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Binary Nanoparticle Superlattices in 3D: from Quantitative Analysis of Crystal Structures to Characterization of Lattice Defects.

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"Bottom-up" assembly of small building blocks into larger ordered structures is a concept, shared across many disciplines, ranging from supra-molecular chemistry to colloidal crystallization. Colloidal building blocks in the nanometer size range are of particular interest since their electronic structure can be tuned by size, shape and composition, giving rise to exceptional optical [1], magnetic [2] and catalytic [3] properties. Furthermore the potential of nanoparticles to self-organize is perhaps the only method whereby one, two, or more types of materials can be arranged on the nanoscale in an ordered three-dimensional geometry with novel opto-electrical properties emerging from interparticle interactions. Understanding and controlling such systems will require a full 3D characterization of the superlattice structure, including lattice defects, which was until now not available. Here we present our results using electron tomography in combination with image and structure analysis for a comprehensive 3D characterization of binary nanoparticle superlattices.

Electron tomography was performed on superlattices with AB, AB_2, and AB_{13} stoichiometry composed of PbSe and CdSe or PbSe and Au nanocrystals (NC). Preparation of the superlattices proceeded according to literature procedures [4] and examples are presented in Figure 1. Image analysis comprised determination of NC positions by cross-correlation and NC sizes from the radial intensity profile. Structure analysis included characterization of crystallinity by local bond order parameters, fitting of lattice vectors, and statistical analysis of NC positions within the unit cell. The results of the image and structure analysis are presented in Table 1. Particle sizes and unit cell parameters could be accurately measured and the structural prototype of the atomic equivalent determined. In addition, a contraction of the unit cell along the direction perpendicular to the support film was found in three of the four lattices. The contraction indicates that the evaporating solvent, retracting through the superlattice, exerts a force thus deforming the NC soft shell. With respect to lattice defects NC vacancies, substitutions, and grain boundaries could be resolved.

In summary, we have developed a methodology for a comprehensive 3D characterization of binary nanoparticle superlattices. The ability to detect lattice contractions and defects, which induce anisotropy in charge carrier transport, will be instrumental in understanding and tuning the opto-electric properties of nanoparticle superlattices. Moreover, we envision that from the measured NC positions a displacement field and thus strain/stress effects can be deduced.

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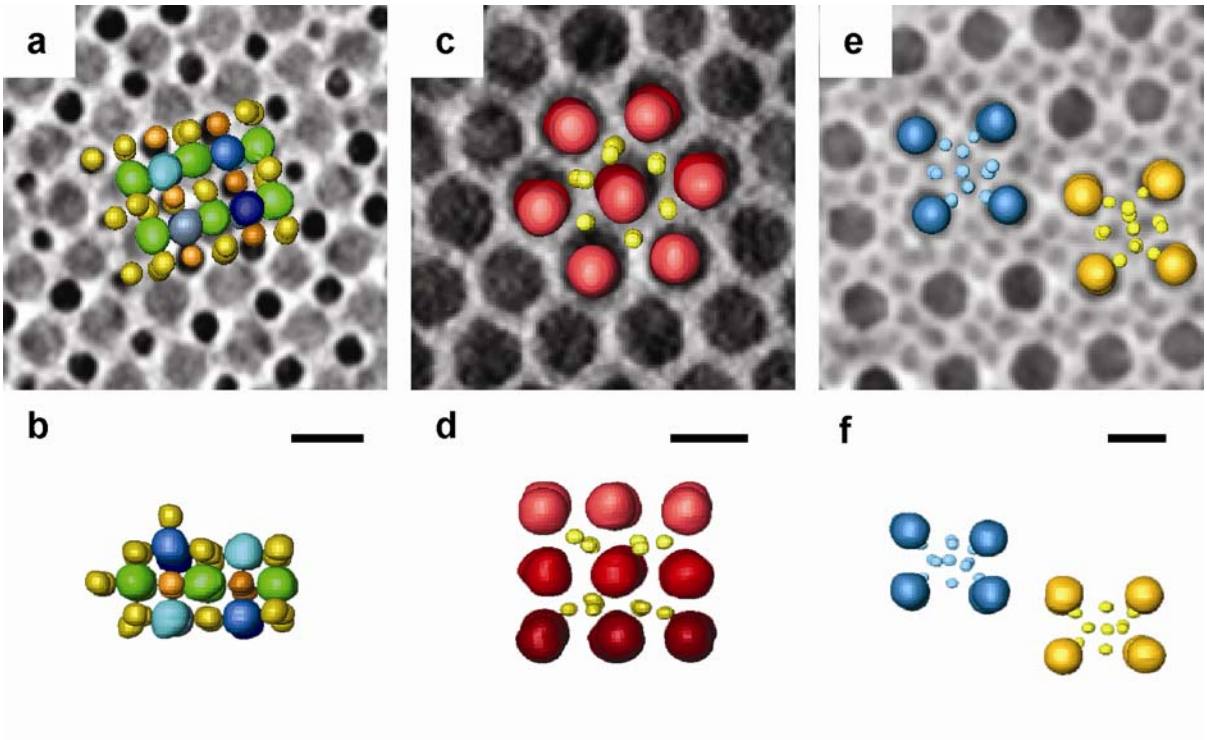

Fig. 1 Numerical cross-sections and segmented region of binary NC superlattices. (a,b) AB lattice composed of PbSe (large) and Au (small), (c,d) AB_2 lattice composed of PbSe (large) and CdSe (small) NC, (e,f) AB_{13} lattice composed of PbSe (large) and CdSe (small). Scale bars are 10 nm.

Table 1 Quantitative analysis of binary nanoparticle superlattices

lattice stoichiometry	particle sizes (mean ± std) [nm] PbSe	CdSe	Au	structural prototype (atomic equivalent)	unit cell vector length (mean ± rms) [nm] A	B	C
AB	6.8±0.5	-	4.6±0.4	CuAu	10.7±0.6	10.5±0.5	10.7±0.6
AB_2	7.1±0.4	-	3.7±0.3	AlB_2	10.0±0.7	10.1±0.6	6.9±0.7
AB_2	9.0±0.3	3.4±0.5	-	AlB_2	11.3±0.7	11.5±0.6	8.4±1.0
AB13	8.8±0.3	3.8±0.4	-	$NaZn_{13}$	13.8±0.5	14.5±0.5	10.3±0.7

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