

## OPTICAL PROPERTIES STABILITY OF CsPbX<sub>3</sub> NANOCRYSTALS EMBEDDED IN POROUS GLASS MATRIX

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### Abstract

All-inorganic perovskite nanocrystals with chemical formula CsPbX<sub>3</sub> (X = Cl, Br, and I) attract much scientific attention since they possess unique optical properties, such as high extinction coefficients and values of emission quantum yield, together with ease of their synthesis and tunability in the chemical composition. However, these nanomaterials are still far from their large-scale applications since they lack stability. Here, it was shown that the use of a nanoporous glass matrix allowed obtaining the samples with blue, green, and red perovskite nanocrystals possessing reproducible optical characteristics which are almost similar to that of their colloidal solution. Such a matrix also prevented the fast degradation of nanocrystals both at the storage in ambient and under UV-light exposure and/or in the conditions of increased humidity.

**Keywords:** Perovskite, nanocrystals, porous matrix, emission, stability, moisture

### 1. INTRODUCTION

The development of chemical routes for the synthesis of nanocrystals with crystal lattice of perovskite-type (PNCs) with chemical formula CsPbX<sub>3</sub> (X = Cl, Br, and I) [1] resulted in the burst of scientific attention since the PNCs possess unique optical and electronic properties: high extinction coefficients, high photoluminescence (PL) quantum yields reaching 1, and high charge carrier mobility [2,3]. Another advantage of these nanomaterials is the tunability of chemical composition together with the ease of fabrication [2] which is important for PNCs future utilization in different areas of photovoltaics and optoelectronics.

However, these materials are unstable and can be easily decomposed under ultra-violet (UV) light exposure and while storing in increased humidity [4,5]. At the moment there several ways to tackle this problem: (i) direct synthesis in polar solvents [6], (ii) passivation of PNC surface via chemical treatment including the ligand engineering [7,8], and (iii) embedding the PNCs into different inert matrices, such as polymers or solid porous matrices [9-11]. In the latter approach, the matrix can be chosen from a wide variety of materials either soft/flexible or hard/solid which can be related to their further application.

Here, we investigate the stability of optical responses of all-inorganic PNCs embedded in nanoporous silicate matrix (NSM) under the UV exposure and increased humidity. The developed idea on PNC protection is of wide interest for their further implementation as active media in solar cells, photodetectors, and light-emitting diodes.

## 2. EXPERIMENTAL

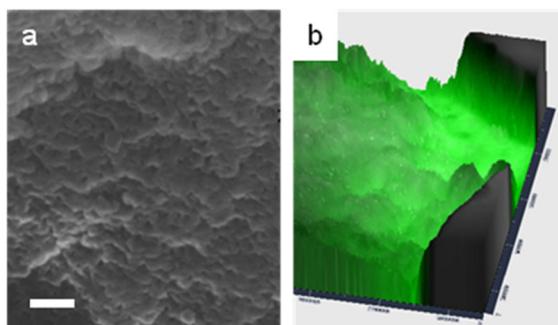
Steady-state spectral measurements of samples were carried out using a UV-3600 spectrophotometer (Shimadzu), a FP-1800 spectrofluorometer (Jasco), and a confocal lasing scanning microscope LSM-710 (Zeiss) equipped with 20× (NA=0.4) objective and a 405 nm laser. For transient photoluminescence measurements a confocal microscope MicroTime 100 (PicoQuant) equipped with 100× (NA=0.95) objective and 405 nm pulsed diode laser implementing time-correlated single photon counting. To estimate the value deviations of each optical parameter the signal from the sample was collected at least in 3 different points.

Cesium carbonate ( $\text{Cs}_2\text{CO}_3$ , 99.9%), lead bromide ( $\text{PbBr}_2$ , 98%), lead chloride ( $\text{PbCl}_2$ , 99.999%), lead iodide ( $\text{PbI}_2$ , 99.999%), octadecene (ODE, 90%), and oleylamine (OIAM, 70%) were purchased from Merck & Co., oleic acid (OA, 85%-92%) was purchased from Fisher. The chemicals were used without any purification. PNCs were synthesized according to the previously reported route [1]. As a result of the synthesis, three colloidal solutions of  $\text{CsPb}(\text{Cl}/\text{Br})_3$ ,  $\text{CsPbBr}_3$ , and  $\text{CsPbI}_3$  with blue, green, and red emission, respectively, were obtained and designated hereafter as b-PNCs, g-PNCs, and r-PNCs. The mean size of PNCs was  $8 \pm 1$ ,  $10 \pm 4$  and  $13 \pm 5$  nm for b-PNCs, g-PNCs, and r-PNCs, respectively.

NSMs were fabricated by the procedure reported in [12]. Before the use, the obtained NSMs were annealed at 100 °C during 1h in a vacuum oven to get rid of moisture and oxygen presented inside the pores.

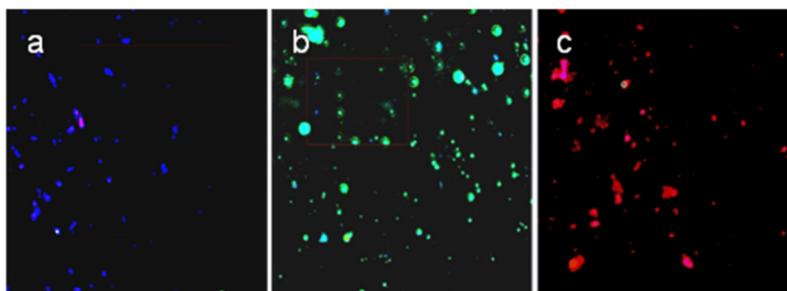
## 3. RESULTS AND DISCUSSION

From SEM image of NSM shown in **Figure 1a** it is seen that the pores are of nanometer-size and homogeneously distributed within NSM' volume. The 3D PL image reconstruction of chopped NSM with g-PNCs shown in **Figure 1b** confirmed the PNCs penetration into NSM pores.



**Figure 1** (a) SEM image of NSM. Scale bar is of 100 nm. (b) 3D PL image of g-PNCs in NSM

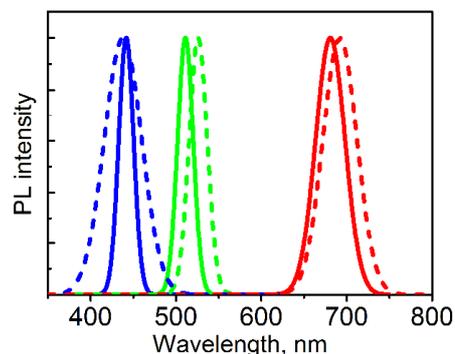
The confocal PL images of samples showed that the PNCs formed agglomerates on the NSM surface which were most probably located at the pore entry. This can be seen as bright spots in the PL images (**Figure 2**).



**Figure 2** PL image of b-PNCs (a), G-PNCs (b), and r-PNCs (c) in NSM. The image size is of 100 × 100 μm

Although the formation of agglomerates on NSM surface is an undesirable process that may affect optical properties of PNCs, however, this helped to close as many pores on the surface as possible which, in turn, resulted in the increased protection from the moisture and oxygen penetration within the porous matrix.

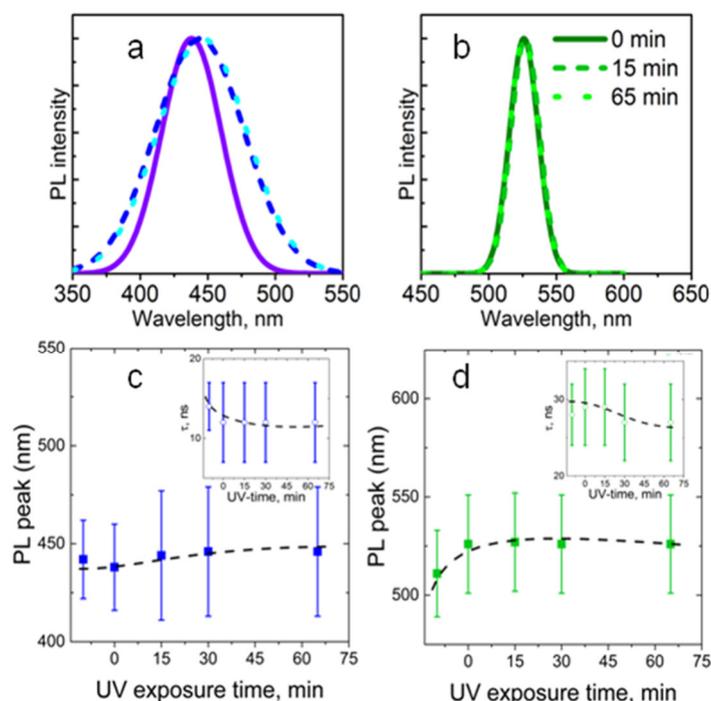
The absorption spectra showed increased optical density in the 400-650 nm spectral region which can be attributed to the presence of the PNCs in the NSM volume. The PL spectra shown in **Figure 3** of PNCs in NSM showed almost unchanged peak positions with the increased full width at half maximum (FWHM). It is worth to mention that the average PL lifetime is almost preserved after the PNCs embedding into the NSMs. This observation suggested that the embedding of PNCs into the NSMs didn't result in the appearance of additional nonradiative channels of charge carriers' recombination. PL parameters of investigated samples are summarized in **Table 1**.



**Figure 3** PL spectra of b-PNCs (blue), g-PNCs (green), and r-PNCs (red) in colloidal solution (solid lines) and in NSM (dashed lines)

**Table 1** Optical parameters of PNCs in colloidal solution and in NSM

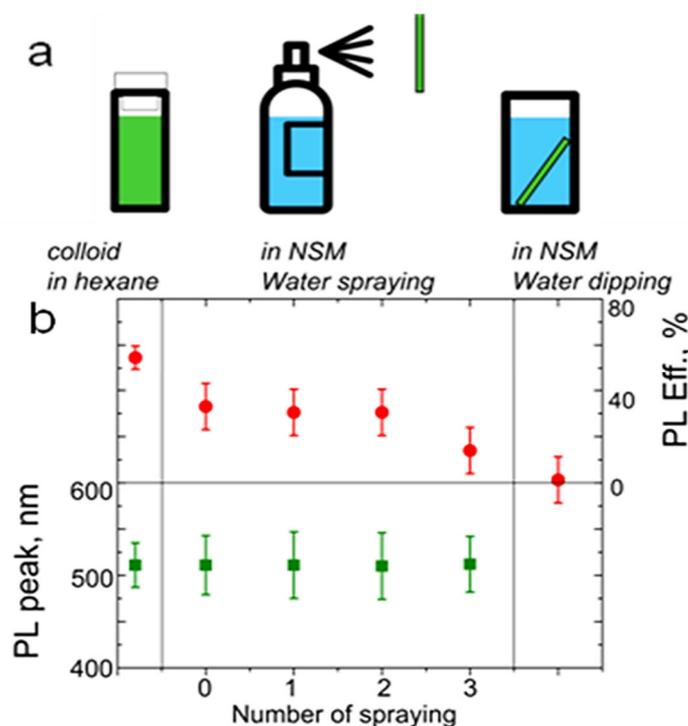
P-NCs	Blue		Green		Red	
	PL peak/ FWHM, nm	PL lifetime, ns	PL peak/ FWHM, nm	PL lifetime, ns	PL peak/ FWHM, nm	PL lifetime, ns
Solution	442/20	14±3	510/20	28±4	680/40	110±6
NSM	438/50	12±1	525/25	24±5	690/50	80±5



**Figure 4** Optical properties of b-PNCs (a and c) and g-PNC (b and d) in NSM: PL spectra (a and b) under UV exposure, time of exposure is listed in b legend; PL peak position (c and d), Insets in c and d show the change in PL lifetime with UV exposure time

First, the samples were examined on the stability of the optical parameters under UV exposure. For that, the NSM samples with PNCs were constantly irradiated by a 405 nm laser. The PL spectra for b-PNCs and g-PNCs in NSM together with the average PL lifetimes are shown in **Figure 4**. For b-PNCs embedded into NSM a broadening of the PL band was observed with almost the same PL peak position. The average PL lifetime decreased slightly during the UV-exposure. For g-PNCs in NSM PL band didn't undergo any significant changes. As it was observed for b-PNCs average PL lifetime also decreased slightly with increased exposure time.

Second, the stability of the optical properties of g-PNC embedded into the NSM was probed under the increased humidity conditions. For that, the distilled water was dispersed at the 20 cm distance from the sample. After the water dispersing, the PL spectrum was measured, and this procedure was repeated 3 times. The changes in emission relative efficiency and PL position with increased humidity are shown in **Figure 5**.



**Figure 5** (a) Sketch of PNCs samples. (b) PL efficiency (red circles) and peak (green squares) change with increased humidity

As it can be seen from **Figure 5** the NSM as a host matrix for PNCs preserved the optical properties of g-PNCs during the increased humidity. However, there was a critical value of humidity reaching which the PL efficiency decreased almost twice. Next, we examined the optical properties of g-PNCs in NSM after dipping the sample into the distilled water. The PL signal disappeared after such a treatment.

#### 4. CONCLUSION

The use of a nanoporous glass matrix allowed obtaining the samples with blue, green, and red perovskite NCs possessing reproducible optical characteristics that are almost similar to that of colloidal solution. Such a matrix also may prevent the fast degradation of nanocrystals both at the storage in ambient and under UV-light exposure and/or increased humidity. Thus, the nanoporous inert solid matrix is a perspective candidate for its implementation as a host matrix for perovskite nanocrystals for photovoltaic and optoelectronic devices with improved performance.

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## REFERENCES

- [1] PROTESESCU, Loredana, YAKUNIN, Sergii, BODNARCHUK, Maryna I., KRIEG, Franziska, CAPUTO, Riccarda, HENDON, Christopher H., YANG, Ruo X., WALSH, Aron and KOVALENKO Maksym V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX<sub>3</sub>, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Letters*. 2015. vol. 15. pp. 3692-3696.
- [2] SHAMSI, Javad, URBAN, Alexander S., IMRAN, Muhammad, DE TRIZIO, Luca and MANNA, Liberato. Metal halide perovskite nanocrystals: synthesis, post-synthesis modifications, and their optical properties. *Chemical reviews*. 2019. vol. 119. pp. 3296-3348.
- [3] JENA, Ajay K., KULKARNI, Ashish and MIYASAKA, Tsutomu. Halide perovskite photovoltaics: background, status, and future prospects. *Chemical reviews*. 2019. vol. 119. pp. 3036-3103.
- [4] ZHOU, Yuanyuan and ZHAO, Yixin. Chemical stability and instability of inorganic halide perovskites. *Energy & Environmental Science*. 2019. vol. 12. pp. 1495-1511.
- [5] OUYANG, Yixin, LI, Yajuan, ZHU, Pengchen, LI, Qiang, GAO, Yuan, TONG, Jianyu, LI, Shi, ZHOU, Qionghua, LING, Chongyi, CHEN, Qian, DENG, Zhengtao, TAN, Hairen, DENG, Weiqiao and WANG, Jinlan. Photo-oxidative degradation of methylammonium lead iodide perovskite: mechanism and protection. *Journal of Materials Chemistry A*. 2019. vol. 7. pp. 2275-2282.
- [6] GENG, Chong, XU, Shu, ZHONG, Haizheng, ROGACH, Andrey L. and BI, Wengang. Aqueous synthesis of methylammonium lead halide perovskite nanocrystals. *Angewandte Chemie International Edition*. 2018. vol. 57. pp. 9650-9654.
- [7] TAN, Yeshu., ZOU, Yatao, WU, Linzhong, HUANG, Qi, YANG, Di, CHEN, Min, BAN, Muyang, WU, Chen, WU, Tian, BAI, Sai, SONG, Tao, ZHANG, Qiao and SUN, Baoquan. Highly luminescent and stable perovskite nanocrystals with octylphosphonic acid as a ligand for efficient light-emitting diodes. *ACS Applied Materials & Interfaces*. 2018. vol. 10. pp. 3784-3792.
- [8] KRIEG, Franziska, OCHSENBEIN, Stefan T., YAKUNIN, Sergii, TEN BRINCK, Stephanie, AELLEN, Philipp, SÜESS, Adrian, CLERC, Baptiste, GUGGISBERG, Dominic, NAZARENKO, Olga, SHYNKARENKO, Yevhen, KUMAR, Sudhir, SHIH, Chih-Jen, INFANTE, Ivan and KOVALENKO, Maksym V. Colloidal CsPbX<sub>3</sub> (X= Cl, Br, I) nanocrystals 2.0: Zwitterionic capping ligands for improved durability and stability. *ACS energy letters*. 2018. vol. 3. pp. 641-646.
- [9] LIANG, Panting, ZHANG, Pan, PAN, Aizhao, YAN, Ke, ZHU, Yongsheng, YANG, Minyan and HE, Ling. Unusual stability and temperature-dependent properties of highly emissive CsPbBr<sub>3</sub> perovskite nanocrystals obtained from in-situ crystallization in PVDF. *ACS Applied Materials & Interfaces*. 2019. vol. 11. pp. 22786-22793.
- [10] MALGRAS, Victor, HENZIE, Joel, TAKEI, Toshiaki and YAMAUCHI, Yusuke. Stable blue luminescent CsPbBr<sub>3</sub> perovskite nanocrystals confined in mesoporous thin films. *Angewandte Chemie International Edition*. 2018. vol. 57. pp. 8881-8885.
- [11] USHAKOVA, Elena V., MATUHINA, Anastasia I., SOKOLOVA, Anastasiia V., CHEREVKOV, Sergei A., DUBAVIK, Aliaksei, MEDVEDEV, Oleg S., LITVIN, Aleksandr P., KURDYUKOV, Dmitry A., GOLUBEV, Valery G. and BARANOV, Alexander V. Enhanced stability of the optical responses from all-inorganic perovskite nanocrystals embedded in a synthetic opal matrix. *Nanotechnology*. 2019. vol. 30. pp. 405206.
- [12] BAGNICH, Sergey A., BOGOMOLOV, V. N., KURDYUKOV, Dmitry A. and PERSHUKOVICH, P. P. Phosphorescence of aromatic compounds in a porous matrix of sodium borosilicate glass and their interaction with the pore walls. *Physics of the Solid State*. 1995. vol. 37. pp. 1642-1645.