

Stoichiometric control of the density of states in PbS colloidal quantum dot solids

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Colloidal quantum dot (CQD) solids have gained great attention recently for their solution processability coupled with high absorption, crystalline robustness and the tailorable electronic structure, yielding great potential for applications in light harvesting or emission. However, full control of the electronic structure has not been achieved, since most air-stable samples of lead-based, supposedly intrinsic semiconductors show dominant n-type conductivity, and efficient p-type transport is only achieved by air exposure. The lack of high quality p-type layers has recently been identified as one of the limiting factors for the solar cell performances. Theoretically, particles with excess lead on their surface show n-type characteristics due to filled midgap states present near the conduction band, while (over)compensating the initial off-stoichiometry turns them p-type. Such an approach seems to provide the solution, but to date there has been no reports about a direct and fine control of the stoichiometry of PbS CQD solids.

In this work, we present how to control the stoichiometry of fully inorganic PbS CQD films using a two-step ligand exchange with iodide and sulfide. The sulfide capping is shown to enhance the coupling between quantum dots through stronger neck formation, causing partial loss of quantum confinement. The variation of the lead-to-sulfur ratio results in fine-tunable changes in the transport properties of the CQD films; the initial electron-dominated transport is turned into balanced ambipolar, while compensating for the initial excess lead, and the hole mobility increases 3-4 orders of magnitude. We explain the increased mobility with a large increase of the DOS of the valence band. The presented method is proven useful in band structure engineering of strongly coupled CQD arrays, adding a new item to the researchers' toolbox.

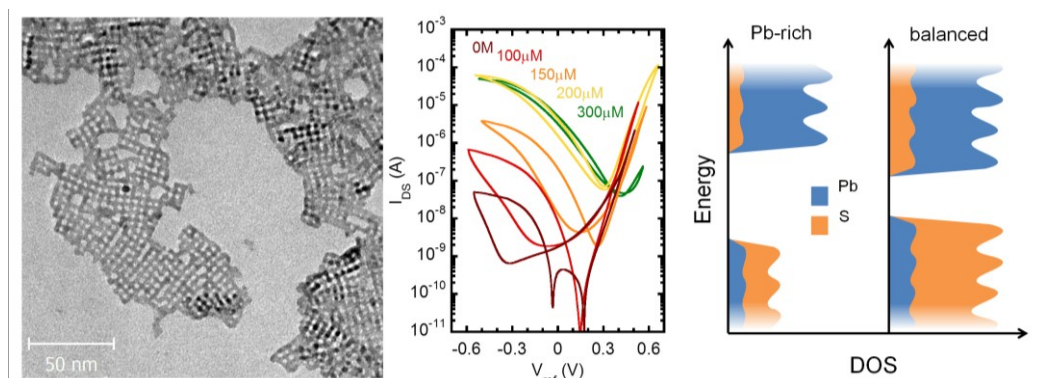


Figure 1. (a) TEM image of a sulfur-rich PbS CQD film; (b) transfer curves showing the tenability of the properties; (c) band structure changes upon stoichiometric compensation.