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Epitaxial Quantum Dot Superlattices: From Synthesis to Characterization to Electronic Structure

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Leveraging the tunability of quantum dots (QDs) for functionalization in next-generation photovoltaics, thermoelectrics, or other devices requires a combined approach of novel synthesis, characterization, and theory. Here, we study thin films of PbSe QDs self-assembled into square superlattices (SLs) and then epitaxially connected by adding a chelating agent which selectively strips organic ligands from the <100> facets (Figs. 1a-d) [1,2]. The presence of epitaxial bridges promotes efficient charge transport by improving coupling between neighboring QDs. However, optimizing transport in these systems, requires characterizing the local QD connectivity and statistical disorder, and determining their relationship to the electronic structure. Using aberration-corrected HAADF-STEM, we analyze several distinct forms of disorder across length scales, and perform calculations to understand their effect on charge transport. Finally, we identify a practical pathway to minimizing the limiting disorder,

Achieving sufficient charge delocalization that an electronic band picture best captures the system's behavior is a crucial but formidable goal in QD SLs. The improved QD coupling resulting from epitaxial connectivity is an important step towards carrier delocalization, however, it depends sensitively on the size of the connecting bridges, which we quantify in Fig. 1e. Importantly, we find 21% of nearest neighbors remain unconnected. Further, we show that unconnected QDs are spaced farther apart than connected QDs (Fig. 1f), with a twofold detrimental impact on carrier delocalization: first, because the QD coupling depends directly on the spacing, and second, because the resulting broadening of the QD-QD spacing distribution diminishes medium and long range SL order, as we discuss below.

To characterize medium and long range order, we extracted QD centroid positions with sub-pixel precision from large field of view, high pixel density STEM images (Figs. 2a-c), then calculated the 2D pair correlation function $G(\boldsymbol{r}) = \int n(\boldsymbol{r}')n(\boldsymbol{r}-\boldsymbol{r}')d\boldsymbol{r}'$ for particle density $n(\mathbf{r})$ (Fig. 1d), which describes the likelihood of finding two particles at a relative displacement $\mathbf{r}$. The anisotropy of the peaks indicates greater shearing disorder than compressive/tensile disorder (Fig. 2d, *inset*), while the broadening of peaks progressively farther from the origin indicates cumulative translational disorder through the SL (Fig. 2e). Quantitative comparison to several models demonstrates that the cumulative disorder is well-described by a paracrystal model (Fig. 2f), which in turn implies the broadening of the nearest neighbor spacing distribution dramatically impacts medium and long range order. Statistical analysis of many datasets shows that translational order is improved by increasing film thickness (Fig. 2. g), suggesting a simple approach to optimizing transport. The expected impact of the improved order with SL thickness is estimated by calculating the charge carrier localization length as a function of translational order using a tight binding Hamiltonian. We find that the localization length improves by an order of magnitude when the film thickness is increased from a QD monolayer to 6 QD layers thick [3, 4].

[1] WH Evers, *et al*., Nano Lett. **13** (2013), p. 2317.
[2] K Whitham, J Yang, BH Savitzky, LF Kourkoutis, F Wise, T Hanrath, Nat. Mater. **15** (2016), p. 557.

[3] BH Savitzky *et al*., Nano Lett. **16** (2016), *p.* 5714.
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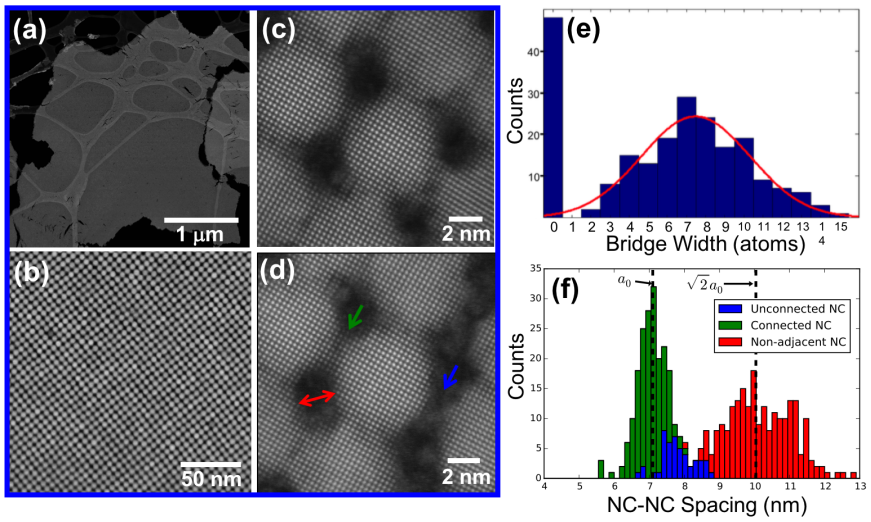

Figure 1. (a-d) STEM images of PbSe QD thin films, forming ~3μm grains (a) of square SLs (b), epitaxially connected via the <100> facets (c) with 21% missing epitaxial bonds (d). **(e)** Distribution of epitaxial bridges, which directly impacts nearest neighbor electronic coupling. A Gaussian fit (*red*) to the nonzero width distribution has a mean of 7.5 atoms and a standard deviation of 2.8 atoms. **(f)** The distribution of QD nearest neighbor spacings, segmented according to epitaxial connectivity. Connected QDs have a mean spacing of 7.0 nm, while unconnected, adjacent QDs have a larger mean spacing of 7.8 nm. More importantly to long range order, the presence of missing bonds increases the standard deviation in nearest neighbor spacings from 3.9 Å to 5.3 Å.

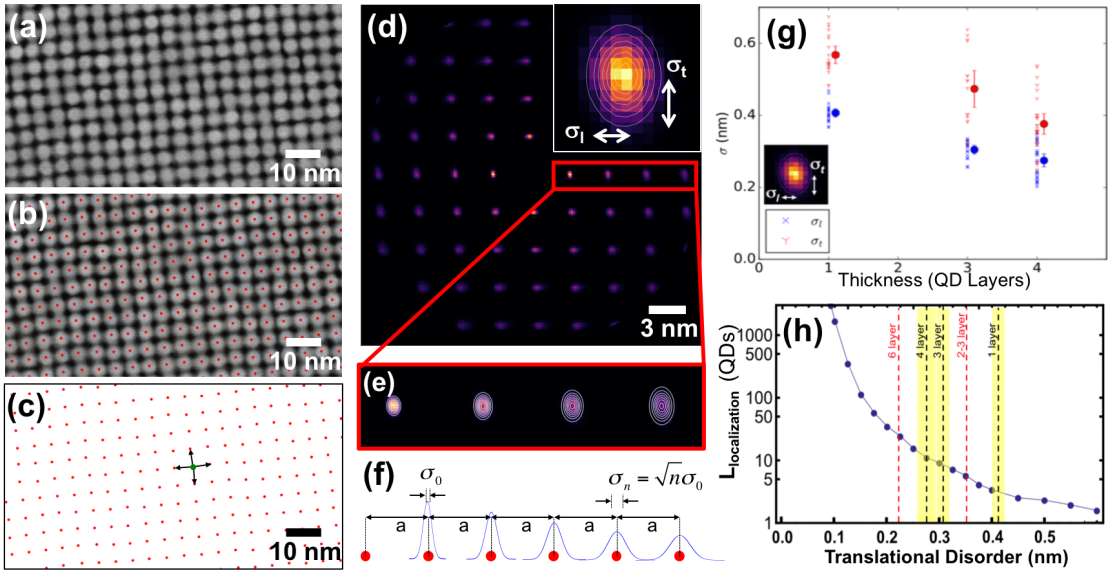

Figure 2. **(a-c)** Calculating the pair correlation function for QD positions from STEM data (a) by first fitting all QD positions (b), then computing the distribution of spacings over all QDs (c). **(d)** The pair correlation function, G(**r**), of QD spacings reveals greater shearing disorder than compressive/tensile disorder (*inset*). **(e)** The growing spread in G(**r**) with increasing spacing between QDs indicates the presence of cumulative disorder, which is quantified and fit to a paracrystal model. **(f)** Schematic of the 1D paracrystal model, in which cumulative disorder results from identical, independently distributed nearest neighbor spacings. **(g)** SL disorder decreases with increasing film thickness, suggesting an approach to controlling disorder. **(h)** Tight binding calculations of the charge carrier localization length, $L_{localization}$, indicate a substantial improvement in delocalization with the observed increase in translational order with growing film thickness.

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