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Water-stable halide perovskite nanocrystals in biological environment

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Abstract. Tetramethyl orthosilicate and triethoxyphenylsilane, which contains hydrophobic phenyl groups, were used as a silica (SiO₂) source in a modified ligand-assisted reprecipitation synthesis approach for the fabrication of water-stable perovskite nanocrystals. Hydrolysis-condensation reaction of tetramethyl orthosilicate and triethoxyphenylsilane results in a formation of 3D siloxane network. Employing triethoxyphenylsilane in the synthesis enhances the hydrophobic properties of the SiO₂ shell, which increases the stability of perovskites in aqueous medium. The stability of the CsPbBr₃@SiO₂ nanocrystals was estimated after 24 h of water exposure by the photoluminescence measurements at different time points. The synthesized CsPbBr₃@SiO₂ nanocrystals were visualized during *in vitro* experiments with murine melanoma B16-F10 cells. Hence, the potential of CsPbBr₃@SiO₂ nanocrystals for bioimaging purposes was observed.

1. Introduction

Recently, perovskite nanostructured materials have attracted significant interest due to their excellent photophysical properties, such as narrow full width at half maximum (FWHM), high photoluminescence (PL) quantum yield (PLQY), tunable emission spectra, etc. There are a number of reports dedicated to the fabrication of optoelectronic devices based on perovskite materials, e.g., light-emitting diodes [1], scintillators [2], lasers [3], solar cells. Moreover, not only the linear optical properties of perovskite nanocrystals (NCs) are worthy of attention, but also their nonlinear optical properties, such as near-infrared-triggered photon upconversion, which can be potentially applied for *in vivo* bioimaging due to an increased penetration depth of near-infrared light [4]. Nevertheless, the instability of perovskites in aqueous medium is still a challenge, which prevents from applying them in bioimaging. This study is



aimed at obtaining lead halide perovskite (CsPbBr_3) nanocrystals coated with a silica shell exhibiting an improved stability in water.

2. Materials and methods

Synthesis of $\text{CsPbBr}_3@SiO_2$ NCs:

The perovskite nanocrystals covered with silica shells ($\text{CsPbBr}_3@SiO_2$ NCs) were synthesized using a modified ligand-assisted reprecipitation (LARP) method [5]. Briefly, lead halide perovskite NCs precursor was obtained by mixing PbBr_2 , CsBr and stabilizers (oleylamine (OAm) and oleic acid (OA)) in dimethylformamide (DMF). Subsequently, the colloidal solution was stirred at 90 °C for 2 hours to obtain a clear, slightly yellow solution. Afterwards, a small amount of ammonia was added to the precursor solution, and then the resulting mixture was injected to the excess of toluene solution that contained a tetramethyl orthosilicate (TMOS) and triethoxyphenylsilane (phTEOS) (molar ratio= 50:50) for the hydrolysis-condensation reaction under vigorous stirring at room temperature. After 10 s, the stirring speed was decreased and kept constant overnight. The obtained CsPbBr_3 NCs were washed with toluene by centrifugation (8000 rpm for 5 min).

A control experiment with non-passivated NCs was performed by Qixuan Z et al [5]. The obtained perovskite sample demonstrated poor stability, decomposing in less than 16 minutes.

Characterization of $\text{CsPbBr}_3@SiO_2$ NCs:

To check the water resistance, a fresh sample of CsPbBr_3 NCs covered with SiO_2 shell ($\text{CsPbBr}_3@SiO_2$ NCs) was sustained in water during 24 h, and then the PL analysis of $\text{CsPbBr}_3@SiO_2$ NCs was performed using CARY 60 UV-Vis spectrophotometer (excitation $\lambda = 400$ nm). The high quality of the obtained $\text{CsPbBr}_3@SiO_2$ NCs was confirmed with scanning transmission electron microscopy (STEM) on Merlin 42-37 microscope, and with high-resolution transmission microscopy (HRTEM) on Tecnai F20 X-TWIN microscope. The elemental analysis was performed using energy-dispersive X-ray (EDX) measurements.

Cell experiments with $\text{CsPbBr}_3@SiO_2$ NCs:

B16-F10 cells were cultured in AlphaMEM medium (37°C, aseptic atmosphere with 95% air and 5% CO_2). $\text{CsPbBr}_3@SiO_2$ NCs incubated with B16-F10 cells were visualized using confocal laser scanning microscopy (CLSM). The cells were seeded into cell imaging dishes. Afterwards, the cells were stained with Rhodamine 800, and the cell nuclei with propidium iodide (PI). Then, $\text{CsPbBr}_3@SiO_2$ NCs were added to the cells and incubated for 24 hours. The stained cells were excited using a HeNe laser ($\lambda = 633$ nm, emission filter: LP $\lambda = 650$ nm). Perovskite NCs were excited using an argon laser ($\lambda = 488$ nm, emission filter: BP $\lambda = 500-550$ nm).

3. Results

CsPbBr_3 NCs covered with SiO_2 shells were visualized with STEM (Fig. 1) and HRTEM (Fig.2). According to the obtained data, the core size distribution of the individually coated $\text{CsPbBr}_3@SiO_2$ NCs is in the range of 20-30 nm, and their shell thicknesses are in the range of 8-20 nm. HRTEM image analysis confirms the good quality and the high crystallinity of the synthesized CsPbBr_3 cores.

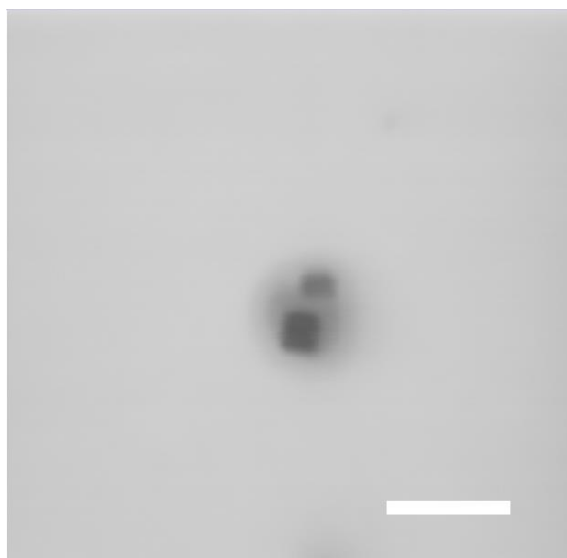


Figure 1. STEM image of a single NC. Scale bar corresponds to 100 nm

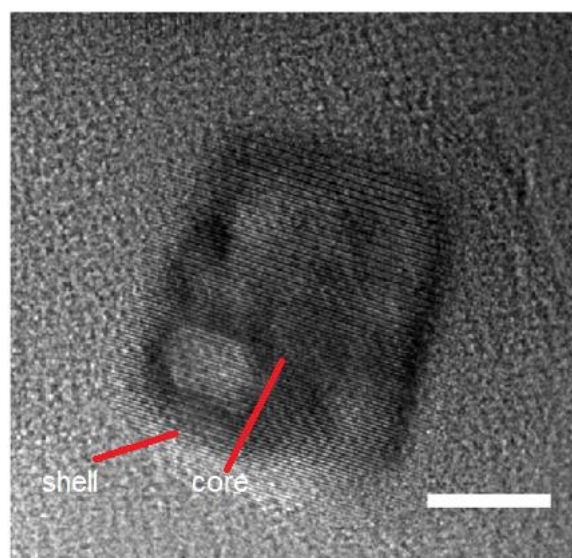


Figure 2. HRTEM image of single NC. Scale bar corresponds to 10 nm

EDX analysis was performed for a single $\text{CsPbBr}_3@SiO_2$ NC (Fig. 3). According to the EDX spectrum, it contains the peaks corresponding to Cs, Pb, Br (perovskite core) and Si (silica shell). To reveal stability of the obtained NCs in aqueous solutions, $\text{CsPbBr}_3@SiO_2$ NCs were sustained in water for 24 h, and the PL measurements were carried out at different time points (0, 1, 4, 24 h) (Fig. 4). According to the obtained PL data, the PL from the perovskite NCs decreased to 25% after 24 h of water exposure. The water resistance of the silica shell formed around CsPbBr_3 NCs can be explained as follows. To obtain a silica shell, TMOS and phTEOS were added to the reaction at 50:50 molar ratio. It should be noted that phTEOS contains phenyl groups, which provide hydrophobic properties and, thus, the improved stability in water.

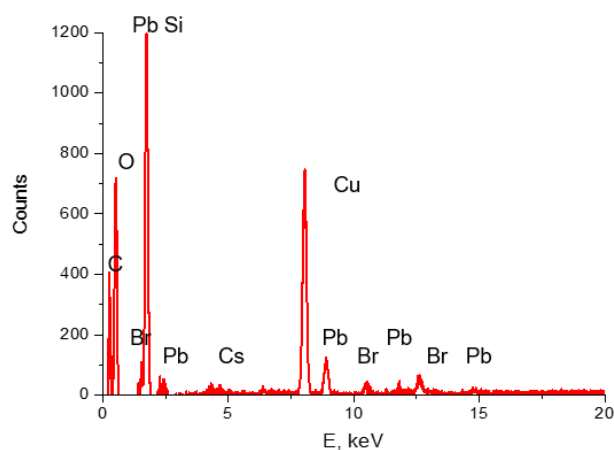


Figure 3. EDX analysis of a single NC

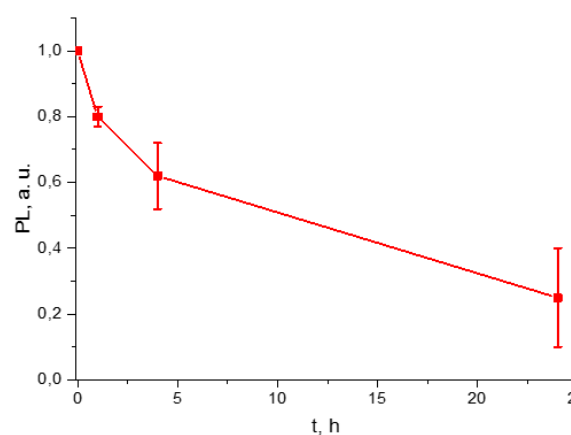


Figure 4. Relative PL intensity in water during 24 h

Further, the stability of $\text{CsPbBr}_3@SiO_2$ NCs was tested in a biological environment; apart from water, it contained organic compounds (ions, enzymes, and proteins), which can induce dissolution of nanomaterials. As a proof of concept, the synthesized $\text{CsPbBr}_3@SiO_2$ NCs were incubated with B16-

F10 cells and visualized with CLSM (Fig. 5). Bright green fluorescence from CsPbBr₃@SiO₂ associated with B16-F10 cells (stained with tetramethylrhodamine) (TRITC) confirmed the stability of perovskite nanocrystals in biological environment.

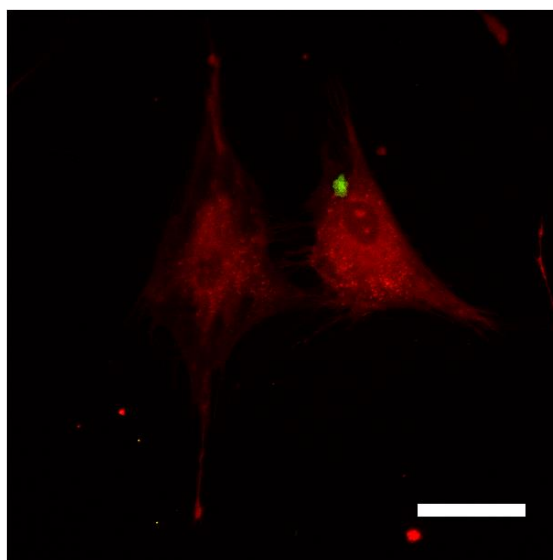


Figure 5. CLSM image of the association of CsPbBr₃@SiO₂ NC (green) with a stained B16 cell (red). Excitation $\lambda = 488$ nm. Scale bar corresponds to 20 μm .

4. Conclusions

To conclude, a synthesis approach to obtain water-stable CsPbBr₃@SiO₂ NCs was developed. For this, TMOS and phTEOS were added in molar ratio 50:50 to the reaction within LARP method. The used ratio of phTEOS and TMOS allows obtaining stable shells, which prevent water penetration to the perovskite core. The water stability of the sample was estimated with PL measurements. The crystal morphology, quality and elemental composition were verified by EDX, STEM, and HRTEM analyses. Moreover, lead halide perovskites were visualized in living cells using confocal laser scanning microscopy. The obtained results prove the good stability of CsPbBr₃@SiO₂ in water and biological environment.

5. Acknowledgments

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References

1. Veldhuis, S.A., Boix, P.P., Yantara, N., Li, M., Sum, T.C., Mathews, N. and Mhaisalkar, S.G., *Adv. Mater.*, 2016, 28: 6804–6834.
2. Chen, Q., Wu, J., Ou, X. et al., *Nature*, 2018, 561, 88–93.
3. Zhu, H., Fu, Y., Meng, F. et al. *Nature Mater*, 2015, 14, 636–642.
4. Liang, L., Chen, N., Jia, Y. et al. *Nano Res.*, 2019, 12, 1279–1292.
5. Qixuan, Z., Muhan C., Huicheng H., et al., *ACS Nano*, 2018, 12, 8, 8579–8587.