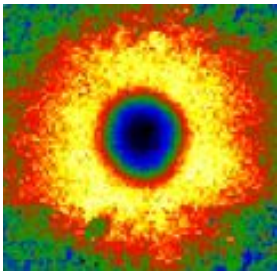

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Post-synthesis band gap halide anion exchange tuning in CsPbBr3 nanocrystals and issues of light-induced phase segregation

This study investigates post-synthesis band gap tuning of CsPbBr3 nanocrystals through halide anion exchange (HAE) with CsI. While effective HAE occurs, phase segregation leads to Br-rich core and I-rich shell formations, impacting optical properties. Comprehending these phenomena enhances the development of precise optoelectronic engineering strategies tailored for semiconductor nanocrystals.

The semiconductor industry's reliance on chemical doping for electrical property engineering is paralleled by the effective tuning of optoelectronic properties in LHPs through halide anion exchange (HAE)1. Post-synthesis tuning of CsPbBr3 nanocrystals alters their bandgap and optical characteristics, offering replaceable and reversible passive optoelectronic elements, e.g. for photovoltaics2, high-resolution displays3, or functional metasurfaces4. The photoluminescence response of CsPbBr3 nanocrystals was tuned by employing post-synthesis treatment with CsI in isopropyl alcohol. These nanocrystals were prepared via the hot-injection method and dropcasted onto silicon substrates.

To examine the resulting optical band gap of the HA exchanged CsPbBr3 nanocrystals, scanning electron microscopy (SEM) imaging and photoluminescence (PL) mapping were employed. The overlay of the two images is incorporated in Figure 1a. Here, the nanocrystals are highlighted by white dashed lines, and their PL response is further post-processed. The raw PL spectrum contains two distinguishable peaks, which we assign, in comparison to the literature and our own expertise, to Br-rich (mapped as green) and I-rich (mapped as red) phases. This suggests light-induced segregation of the nanocrystals. However, several sites appear to change their PL response according to the prospect of band gap tuning, as seen in Figure 1d, where several spectra are shown with Br-rich, I-rich, and mixed PL responses. The mixed PL responses exhibit much lower intensities than the rich phases.

To unravel the nature and impact of the phase segregation, time-of-flight secondary ion mass spectrometry (ToF-SIMS) was utilized to image the spatial distribution together with the depth profile of Br and I ions, as seen in Figures 1b and 1c, respectively. Here, the Br ions are detected at the sites of the nanocrystals as expected. However, I ions seem to follow a random pattern across the sample with a preference for occurrence on the edges of the nanocrystals. Moreover, upon examining the depth profile of Br and I ions in Figure 1e and comparing it with the depth PL profile in Figure 1f, we see a strong Br signal present on the surface with I signal rapidly decreasing when reaching certain depth. It is evident that the HAE mainly occurs on the outer shell of the nanocrystal which becomes I-rich. The shell reaches a certain saturation depth and leaves the core of the nanocrystal purely made of the Br-rich phase.

To summarize, the correlative optical and chemical imaging of HAE CsPbBr3 nanocrystals revealed that light-induced phase segregation takes place leading to formation of Br-rich and I-rich phases. The band gap tuning of individual HAE CsPbBr3 nanocrystals was found to be existent and prevalent even after light illumination at several sites, however, it was regarded as inefficient and random. Additional sensitive chemical mapping reveals that phase segregation primarily occurs on the outer shell of the CsPbBr3 nanocrystals, saturating at an effective depth. This indicates that, rather than engineering the bandgap and PL response of the CsPbBr3 NCs, non-selective mixing was prevalent due to phase segregation.

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