Exciton diffusion in cesium lead halide perovskite nanocrystals organized in ordered nanoscale assemblies

Erika Penzo [a], Anna Loiudice [b], Edward Barnard [a], Nicholas Borys [a], Raffaella Buonsanti [b], Adam Schwartzberg [a], Alexander Weber-Bargioni [a], and Stefano Cabrini [a]

[a] *The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley CA, 94720, USA*
[b] *École Polytechnique Federale de Lausanne, 1950, Sion, Switzerland*
email: epenzo@lbl.gov

Fully inorganic cesium lead halide perovskite nanocrystals (NCs) are a novel colloidal material displaying remarkably bright photoluminescence (PL) characterized by high quantum yield (QY) of 50-90% and narrow emission line widths of 12-42 nm. In addition, compositional control and quantum-size effects allow for the precise and continuous tuning of bandgap energies over the entire visible spectral region. The cubic perovskite crystal structure results in NCs with cubic shape, 4-15 nm in side length[1].

Taking advantage of their affinity for hydrophobic surfaces, these NCs can be assembled in highly ordered monolayers in which the cubic NCs are organized in arrays with parallel edges (Fig. 1a). The close proximity of this arrangement and the high polarizabilty of these NCs allow for efficient exciton migration between adjacent NCs through Förster Resonant Energy Transfer (FRET)[2]. The monolayer layout confines the available paths for exciton transport in two dimensions, enabling the accurate study of the transport effects and mechanism using super-resolution based optical imaging techniques combined with steady-state and time-resolved spectroscopy. Evidence of FRET-like transport is found in accelerated relaxation times and spatial expansion of the excited state ensemble. As shown in Fig. 1b and 1c, when excited with a 450 nm laser, the PL produced by the NCs organized in a monolayer is observed on an area significantly larger than the dimensions of the laser excitation spot, indicating FRET-mediated long-range exciton migration.

Combining lithographic patterning and self-assembly, the $CsPbBr_3$ NCs can be organized and confined even further. Trenches 60 nm deep and 250 nm, 100 nm and 50 nm wide are patterned with electron beam lithography and inductively coupled plasma (ICP) etching. A 60 nm thick layer of amorphous Si is deposited by plasma-enhanced chemical vapor deposition (PECVD) on a 20 nm thick alumina layer deposited by atomic layer deposition (ALD). The alumina works as an etch-stopping layer producing etched features with sharp corners and a flat bottom (Fig. 2a). The patterned surface is coated with a 10 nm thick hydrocarbon polymer to increase the affinity with the NCs solution and the NCs ligands (oleylamine and oleic acid). Due to capillary forces the NCs form separate monolayers on the top and on the bottom of the trenches, where the reduced available space improves the alignment of the NCs into orthogonal arrays, extending the scale of the organized monolayer domains and guiding the exciton diffusion along preferred directions (Fig. 2).

This system allows for the first demonstration of such long-range spatially controlled FRET mediated exciton transport in NCs solids opening up new possibilities for high functionality optoelectronic devices based on cesium lead halide perovskite NCs.

[1] L. Protesescu, et al. Nano Letters 15 (2015) 3692-3696.
[2] G. M. Askelrod, et. al. Nano Letters 14 (2014) 3556-3562.

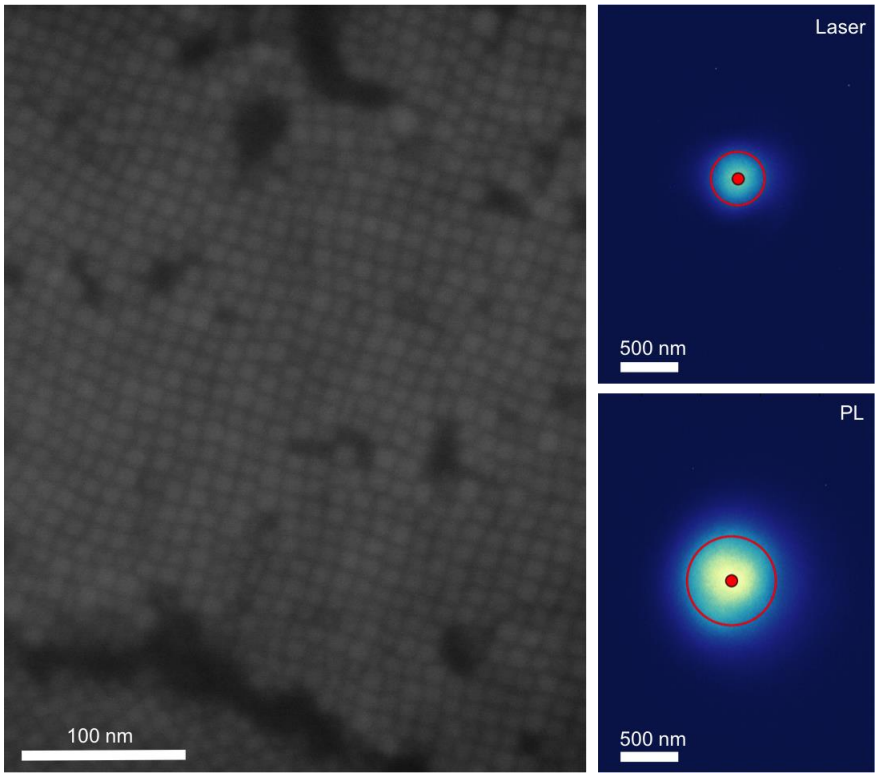

Figure 1. a) SEM image of a monolayer of $CsPbBr_3$ NCs. b) CCD image of the excitation laser spot (λ = 450 nm). c) CCD image of the NCs PL produced by the excitation laser in b) on the sample in a). The red circle is the FWHM of a two-dimensional Gaussian fit.

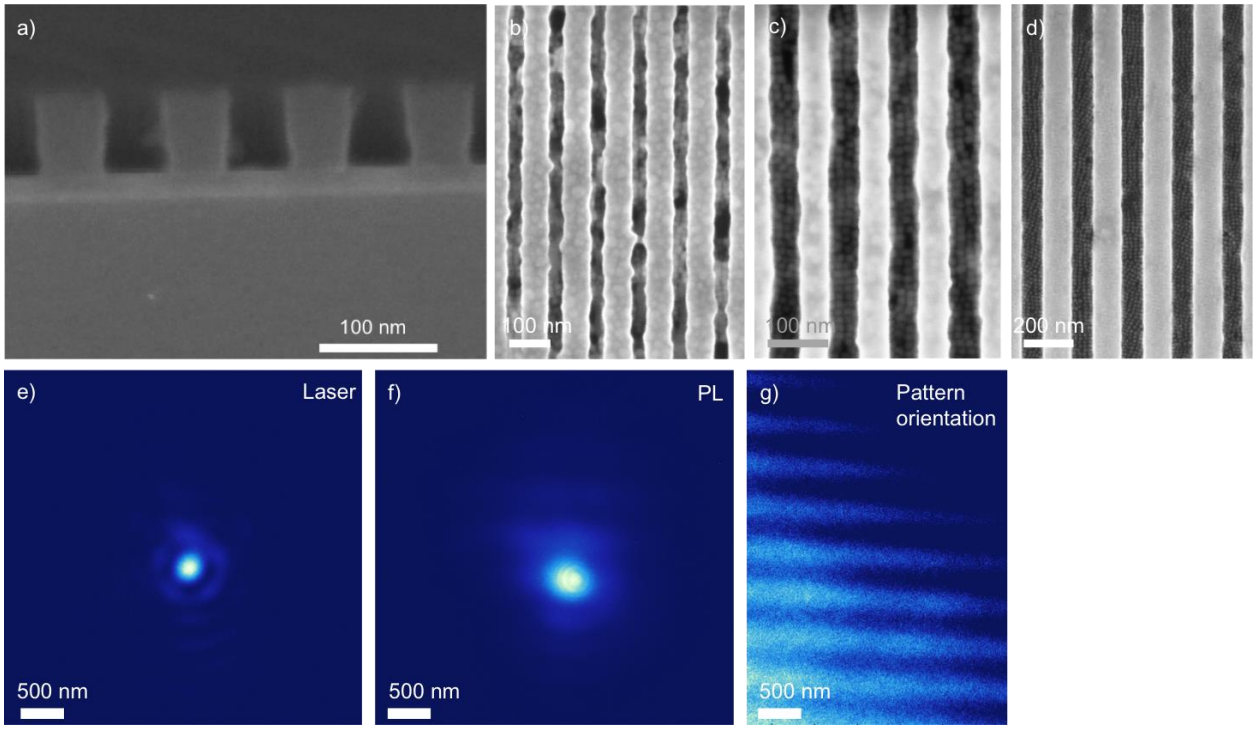

Figure 2. a) Cross-section SEM image of 60 nm deep, 50 nm wide patterned trenches. b) c) and d) Top-view SEM images of $CsPbBr_3$ NCs assembled inside respectively 30 nm, 50 nm and 90 nm trenches. e) and f) CCD image of the excitation laser spot and of the NCs PL produced by NCs assembled on 250 nm trenches oriented as shown in g).