

ADVANCED MATERIALS

Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.201501156

Identifying and Eliminating Emissive Sub-bandgap States in
Thin Films of PbS Nanocrystals

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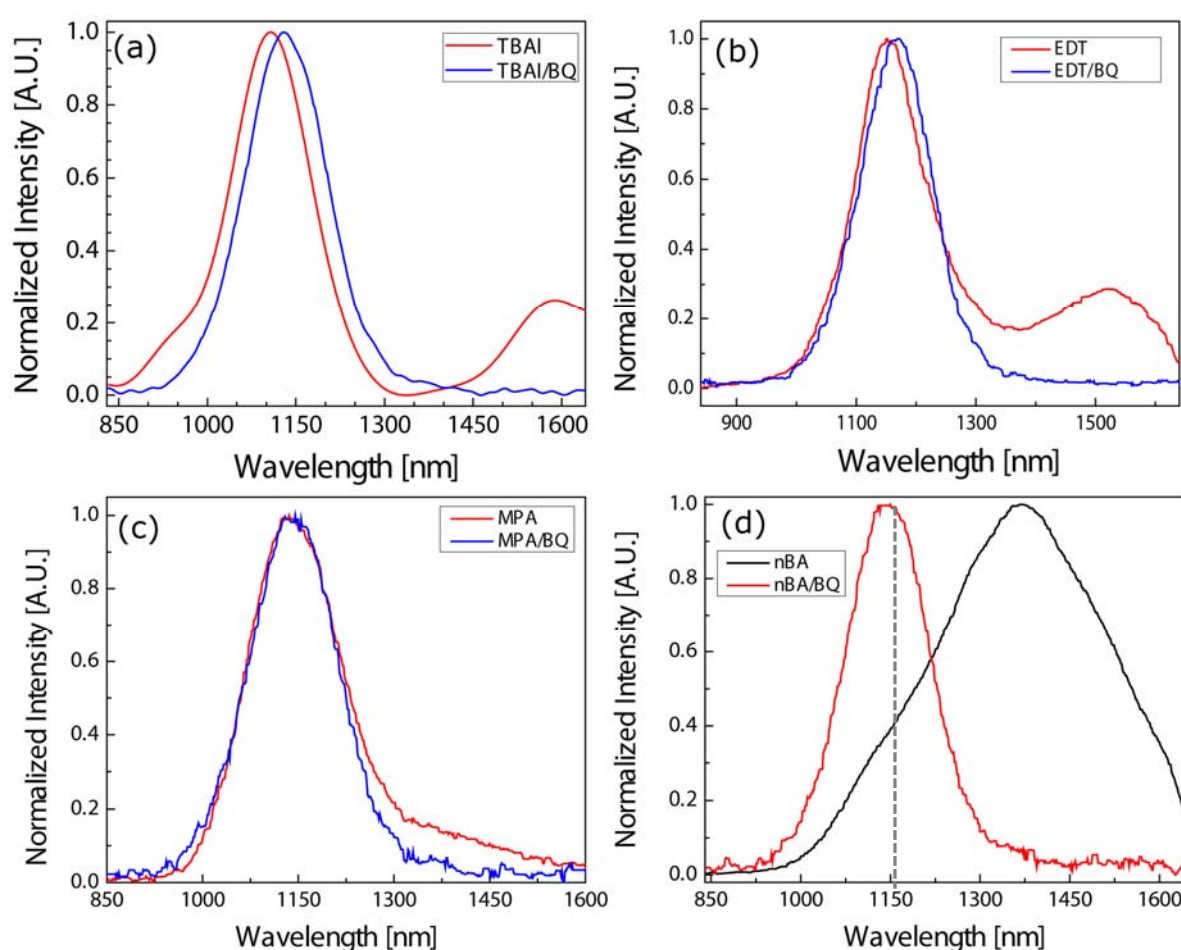


Figure S1. The comparison of each ligand treated sample before and after BQ treatment. PL from (a) TBAI- (b) EDT- (c) MPA- and (d) nBA-treated sample. We added a line for (d) for easy comparison of peak position for nBA/BQ-treated and peak shoulder position for nBA-treated sample.

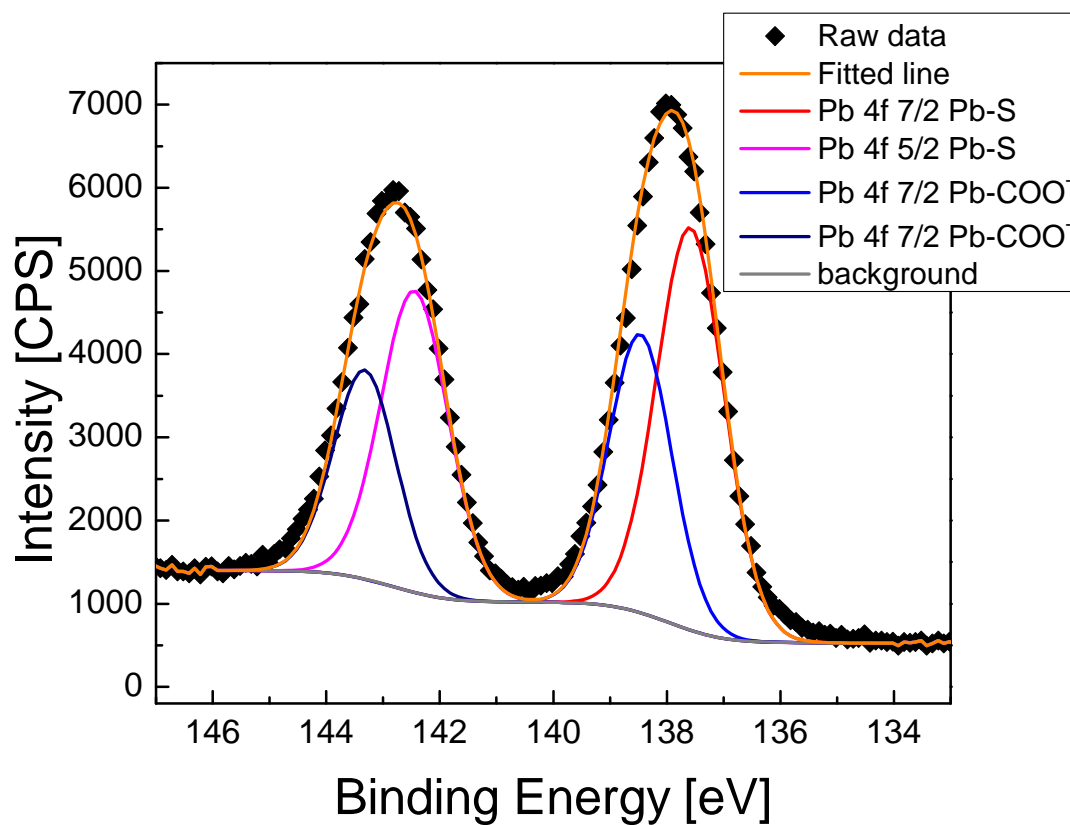


Figure S2. The deconvoluted spectrum of PbS QD thin films with native OA ligands. The spectrum is well fitted with the sum of the peaks from Pb-S and Pb-carboxylates.^[1]

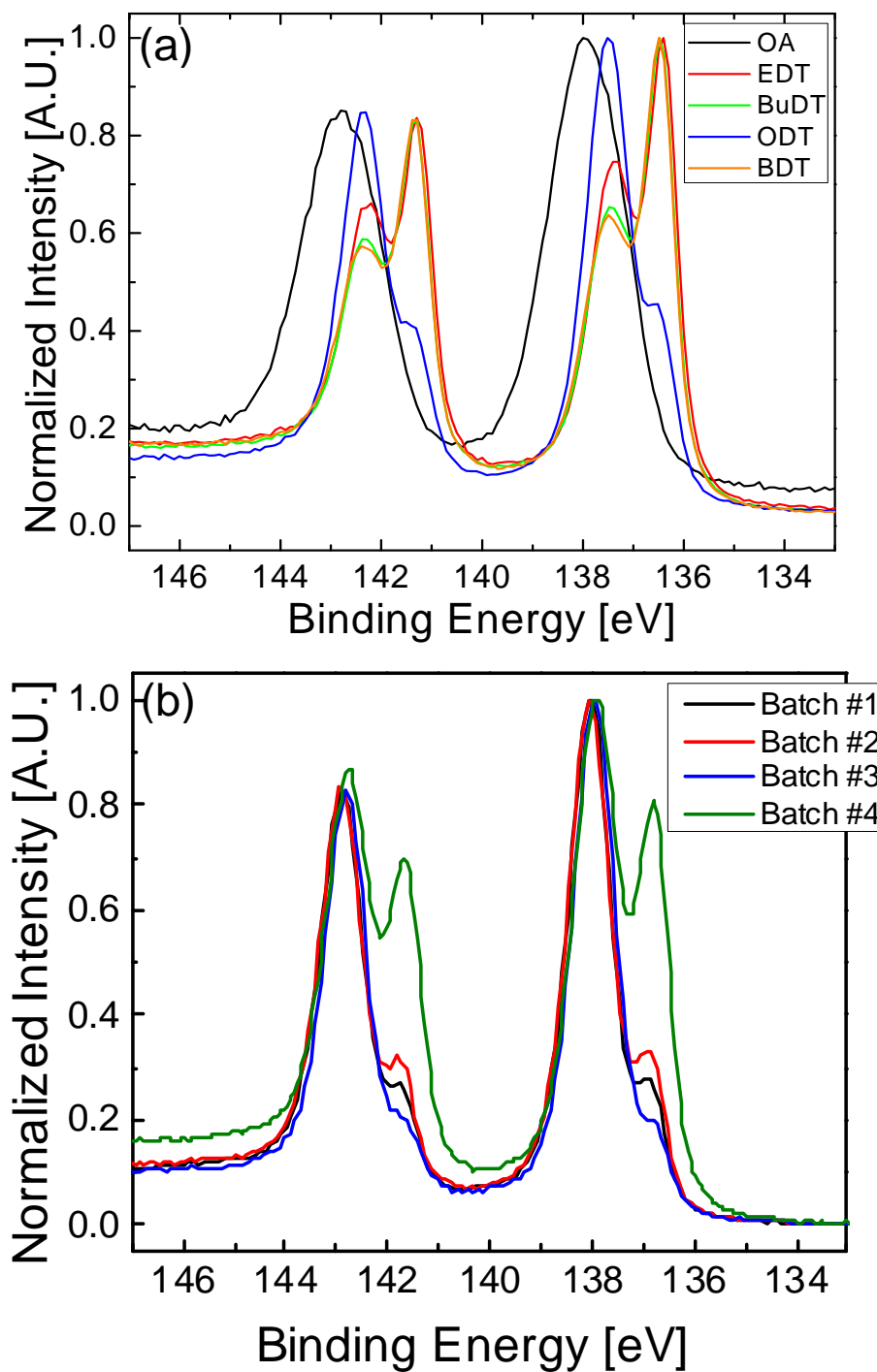


Figure S3. (a) The XPS results of PbS QD thin films with different length of dithiol ligands are compared with oleic acid (OA) ligand : 1,2-ethanedithiol (EDT), 1,4-butanedithiol(BuDT), 1,8-octanedithiol(ODT), and 1,3-benzendithiol (BDT). Under-charged Pb atoms exist regardless of

the length of dithiol ligands. (b) XPS results show the under-charged Pb atoms in TBAI-treated PbS QDs result from four different synthetic batches.

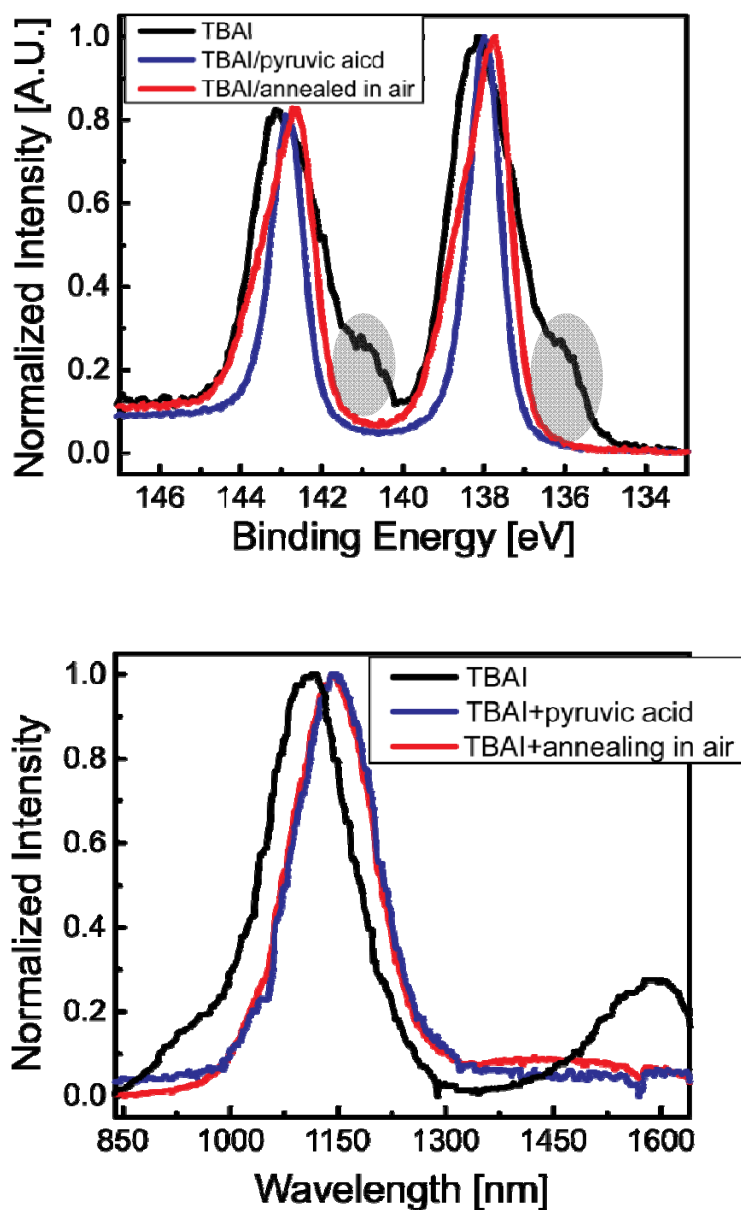


Figure S4. The XPS results (upper panel) of TBAI-treated PbS QD thin films with different oxidation methods: TBAI-treated films as a reference (black), TBAI-treated films followed by 0.8 % (v/v) pyruvic acid treatment^[2] (blue), which is a well-known oxidant in metabolic pathways in muscles,^[3] TBAI-treated films followed by annealing at 80°C in air for 30min (red). Less-charged Pb features (marked as grey) at the shoulder of Pb-S peak are disappeared with

pyruvic acid treatment and air-annealing. The PL (lower panel) shows that the emission from sub-bandgap states removed after the treatment.

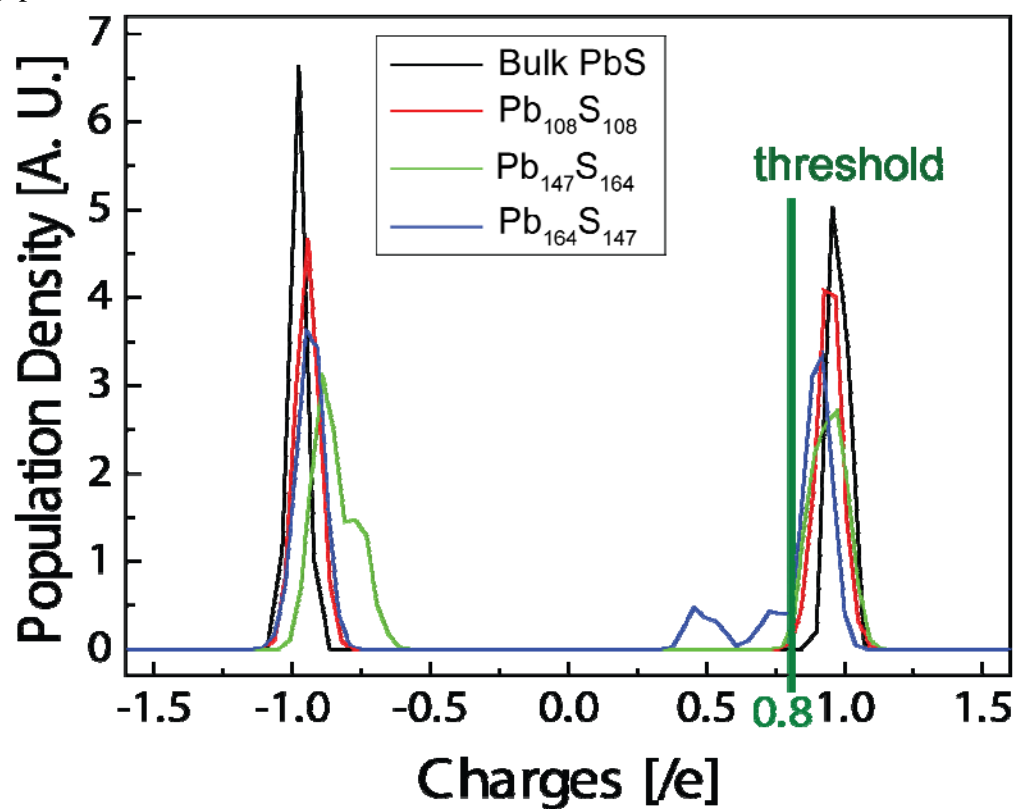


Figure S5. The simulated charge distribution of different Pb-to-S ratio samples to show that the level of charge threshold for under-charged Pb species is 0.8

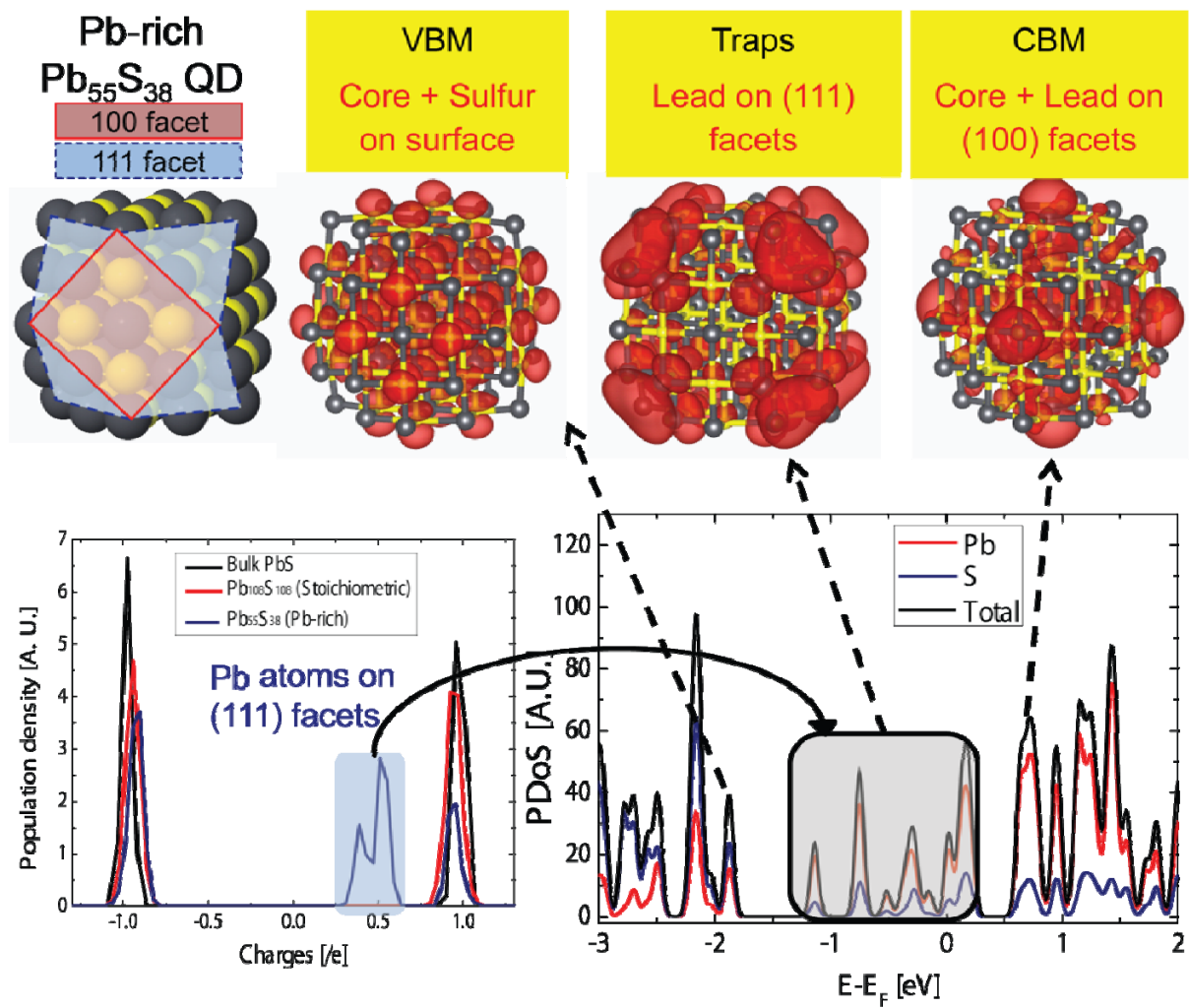


Figure S6. The DFT results shows that under-charged Pb species are located on the (111) facet, and induce sub-bandgap states.

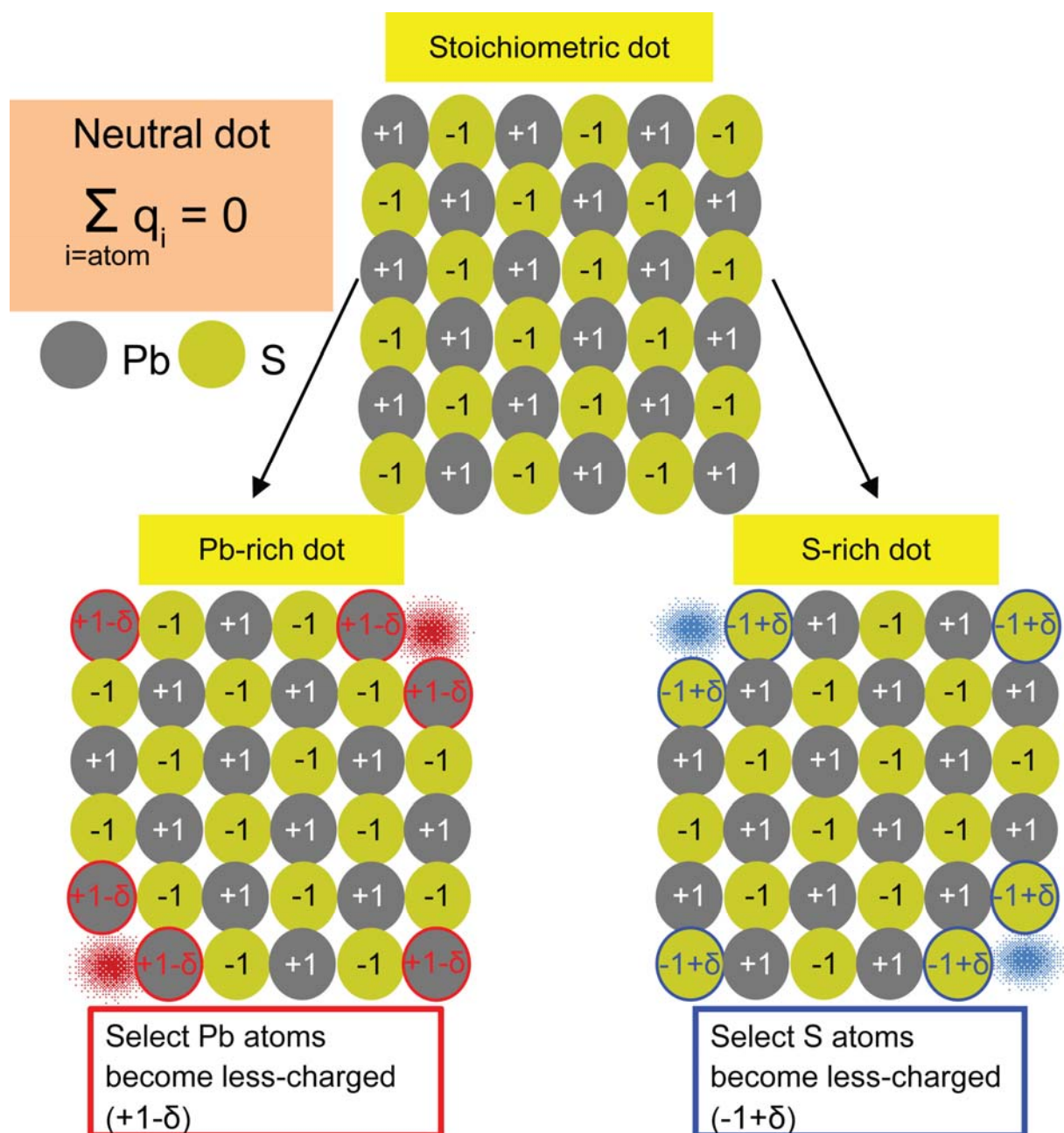


Figure S7. A schematic illustration of the origin of under-charged species with off-stoichiometry.

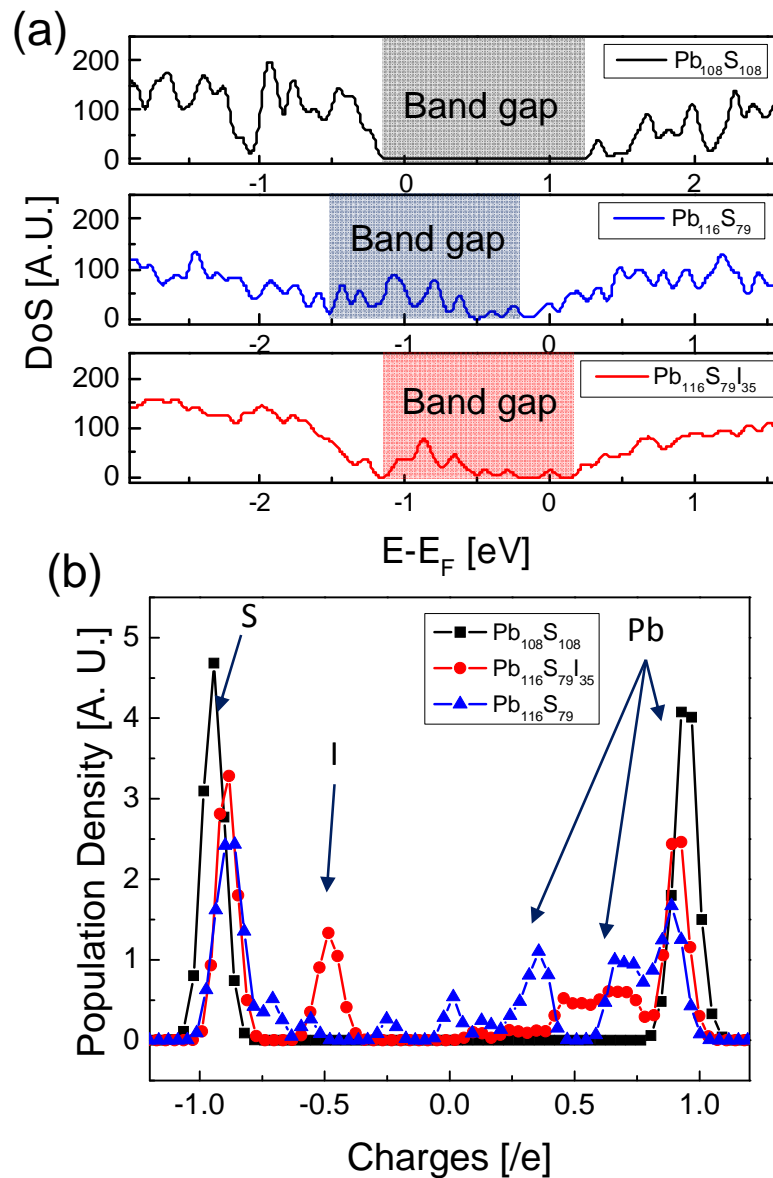


Figure S8. (a) DoS and (b) Bader analysis for the comparison of bare QDs and iodine passivated QDs. Iodide ligands suppress under-charged Pb species, and sub-bandgap states in off-stoichiometric PbS QDs. As a reference, calculations on stoichiometric QDs show no sub-bandgap states and no reduced Pb atoms.

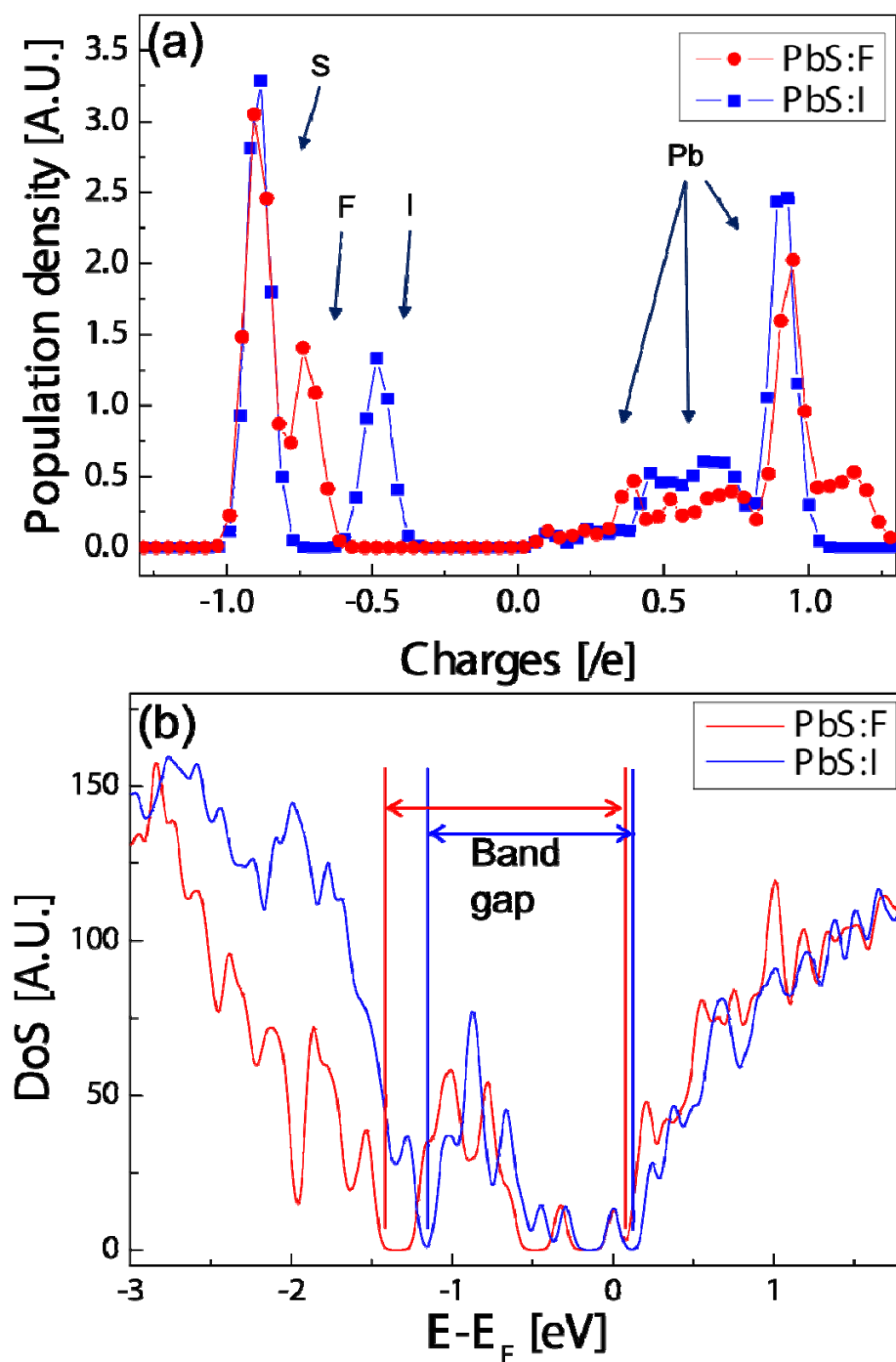


Figure S9. DFT results show that iodine and fluorine ligands induce different suppression of under-charged Pb species and a different profile of sub-bandgap states.

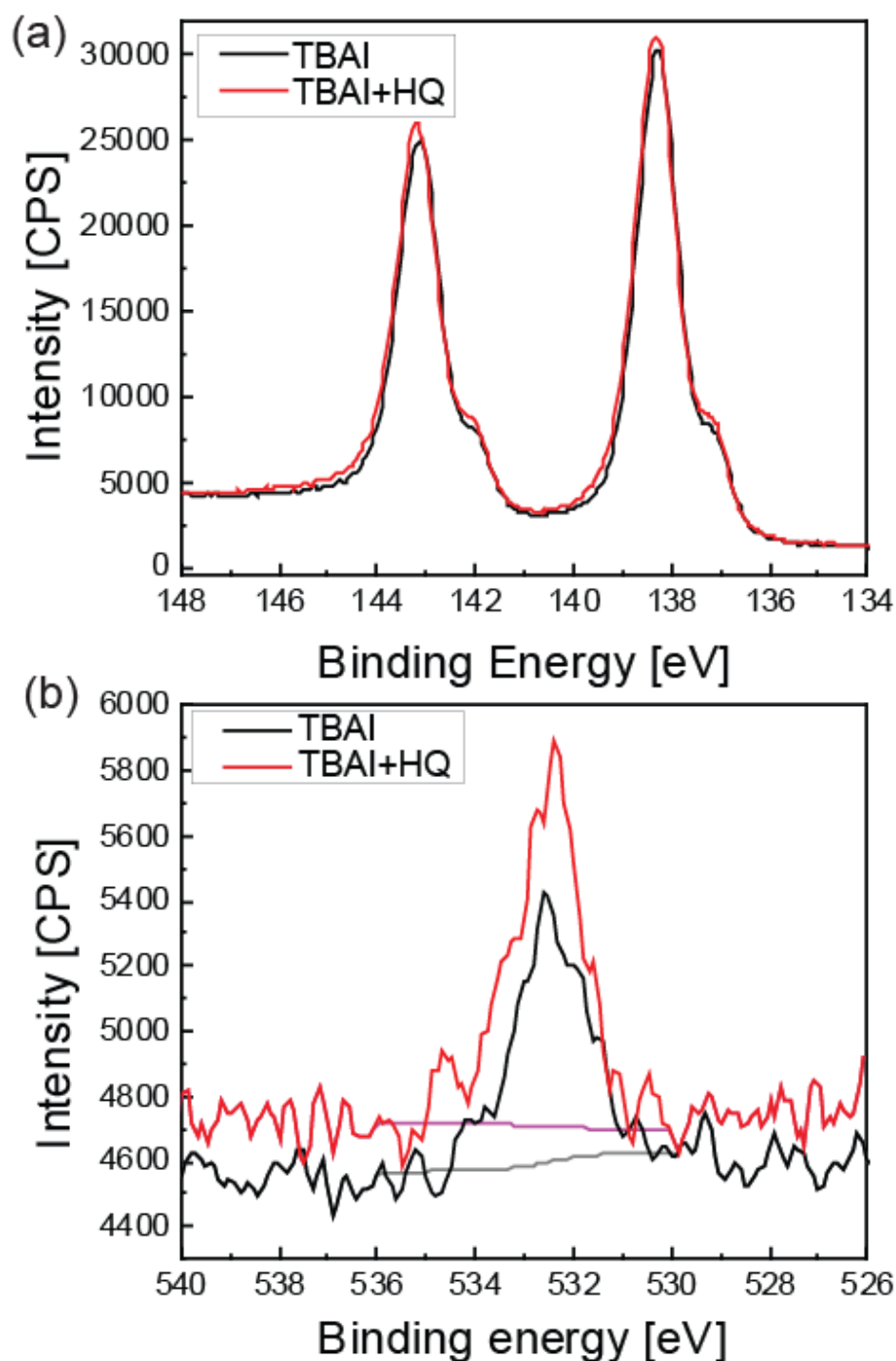


Figure S10. XPS results of TBAI-treated samples with and without 1,4-hydroquinone (HQ) treatment. HQ is a product from the reduction of BQ. Minimal change in the spectral features of (a) Pb 4f and (b) O 1s is observed before and after the HQ treatment. This result indicates limited binding of HQ on the QD surface. O-to-Pb ratio with background correction increases 9% after the HQ treatment. We suspect that oxygen in the samples are originated from residual OA ligands or air-exposures during the sample transfer to XPS chamber.

References

- [1] a) J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Eden Prairie, MN, **1992**. b) NIST X-ray Photoelectron Spectroscopy Database, Version 4.1 (National Institute of Standards and Technology, Gaithersburg, 2012); <http://srdata.nist.gov/xps/>.
- [2] G. H. Carey, I. J. Kramer, P. Kanjanaboos, G. Moreno-bautista, O. Voznyy, L. Rollny, J. A. Tang, S. Hoogland, E. H. Sargent, *ACS Nano* **2014**, *8*, 11763.
- [3] J. M. Berg, J. L. Tymoczko, L. Stryer, *Biochemistry*, W. H. Freeman And Company, New York, **2002**.