Counterion-Mediated Ligand Exchange for PbS Colloidal Quantum Dot Superlattices

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Colloidal quantum dot (CQD) solids represent a popular topic in the field of emerging photovoltaics for the past decade due to their tunable bandgap, high absorbance and the possibility of solution processing. Exchanging the ligands is a crucial step in the fabrication of high quality CQD solids, since the resulting interparticle distance, surface passivation and order will tailor both the optical and electronic properties. Although many reports investigate the devices fabricated using different ligands, the process of ligand exchange itself and the influence on the device properties have not gained enough attention.

In this work, we compare the ligand exchange process in CQD thin films using ammonium, methylammonium and tetrabutylammonium iodide, and shed light to the mechanism of the ligand exchange. [1] We obtain two- and three-dimensional square-packed PbS CQD superlattices with epitaxial fusion of the nearest neighbor CQDs as a direct outcome of the ligand-exchange reaction, and show that the order in the layer can be controlled by the nature of the counterion. Furthermore, we demonstrate that the acidic species (both solvent and counterion) mediate the removal and replacement of the carboxylates bound to lead-chalcogenide surface. A non-acidic counterion eventually leads to higher order, but also poorer carrier transport in the QD thin film due to incomplete ligand exchange. Finally, we show that single-step blade-coating and immersion in a ligand exchange solution can be used to fabricate well performing bottom-gate/bottom-contact PbS CQD field effect transistors with record subthreshold swing.

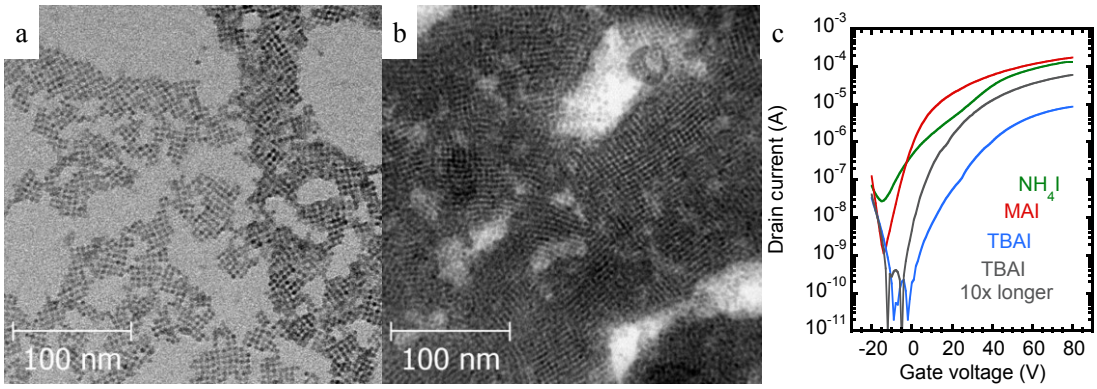

Figure 1. TEM images of of PbS collidal quantum dots treated with (a) methylammonium-iodide and (b) tetrabutylammonium-iodide; (c) the influence of the ligand counterion on the transport properties

[1] D. M. Balazs, et al. ACS Nano, 2015, 9, 11951