provides a short curing time, allowing perovskites to be quickly covered with the polymer material. Once fixed in a polymer network, NCs are protected from ambient conditions such as heat, cold, light, and moisture, which can lead to degradation. This protection is expected to maintain a constant photoluminescence intensity, which is important for further applications [8 - 13].

In this research study, composites of PeNCs $CsPbX_3$ (X = Br, Cl) were incorporated into polyacrylate to improve the optical properties and stability of PeNCs for further practical applications (e.g., energy harvesting, scintillation detection, and imaging instruments). Our results demonstrate various options for enhancing the stability of PeNCs-polyacrylate composites under different external conditions.

2. Experimental

Materials. For the synthesis of $CsPbX_3$ (X = Br, Cl) the following materials were used: lead bromide (II) ($PbBr_2$, 99.99%); cesium bromide (CsBr, 99.999%); lead chloride (II) ($PbCl_2$, 99.99%); cesium chloride (CsCl, 99.999%); oleic acid (90%); n-octylamine (99%) from “Sigma-Aldrich” (Germany); toluene (anhydrous, 99.8%) from “CARLOERBA Reagents” (Germany), and dimethylformamide (DMF) from “Macrochem” (Ukraine); acrylic Norland Optical Adhesive (NOA 83H) from “Norland Products” (USA). The chemicals were all analytical reagents and used as received.

Table 1 Ratio of the quantity of initial components and concentration PeNCs in resulting compositer

acrylic NOA 83H (g)	colloid of PeNCs (μL)	concertation of PeNCs in composite, (w/v %)
0.5	5	0.005
0.5	10	0.01
0.5	20	0.02
0.5	30	0.03

Synthesis of $CsPbX_3$ *(X = Br, Cl).* were made using the ligand-assisted re-precipitation (LARP) technique [8, 9], which can be performed under ambient conditions at room temperature. By employing the LARP technique, it is possible to synthesize highly luminescent PeNCs with fascinating optical properties. These properties can be achieved by varying the ratio of initial precursors and the starting parameters of the synthesis procedure. This approach involves using precursors that are soluble or decomposable in solvents at low temperatures, producing monodisperse nanocrystals in “free” colloidal states, which is important for the development of high photoluminescence composites.

At first stage, solutions of the initial precursors of the following compositions were prepared: 0.1 mmol of CsBr and 0.2 mmol of $PbBr_2$ for $CsPbBr_3$; 0.1 mmol of CsCl and 0.2 mmol of $PbBr_2$ for $CsPbBr_2Cl$; 0.1 mmol of CsBr and 0.2 mmol of $PbCl_2$ for $CsPbBrCl_2$; 0.1 mmol of CsCl and 0.2 mmol of $PbCl_2$ for $CsPbCl_3$ were dissolved in 5 mL of DMF using ultrasonic treatment. Then, 20 μl of n-octylamine and 0.5 mL of oleic acid were added to the mixture to obtain a transparent and colorless mixture of precursors. After that, 100 μL of the mixture of precursors was added to 10 mL of toluene with intensive stirring at room temperature (20-25°C). As a result, a toluene colloidal solution of $CsPbBr_3$ PeNCs, $CsPbBr_2Cl$ PeNCs, $CsPbBrCl_2$ PeNCs, $CsPbCl_3$ PeNCs of a bright yellow-green color, blue-green color, blue-violet color and light violet (under UV lamp) were obtained, respectively.

Synthesis of PeNCs-polyacrylate composite. The method of obtaining samples of composite was implemented as follows: the initial toluene colloidal solution of PeNCs (100 μL of the mixture of precursors in 10 mL of toluene) was added to the acrylic NOA 83H (the corresponding quantity are given in Table 1) and intensively

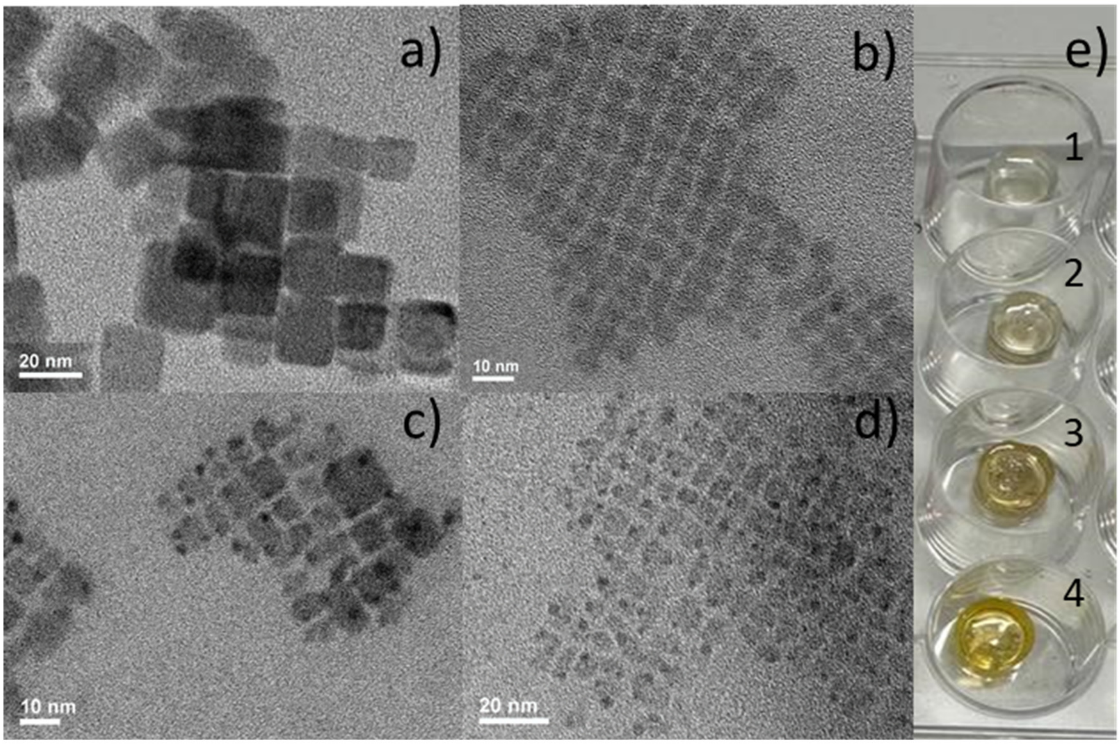

Fig 1. TEM images of PeNCs: a) $CsPbBr_3$, b) $CsPbBr_2Cl$, c) $CsPbBrCl_2$, d) $CsPbCl_3$. e) Picture of the $CsPbBr_3$-polyacrylate composite: 1 - 0.005 w/v %, 2 - 0.01 w/v %, 3 - 0.02 w/v %, 4 - 0.03 w/v %.

mixed, after which it was poured into a mold and polymerized under the ultraviolet lamp for 3 min. As a result, transparent composites were obtained. The mass fractions of PeNCs in synthesized PeNCs-polyacrylate composite were in region 0.005-0.03 w/v % (where w is the mass of PeNCs in g; v is the volume of polymer in ml) (Table 1). The concentrations of the PeNCs in formed composites were controlled by the gravimetric method.

Characterization and optical measurements. Transmission electron microscope (TEM) images of the PeNCs were obtained using TEM JEM 2200fs (JEOL, Japan). Photoluminescence spectra were registered using a spectrophotometer FluoroMax Plus (HORIBA, Japan), excitation wavelengths λ_{ex} = 300 – 380 nm were used for all the sample. Ultraviolet lamp UVASPOT-400/T (Dr. Hönle AG, Germany) was used for polymerization of PeNCs-polyacrylate composite.

3. Results and discussion

The TEM images of obtained PeNCs and pictures of the prepared PeNCs-polyacrylate composites (as an illustration, for PeNCs $CsPbBr_3$) are shown in Fig. 1. The LARP technique was producing monodisperse PeNCs composition of $CsPbBr_3$, $CsPbBr_2Cl$, $CsPbBrCl_2$, $CsPbCl_3$ mainly in the form of cubes with an edge length of 10-25 nm (depending on composition of NCs). This shape is consistent with the fact that PeNCs crystallize in the cubic phase. Also, no hexagonal-shaped NCs were observed in the TEM images, which could correspond to another phase.

A high photoluminescence response was obtained from all PeNCs colloidal solutions with luminescence maxima ranging from 409 nm to 521 nm (Fig. 2). A blue shift in the photoluminescence maximum appeared for all composite materials. This is a result of preventing NCs' agglomeration due to their incorporation into the polymer, which separates the small NCs and allows the quantum-confinement effect to be observed.

The photoluminescence maxima near 450 nm and wide photoluminescence spectra of composites can be explained with the luminescence of polyacrylate with an excitation wavelength λ_{ex} = 300 – 380 nm (Fig.2).

The important point before stability studies is to investigate an optimal concentration of luminescent NCs in polymer, after which a self-quenching takes place. For this purpose, samples of PeNCs-polyacrylate composite with different concentrations of PeNCs in polymer

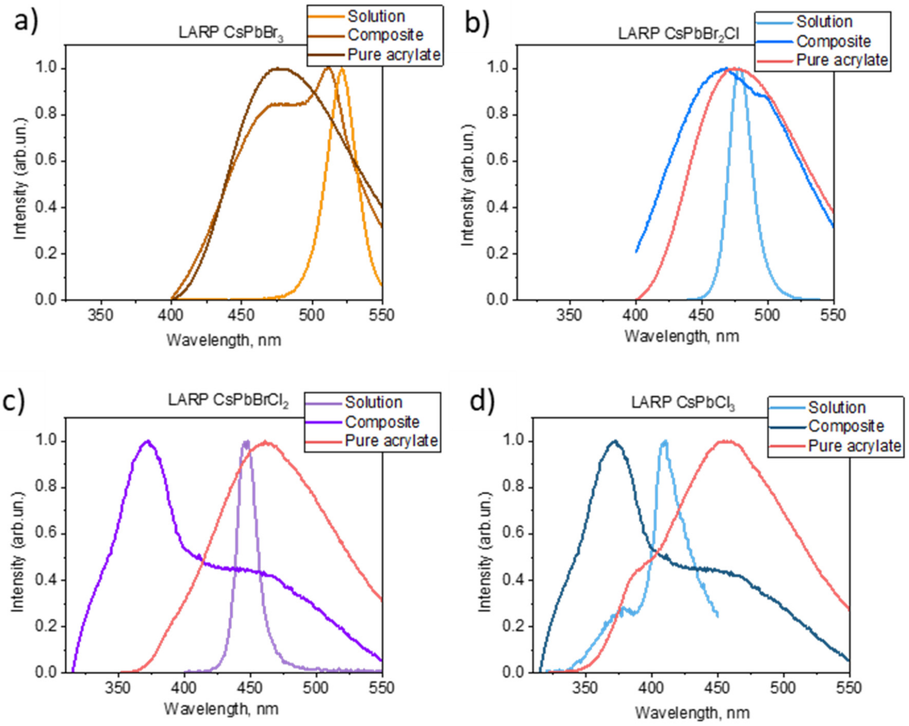

Fig. 2. Photoluminescence spectra of PeNCs colloidal solutions (Solution), PeNCs-polyacrylate composite (Composite): a) $CsPbBr_3$, b) $CsPbBr_2Cl$, c) $CsPbBrCl_2$, d) $CsPbCl_3$, and pure polyacrylate (Pure acrylate) .

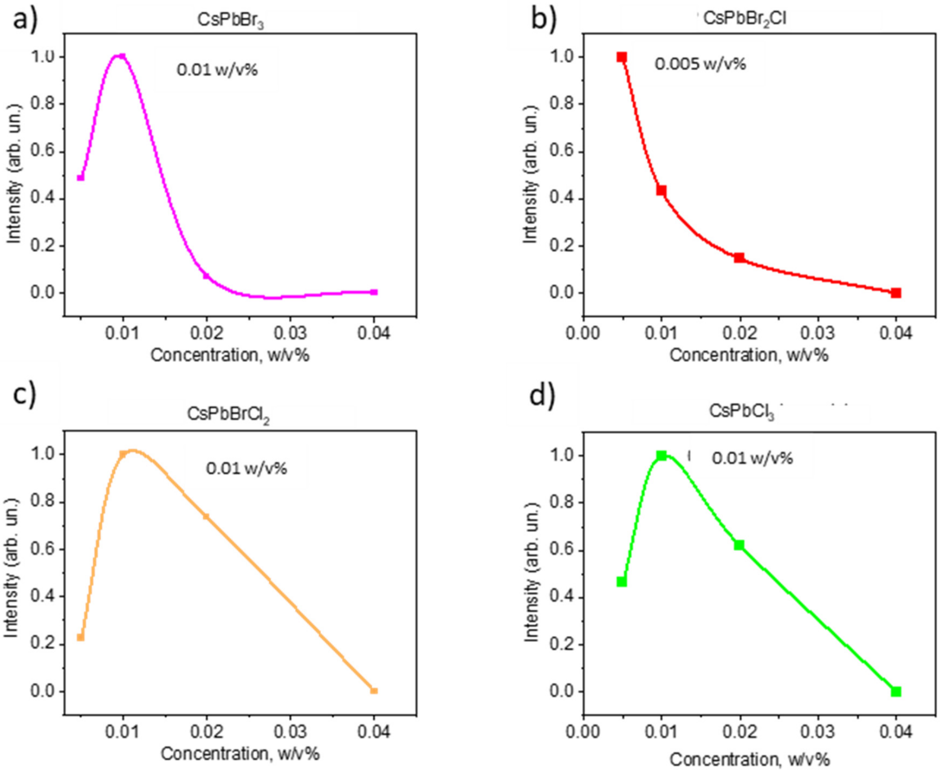

Fig. 3. Dependence of photoluminescence intensity on PeNCs concentration in samples of PeNCs-polyacrylate composite: a) $CsPbBr_3$, b) $CsPbBr_2Cl$, c) $CsPbBrCl_2$, d) $CsPbCl_3$.

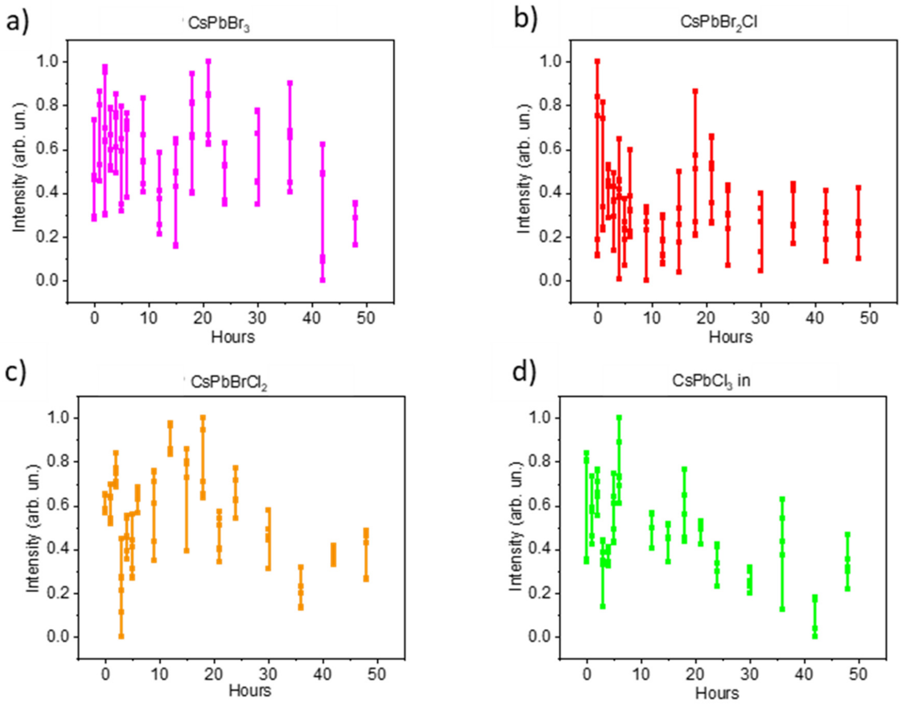

Fig 4. Dependence of photoluminescence intensity on storage time at a temperature +60°C of PeNCs-polyacrylate composite: a) $CsPbBr_3$, b) $CsPbBr_2Cl$, c) $CsPbBrCl_2$, d) $CsPbCl_3$.

ranging from 0.005 w/v% to 0.03 w/v% were made and photoluminescence spectra were measured (Fig. 3).

The optimal concentration of PeNCs in a composite depends on the type of polymer they are incorporated into and the composition of the PeNCs, as is commonly known. Fig. 3 is shown, that with the increase of a concentration of PeNCs in the polymer matrix, the photoluminescence intensity decreases after some point. One can conclude that the optimal concentrations of PeNCs in an investigation polymer these values are 0.01 w/v% for $CsPbBr_3$, $CsPbBrCl_2$, $CsPbCl_3$ and 0.005 w/v% for $CsPbBr_2Cl$, after which self-quenching occurs for PeNCs in polyacrylate composite.

For estimating the stability of PeNCs-polyacrylate composites were compared the photoluminescence intensity after keeping composites with NCs concentration of 0.01 w/v% under different external conditions. Different ambient conditions such as heating to +60°C (Fig.4), cooling to -20°C (Fig.5), storage at room temperature in darkness to reduce the effect of sunlight (Fig.6), and keeping in the open air (Fig.7), where the light and moisture can affect the materials. Each sample of the composite was measured five times due to the potential heterogeneous distribution of PeNCs in the polymer. This can be explained by the migration of the NCs within the polymer volume (initially liquid) while it is not fully polymerized, causing variations in photoluminescence intensity in different parts of the PeNCs-polyacrylate composite. A decrease in photoluminescence intensity of the polyacrylate composite indicates the degradation of PeNCs, whereas its permanence signifies the stability of their optical properties within the composite.

For PeNCs-polyacrylate composite photoluminescence intensity can be kept stable up to 40 h of exposure to heat up to +60° (see Fig. 4). However, there is a decrease in photoluminescence intensity for $CsPbCl_3$-polyacrylate composite and $CsPbBrCl_2$-polyacrylate composite comparable to $CsPbBr_3$-polyacrylate composite and $CsPbBr_2Cl$-polyacrylate composite, where intensity is more stable even after 40h.

Cooling till –20°C is all type PeNCs-polyacrylate composite does not lead to destruction of the PeNCs, as shown in Fig. 5. Under these conditions for $CsPbCl_3$-polyacrylate composite and $CsPbBrCl_2$-polyacrylate composite this time is 30h, for $CsPbBr_3$-polyacrylate composite and $CsPbBr_2Cl$-polyacrylate composite – up to 50h. Fig. 4 and Fig.5 show, that polyacrylate matrix improves stability of PeNCs of all compositions. However, changing from Br- to Cl- in the structure of these PeNCs makes them less

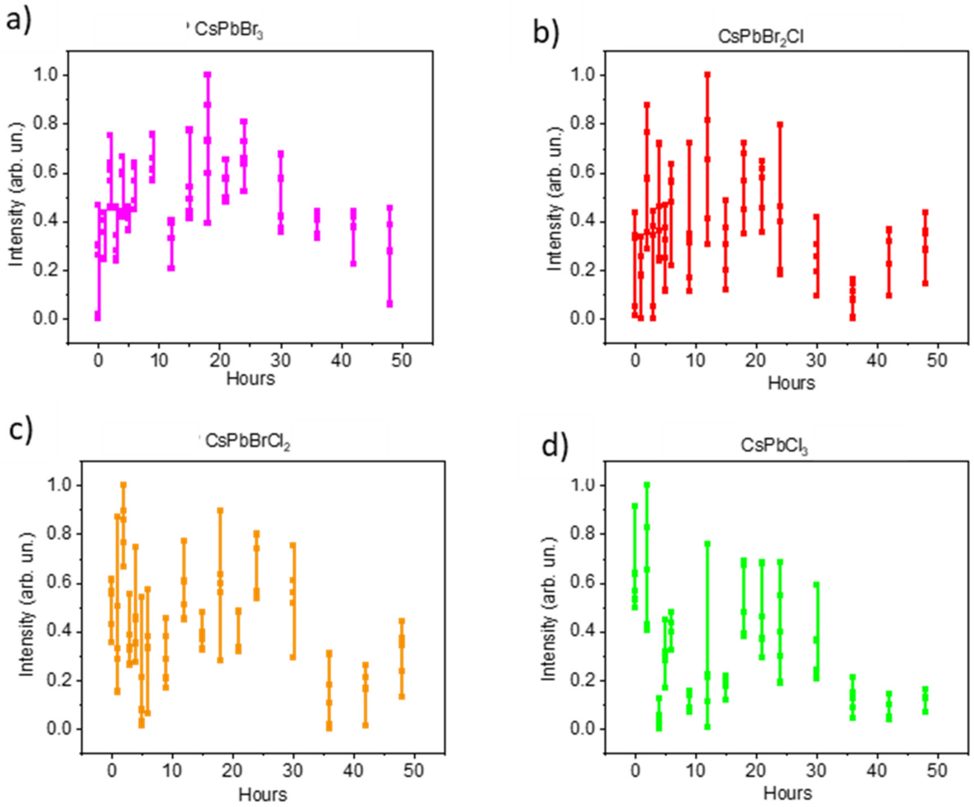

Fig 5. Dependence of photoluminescence intensity on storage time at a temperature -20°C of PeNCs-polyacrylate composite: a) $CsPbBr_3$, b) $CsPbBr_2Cl$, c) $CsPbBrCl_2$, d) $CsPbCl_3$.

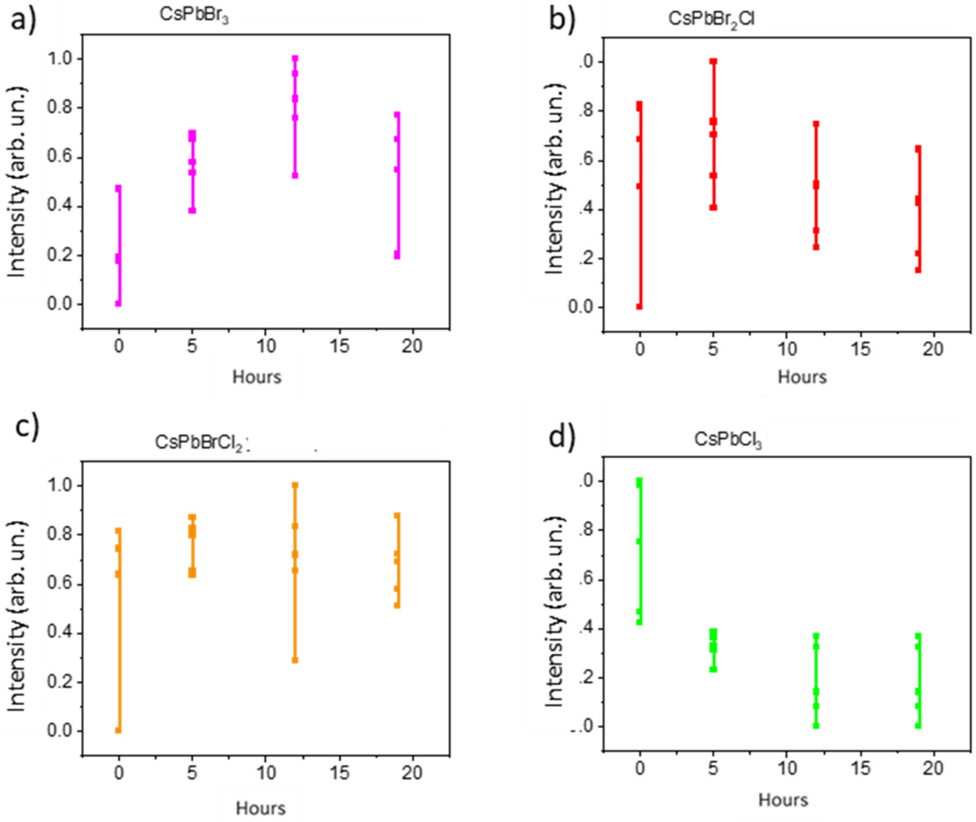

Fig. 6. Dependence of photoluminescence intensity on storage time in darkness of PeNCs-polyacrylate composite: a) $CsPbBr_3$, b) $CsPbBr_2Cl$, c) $CsPbBrCl_2$, d) $CsPbCl_3$.

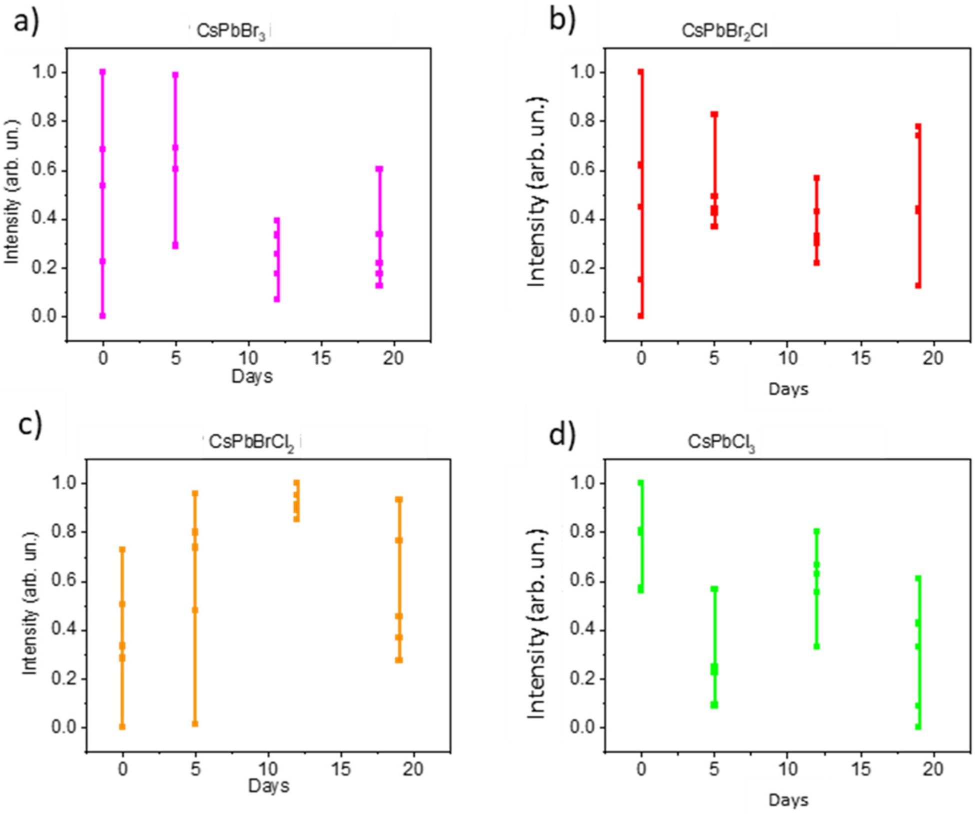

Fig. 7. Dependence of photoluminescence intensity on storage time on the open air of PeNCs-polyacrylate composite: a) $CsPbBr_3$, b) $CsPbBr_2Cl$, c) $CsPbBrCl_2$, d) $CsPbCl_3$.

stable to heating and cooling, even after incorporation into a polymer.

After keeping of PeNCs-polyacrylate composites in a dark place during for 26 days, a decrease in photoluminescence intensity is observed for $CsPbCl_3$-polyacrylate composite (Fig. 6) and other polyacrylate composites are showing improved stability of photoluminescence intensity.

For PeNCs-polyacrylate composites, that were exposed to the open air show constant photoluminescence intensity more than 20 days, which means an improvement of PeNCs stability in polymer (see Fig. 7).

There is no big difference between the graphs in Fig. 6 and Fig.7 for all PeNCs-polyacrylate composites. This means, that inside composite material, PeNCs are not affected by sunlight. Only NCs of $CsPbCl_3$ show a slight decrease in photoluminescence intensity, comparable to that, which were kept in sunlight, which depends on the composition of PeNCs.

So, the proposed approach of using UV irradiation for curing polyacrylate, while potentially harmful to PeNCs, offers the advantage of a shorter curing time and rapid coverage of PeNCs with a polymer material. Once fixed in a polymer matrix, PeNCs are protected from ambient conditions such as heat, cold, light, and moisture, which can lead to degradation. This protection is expected to maintain a constant photoluminescence intensity, crucial for further applications in optical systems for various purposes.

4. Conclusions

In this work, were investigated a set of PeNCs-polyacrylate composites, where the PeNCs are NCs of common formula $CsPbX_3$ (X = Br, Cl) with the form of cubes size of 10-25 nm and a bright emission range from 409 nm to 521 nm (depending on the composition of NCs). Concentrations of self-quenching of PeNCs were investigated and determined that the optimal concentrations of PeNCs in the polymer are 0.01 w/v%, after which self-quenching occurs for PeNCs in polyacrylate composite. It was shown that polymer material has an impact on the optical properties of PeNCs - with varying compositions of the polymer and its' curing time it became possible to change the photoluminescence maxima of PeNCs, control their size, and improve their stability.

These studies show that daily light does not have an effect on PeNCs in the polyacrylate composites. There is no significant difference between the photoluminescence intensity of PeNCs of one composition, which were kept in darkness and on the daylight, which means that inside polymer materials PeNCs have the same stability for both ambient conditions. So, created PeNCs-polyacrylate composite appear to be very promising in a wide range of technological applications including light-emitting diodes, lasers, photovoltaics, photosensors, photocatalysts, luminescence and scintillation detectors.

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