

# Single-object and ensemble properties of all-inorganic perovskite nanocrystals

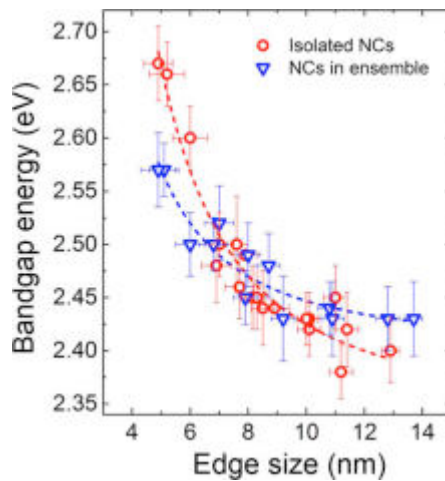
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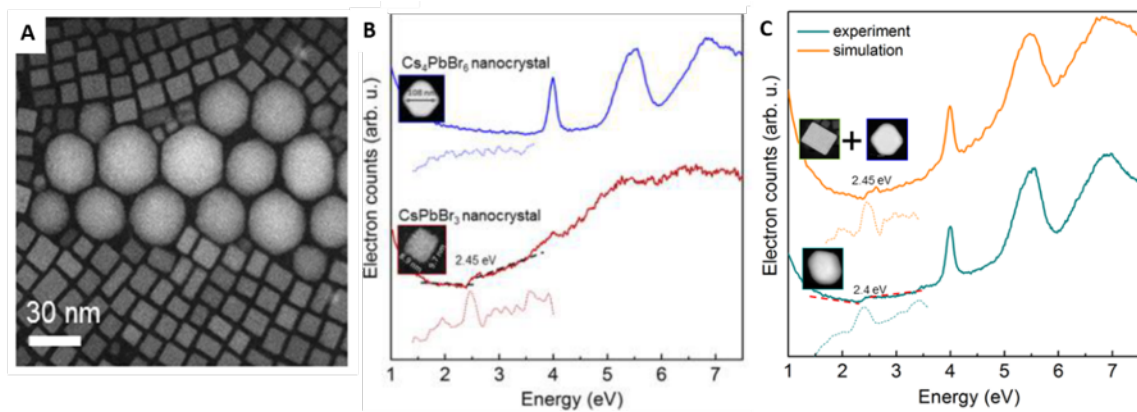
All-inorganic cesium lead halide perovskite nanocrystals ( $\text{CsPbX}_3$  NCs,  $X = \text{Cl, Br, I}$ ) have attracted much attention recently due to their high photoluminescence quantum yields (50-90%) and narrow emission bands with wide tunability. They combine the advantages of perovskites and quantum dots creating an exceptional material for low-cost optoelectronic and photovoltaic devices. By using high-resolution induced absorption and emission spectroscopies, we obtain detailed information on carrier dynamics in perovskite NCs [1], their water-resistant encapsulation [2], and on energy exchange within their ensembles [3]. Further, conducting low-voltage electron energy loss spectroscopy (EELS) on individual NCs, we provide novel insights regarding three important aspects of their microscopic behavior:

- (i) We explicitly demonstrate the relation between NC size and shape with their bandgap, and that the effective coupling between proximal NCs causes band structure modifications as shown in Figure 1 [4].



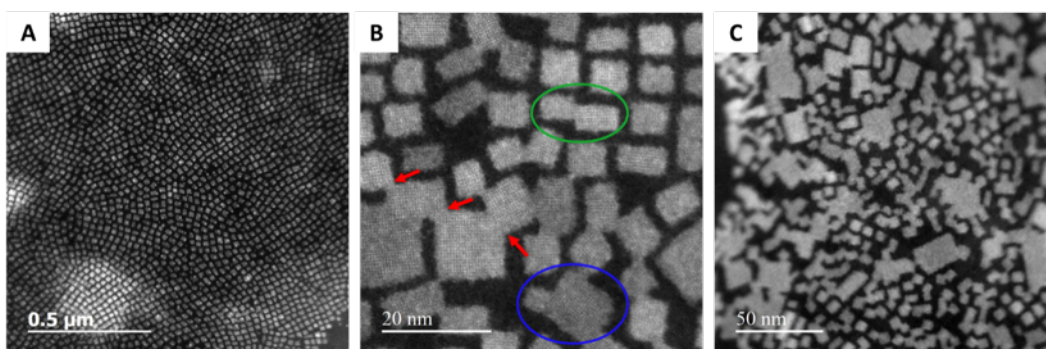
**Figure 1.** The bandgap energies of single NCs that are either isolated (red dots) or in an ensemble (blue triangles), as determined from low-loss EELS measurements on single NCs, plotted as a function of their sizes.

- (ii) The synthesis of  $\text{CsPbX}_3$  NCs inevitably yields simultaneous formation of other nanostructures: insulating  $\text{Cs}_4\text{PbBr}_6$  nanohexagons and hybrid nanospheres [5]. While  $\text{CsPbBr}_3$  is a direct bandgap semiconductor emitting visible light,  $\text{Cs}_4\text{PbBr}_6$  is an insulator with a large indirect bandgap and absorption/emission in the UV region. Since NCs of both materials co-grow independently and simultaneously during one growth process, optical characteristics of  $\text{CsPbBr}_3$  can be easily mixed and erroneously attributed to  $\text{Cs}_4\text{PbBr}_6$  (see Figure 2).



**Figure 2.** A) DAF image of a mixture of  $\text{CsPbBr}_3$  nanocubes and  $\text{Cs}_4\text{PbBr}_6$  nanohexagons. B) Valence-loss EEL spectra representing the absorption of a  $\text{CsPbBr}_3$  nanocube (red) and a  $\text{Cs}_4\text{PbBr}_6$  NC (blue). Their bandgap energy is determined from the peak of the first derivative of the EEL spectrum, that appears due to the abrupt onset in absorption (indicated by the dotted lines). C) Valence-loss EEL spectrum of a spherical nanocrystal (green) formed upon the merging of a nanocube and a nanohexagon.

- (iii) Drop-casted NCs merge spontaneously at room conditions by seamless stitching when aligned (see Figure 3); the merging process can be accelerated by humidity and mild-temperature treatments, and arrested with electron beam irradiation [6]. Being of a cubic shape with a narrow size distribution, NCs are ideally suited to form close-packed layers and/or multilayer structures. The spontaneous merging opens new possibilities of advanced concepts for controlled but autonomous assemblage of NCs, as a step towards the development of high-quality films (homogeneous films in bandgap and thickness, good crystallinity, good contact between NCs, full bandgap control, good electrical properties with high carrier mobility, ...).



**Figure 3.** HRTEM images of CsPbBr<sub>3</sub> NCs. A) Fresh drop-casted nanocrystals on a graphene grid. B) Merging can happen between nanocrystals of similar (green circle) or different size (blue circle), the red arrows point at the boundaries of connecting NCs. C) The same sample after one week stored at ambient conditions.

- [1] E. M. L. D. de Jong *et al.* J. Phys. Chem. C 2017, **121**, 1941.
- [2] L. Gomez *et al.* Nanoscale **2017**, 9, 631.
- [3] C. de Weerd *et al.* J. Phys. Chem. C 2016, **120**, 13310.
- [4] J. Lin *et al.* Nano Lett. **2016**, 16, 7198.
- [5] C. de Weerd *et al.* C **2017**, 121, 19490.
- [6] L. Gomez *et al.* to appear in ACS Appl. Mater. Interf. **2018**.