Synthesis and postsynthetic anion exchange of CsPbX$_3$ (X = Cl, Br, I) quantum dots

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Abstract. CsPbX$_3$ (X = Cl, Br, I) quantum dots were synthesized using hot-injection method at various temperatures (50–200°C), resulting in quantum dots size change and corresponding photoluminescence shift. During anion exchange, continuous formation of intermediate solid solutions was observed resulting in fine adjustment of photoluminescence peak position. Dynamics of photoluminescence spectra under continuous laser irradiation for anion exchange was studied. It is necessary for anion exchange that halide should be in ionic, not molecular, form.

1. Introduction
Nanomaterials never cease to amaze. Even when we think we have seen all the terrific properties and thought about all possible applications, there appears something spectacular. High quantum yields of up to 90%, possibility to tune photoluminescence over the entire visible spectra, the absence of the blinking effect and narrow emission spectral widths – all these interesting properties are present in novel optoelectronic materials, CsPbX$_3$ (X = Cl, Br, I) quantum dots (QDs) [1]. Fully inorganic perovskites attracted emphasis since organic/inorganic hybrid perovskites, such as CH$_3$NH$_3$PbI$_3$, showed staggering power conversion efficiencies above 20%, so it became the only one logical step to synthesize all-inorganic perovskite QDs because of a higher stability they show compared to hybrid ones [2].

Figure 1. Cubic ABX$_3$ perovskite lattice (A = Cs, B = Pb, X = Cl, Br, I).

Figure 2. Photoluminescence spectra of CsPbBr$_3$ (left group of graphs) and CsPbI$_3$ (right group of graphs) QDs synthesized at different temperatures (50–200°C).
2. Synthesis of CsPbX$_3$ QDs
All CsPbX$_3$ QDs crystallize in cubic phase of the perovskite lattice (Figure 1), which is the high-temperature state for bulk compounds. QDs were synthesized via hot injection method using Cs-oleate and PbX$_2$ as precursors and dodecane as a medium. Since the growth of QDs happens exceedingly fast (within 1–3 s), the average size of QDs is rather controlled by reaction temperature. Photoluminescence spectra of CsPbBr$_3$ and CsPbI$_3$ QDs synthesized at various temperatures (50–200°C) are shown in Figure 2.

3. Postsynthetic anion exchange
The enchanting special thing about CsPbX$_3$ (X = Cl, Br, I) QDs is that we can significantly tune photoluminescence spectra using postsynthetic anion exchange [3]. Photoluminescence peak position depends on which halogen atom (Cl, Br or I) is in the QD structure. Halogen atoms ability to easy substitute each other can be used to obtain intermediate energy gap values. Due to the significant difference between Cl$^-$ and I$^-$ ionic radii there is no possibility to obtain CsPb(Cl/I)$_3$, yet CsPb(Cl/Br)$_3$ and CsPb(Br/I)$_3$ systems are feasible. The best option, in this case, is to synthesize CsPbBr$_3$ QDs with subsequent addition of lead chloride and lead iodide solutions to carry out anion exchange. Corresponding photoluminescence spectra are shown in Figure 3. As it can be seen fast anion exchange provides the possibility to the fine tuning of photoluminescence spectra over the entire visible spectra. In Figure 4 are shown dynamics of photoluminescence spectra under continuous laser irradiation for anion exchange from CsPbBr$_3$ to CsPbI$_3$. The following shift of photoluminescence spectra and broad peaks between initial and final states are connected with the continuous formation of CsPbBr$_{1.5}$I$_{1.5}$ solid solutions. Note that photoluminescence intensity of CsPbI$_3$ stays comparable to the CsPbBr$_3$. However, change in solid solution's composition leads to absorption spectra shift, which causes absorption coefficient change on excitation wavelength (405 nm). Especially clearly it is seen in case of CsPb(Cl/Br)$_3$ QDs: chlorine concentration increase in these solutions leads to absorption coefficient decrease on excitation wavelength and applicable luminescence intensity reduction (Figure 5). Talking about CsPb(Br/I)$_3$ QDs, the same effect causes absorption coefficient increase and leads to the fact that charge carrier excess energy converts to the thermal energy, accelerating diffusion balance. Therefore, the process time for CsPb(Cl/Br)$_3$ QDs is three times slower.

Figure 3. Photoluminescence spectra of CsPbX$_3$(X = Cl, Br, I) synthesized using anion exchange.
Figure 4. Dynamics of PL spectra under continuous laser irradiation for anion exchange CsPbBr$_3$ to CsPb(Br/I)$_3$, the legend corresponds to time (in minutes) since injection of PbI$_2$ precursor.

Figure 5. Dynamics of PL spectra under continuous laser irradiation for anion exchange CsPbBr$_3$ to CsPb(Cl/Br)$_3$, the legend correspond to time (in minutes) since injection of PbCl$_2$ precursor.

Note that it is necessary for anion exchange that halide should be in ionic, not molecular, configuration. When adding molecular iodine to the colloidal solution of CsPbBr$_3$ QDs instead of anion exchange etching of surface ligands occurs leading to luminescence intensity decrease (Figure 6). Surface etching is also confirmed by the fact that precipitation of more large-scale CsPbBr$_3$ QDs happens as the result of interaction with molecular iodine. Thus, CsPbBr$_3$ can be used as sensors in iodine electrolytes – shift of peak position indicates dissociated iodine presence, intensity modification – concentration of molecular iodine.
Figure 6. Dependence of photoluminescence intensity maximum versus iodine concentration $C$ (the inset shows photoluminescence spectra evolution increasing iodine concentration).

4. Conclusion
As it was shown in this work, postsynthetic anion exchange allows to use one initial halogen source solution to obtain different solid solution systems, which means capability to achieve wanted luminescence wavelength. Possibility of anion exchange using molecular iodine was studied and it can be seen that anion exchange happens only if halogen is in ionic form. Adding molecular iodine leads to luminescence intensity decrease.

Taking into account all the captivating properties of these materials, it is easy to see possible applications. For LEDs and lasers, we can use the ability to adjust photoluminescence spectra, high quantum yield, and narrow emission linewidths, for solar cells – significant light absorption by these structures.

References
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