Supporting Information:

Diversity of Sub-Bandgap States in Lead-Sulfide Nanocrystals: Real-Space Spectroscopy and Mapping at the Atomic-Scale.

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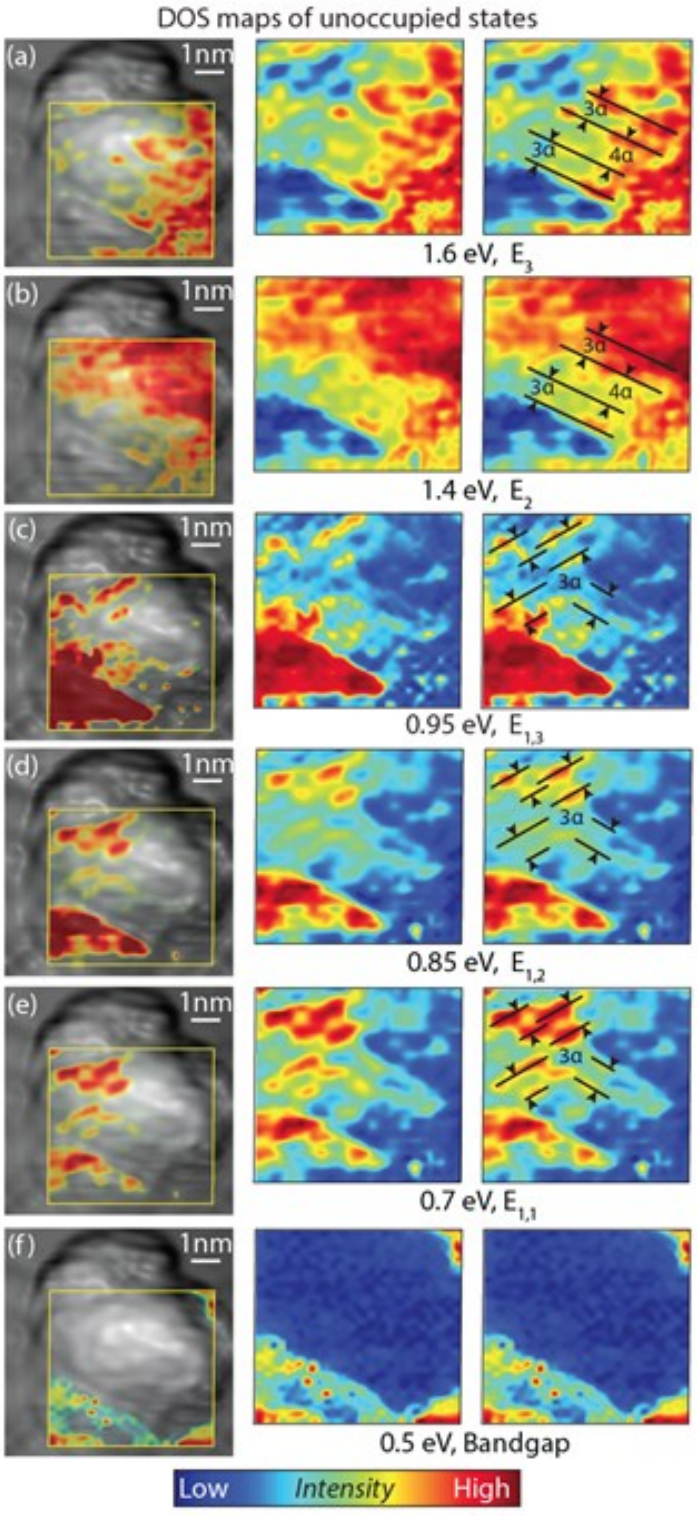
Figure S1 (Right) shows the prominent unoccupied states for NC1. Subfigures (a-f) include (from left to right) a combination of topography(grayscale), and DOS map(color) overlay (where the yellow outline encloses the area of DOS mapping), DOS map only, and DOS map with black lines showing DOS features that are in registry with NC1 crystallographic features from Figure 1g in the main text. Parameter α is defined as the distance between two neighboring {211} planes, as shown in the model in Figures 6a and b in the main text. STS measurements taken with set-point 1.6 V bias, 30 pA tunnelling current. STM topography image measured with set-point 2.0 V bias, 2 pA tunneling current.



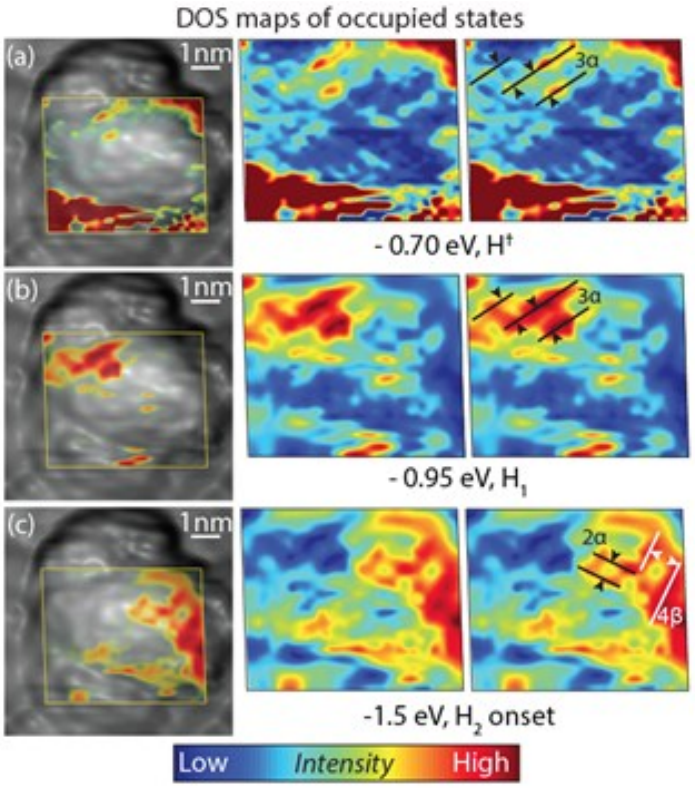


Figure S2 (Right) shows the prominent occupied states for NC1. Same area and representation as Figure S1 for the occupied states of NC1. Parameter β is defined as the distance between two neighboring {110} planes, as shown in the model in Figures 6c and d in the main text. Set-points of STM topography image and STS maps same as in Figure S1.

Figure S3 (Right) shows the prominent unoccupied states of NC2. Same representation as in Figure S1 for NC1. Parameter β is defined as before for figure S2, and as shown in the model in Figures 6c and d in the main text. STM topography measured with set-point 2.0 V bias, 1 pA tunneling current. STS maps measured with set-point 1.5 V bias, 20 pA tunneling current.

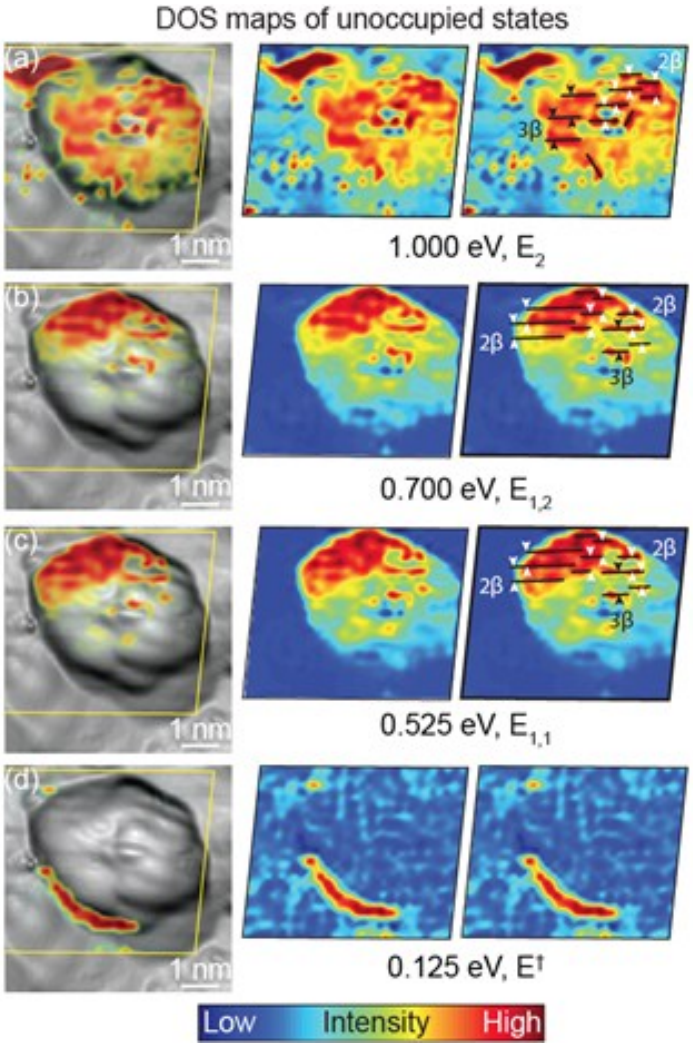


Figure S4 (Right) shows the prominent occupied states of NC2. Same representation as in Figure S3 for NC2. Parameter α is defined as the distance between two neighboring {211} planes, as shown in the model in Figures 6a and b in the main text. Set-points of STM topography image and STS maps same as in Figure S3.

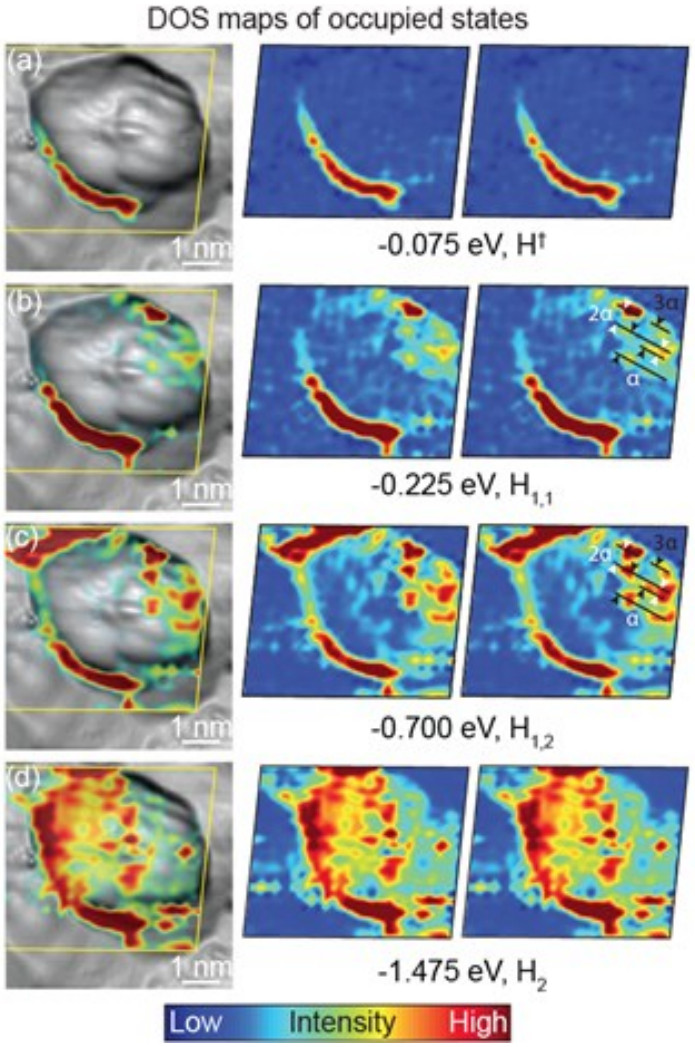
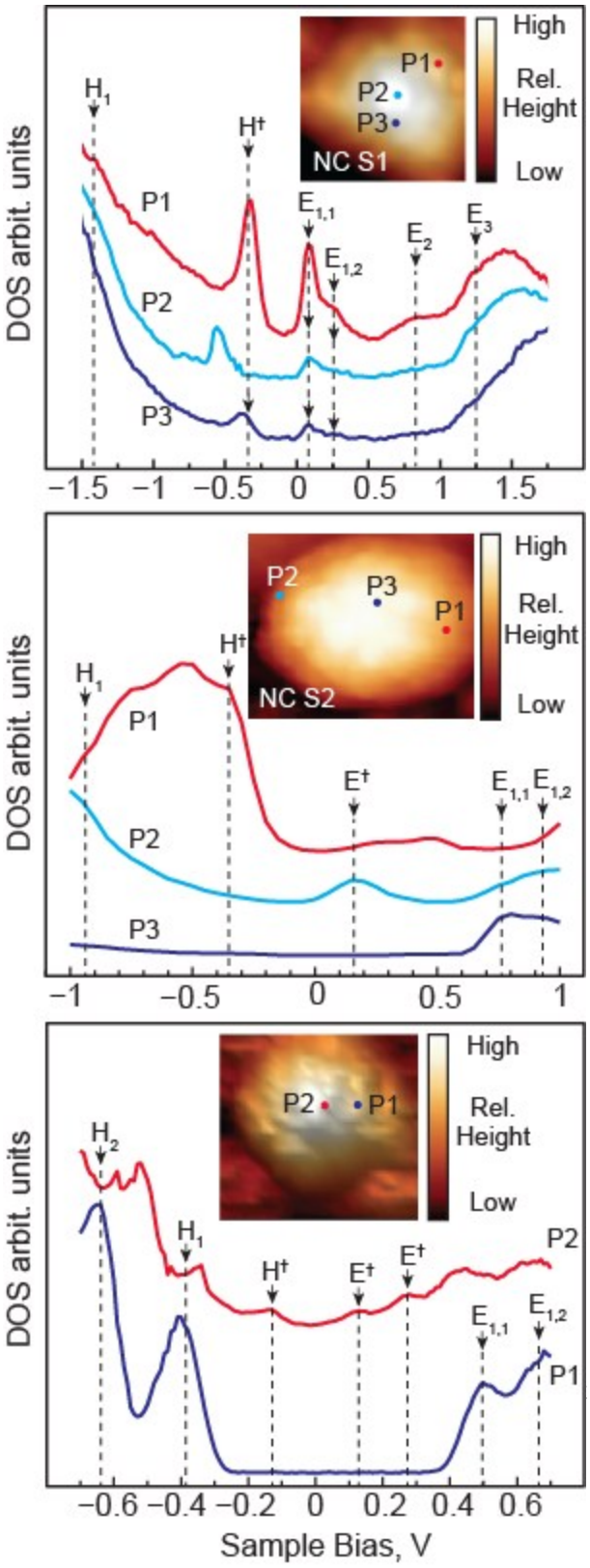


Figure S5 (Right) shows examples of PbS NCs displaying localized defect-related states in their DOS. Unoccupied $E_{1,n}$ and occupied H_1 states show marked intensity differences depending on location, and are associated with the reconstruction of polar PbS (111) surfaces or regions of marked non-stoichiometry in which excess S (Pb) atoms at the surface lead to sub-bandgap states broken off from the valence(conduction) bands. These observations are in keeping with and further support conclusions made with regard to the sub-bandgap states observed for NCs discussed in the main journal article.



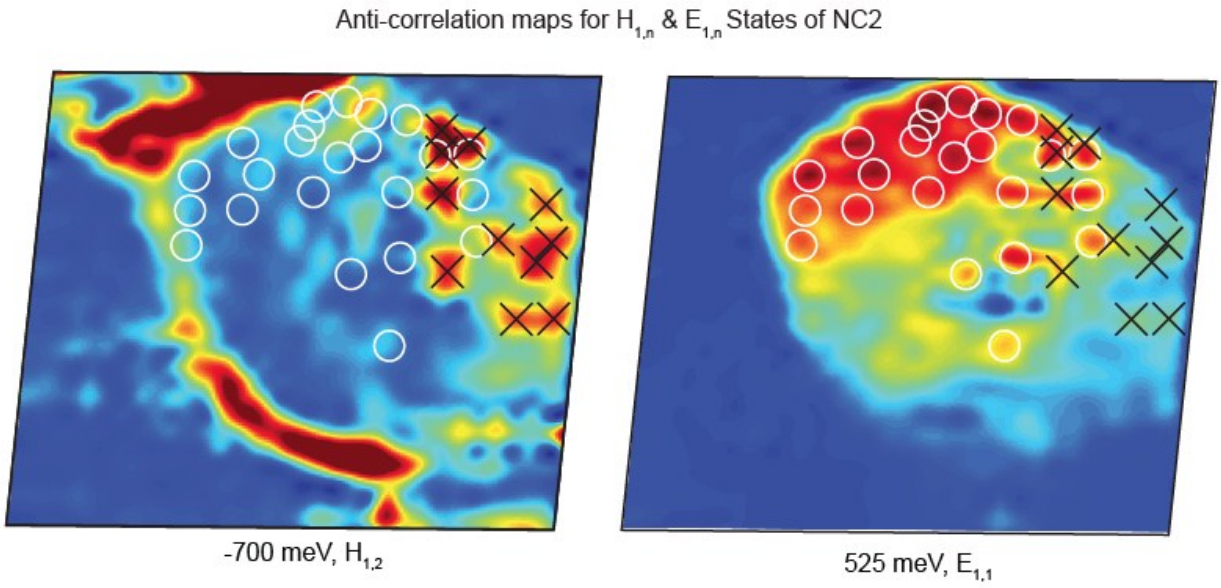


Figure S6 DOS maps for $H_{1,n}$ and $E_{1,n}$ states of NC2 showing anti-correlation in their spatial distributions. White circles (black x's) mark locations of local high intensity for states $E_{1,n}$ ($H_{1,n}$)

DOS intensity maps for the sub-bandgap states of NC2 (Figure S6), show that the locations of high intensity for states $H_{1,n}$ in general correspond (on the atomic scale) to locations of low intensity for states $E_{1,n}$, and vice-versa suggesting that $H_{1,n}$ and $E_{1,n}$ patterns are carried by atoms corresponding to different elements. Theoretical calculations predict that $H_{1,n}$ and $E_{1,n}$ patterns result from non-stoichiometric surface S and Pb atoms respectively.[1]

References

(1) Kim, D.; Kim, D.-H.; Lee, J.-H.; Grossman, J. C. Impact of Stoichiometry on the Electronic Structure of Pbs Quantum Dots. *Physical Review Letters* **2013,** *110*, 196802.