Microfluidic Reactors Providing Insights into the Synthesis of $FAPb(Br/I)_3$ Nanocrystals

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We employ droplet-based microfluidic reactors [1,2] in conjunction with real-time fluorescence spectroscopy to investigate the synthesis of $FAPbI_3$, $FAPbBr_3$ and mixed $FAPb(Br/I)_3$ nanocrystals (FA = formamidinium) [3]. In the case of pure bromide and iodide we demonstrate that an excess of FA is necessary to obtain sharp emission peaks with minimal full-width-half-maximum while a FA-deficit favors platelet-like emission. We identify optimal temperatures and surfactant concentrations for both compositions and find that $FAPbBr_3$ favors higher temperature and oleic acid concentrations while $FAPbI_3$ in contrast requires low temperature and surfactant content. In addition to the synthesis with PbI_2- or $PbBr_2$-derived precursor we test the individual influence of Pb and halogen on the synthesis by using separate Pb and halogen precursors and show how their content in the reaction solution influences the crystal habit. Kinetic studies demonstrate that the synthesis of $FAPbBr_3$ seems to proceed via initial formation of platelets while $FAPbI_3$ proceeds directly via a cubic habit. (Fig 1)

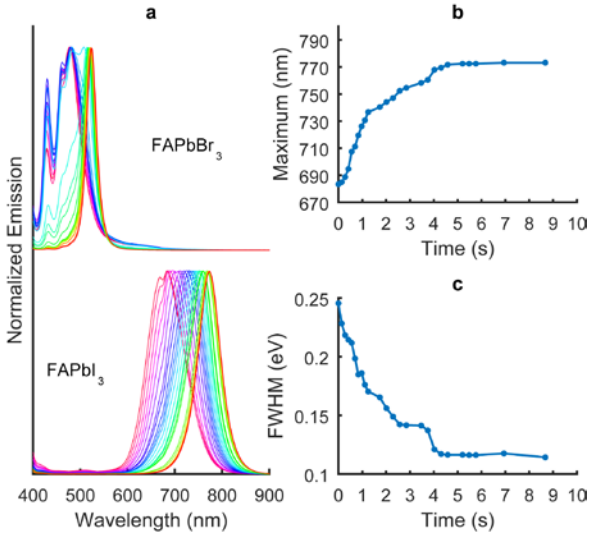

Fig. 1 (a) Emission spectra obtained online during the synthesis of FAPbBr3 and FAPbI3 nanocrystals (both at 80°C). (b, c) Development of the emission maximum and fwhm during FAPbI3 synthesis.

In th case of mixed crystals we show that full compositional tuning of the emission maximum is possible by adjusting the I/Br ratio in the reaction solution. However, we see that the quality of the emission rapidly deteriorates around 650 nm towards higher energies. The data show that the synthesis of the mixed crystal favors the same synthetic conditions as pure $PAPbI_3$. Kinetic studies of the formation of mixed crystals indicate an initial formation of pure $FAPbI_3$ crystals with subsequent incorporation of bromide.

1) R. Maceiczyk *et al*., *React. Chem. Eng.*, **2016**, 1, 261-271.
2) I. Lignos *et al.*, *Nano Letters*, **2016**, 16, 1869–1877.
3) L. Protesescu *et al*., *J. Am. Chem. Soc.*, **2016**, 138, 14202–14205