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Understanding and Designing Crystallographically Oriented Nanocrystal Assembly and
Atomic Attachment

by

Justin C Ondry

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor A. Paul Alivisatos, Chair

Professor Peidong Yang

Professor Alex Zettl

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Abstract

Understanding and Designing Crystallographically Oriented Nanocrystal Assembly and Atomic Attachment

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Justin C Ondry

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor A. Paul Alivisatos, Chair

Colloidal semiconductor nanocrystals, often called quantum dots are small chunks of a bulk semiconducting material. Due to the small size of these materials, quantum mechanical effects modify their properties giving them atomic-like electronic energy levels. If these nanocrystals are brought close enough for the atomic-like states to couple, an artificial molecule or artificial solid may result from the coupling. Thus the assembly would display emergent properties distinct from the isolated nanocrystals. This may allow for the preparation of materials which have properties not displayed in natural materials.

One difficulty is that in order for the coupling to be strong enough to see delocalized states, the nanocrystals must be atomically fused with an inorganic bridge. This attachment is irreversible and thus if the attachment is imperfect, it can trap atomic scale defects such as dislocations at the interface. These atomic scale defects will also interact with carriers potentially preventing the emergence of delocalized states. Currently there isn't a framework for understanding defects in imperfectly attached nanocrystals. As such it is difficult to rationally improve quality in these materials or identify new routes high quality attachment of semiconductor nanocrystals. To this end we aim to better understand the attachment of nanocrystals with a focus on the defects which may form and how to remove those defects.

In this thesis, Chapter 1 outlines the important concepts related to the electronic properties of solids, confined semiconductor physics, nanocrystal synthesis and crystal defects needed to understand the work in this thesis. In Chapter 2, we study the oriented attachment of PbTe using *in-situ* transmission electron microscopy (TEM) to identify optimal attachment facets to minimize defect formation. In Chapter 3, we develop methods to attach CdSe nanocrystals on their prismatic facets, study the defect which form, and understand their removal mechanisms using *in-situ* TEM. The insights from these two studies are used in Chapter 4 to design a clean sheet approach to assemble and atomically attach CdSe/CdS nanocrystals into superlattices with long range translational and orientational order. Finally

in Chapter 5, we discuss the outlook for preparing attached nanocrystal superlattices for realizing artificial band structures.

To My Skis

For getting me out of the lab when I needed it most

More Seriously

To all of those who have been with me for this journey, especially those who now exist in
memories

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Acknowledgments

A PhD dissertation is one person's attempt to create a small unit of knowledge which humanity previously did not have. The small unit of knowledge is not created in a vacuum (unless vacuum chambers are involved), instead it is built on a foundation of human knowledge built over centuries. A fledgling PhD student must first learn everything in the foundation of their project, i.e. they must learn how to learn, and this is no easy task.

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Chapter 1

Properties, Structure, and Defects of Semiconductor Nanostructures and Their Assemblies

1.1 Overview

One overarching goal of this work is to understand how to assemble colloidal nanocrystals into strongly coupled atomically attached arrays. If the coupling is strong enough, a mini-band structure can be engineered in these materials. The properties of the mini-band can be tuned by nanocrystal size, composition, and superlattice geometry. Ultimately it is predicted these mini-band structures may house Dirac cones and non-trivial flat bands which may prove useful for next generation electronics. To realize this goal, materials of sufficient quality (i.e. minimal defects) must be synthesized. In this thesis, we will understand the defects in attached nanocrystal assemblies and use *in-situ* transmission electron microscopy to understand how to remove those defects. Finally we will use the insights from *in-situ* studies to do a clean sheet redesign of new nanocrystal assembly and attachment strategies.

To understand the interplay of the many different aspects related to nanocrystal assembly, attachment, and band engineering, we first do a brief introduction to the various topics. We start by building an understanding of the band structure of solids and the structure of common semiconductors. Next we develop the language of crystallography to rationally describe planes and directions in different crystal structures. Confined semiconductors will form the basis of artificial lattices and thus we understand the effect of spatial confinement on semiconductor structures. We focus on the synthesis and electronic structure of 0D semiconductor quantum dots which can be the “artificial atom” basis for artificial solid. These nanocrystals can be self assembled and atomically fused through a crystal growth mechanism known as oriented attachment. Finally we develop the language of dislocation theory to understand defects which result from imperfect oriented attachment. Together these concepts will be used to understand and engineer properties of semiconductor nanocrystal superlattices.

1.2 Semiconductors From a Chemistry Perspective

Semiconducting materials are the backbone of modern electronics, in part because they are highly amenable to modifications (i.e. addition of part per billion concentrations of impurity atoms) which drastically alter their properties. For example, the conductivity of silicon can be varied over nearly 6 orders of magnitude through appropriate chemical modifications. This rational tunability has allowed the engineering of transistors and other important circuit elements essentially by patterning areas of different conductivity in a silicon substrate. Properties of other materials classes such as metals and insulators, are essentially limited to their intrinsic properties and as such don't have the necessary tuneable properties for device engineering. Understanding and further expanding the tunability of semiconducting materials is always a goal since it may allow additional functionalities.

To begin, we first must understand the origins of semiconductor properties to exploit them. While there are many frameworks for thinking about the properties of solids, we will build up from the properties of individual atoms.^{1,2} This approach is convenient since it highlights the modularity of individual atoms and their arrangement independently tuning properties. Bonding in molecules is often described using the wavefunctions of the atomic species, and interactions between atoms (bonds) are simply linear combinations of the atomic orbitals (LCAO). This builds an intuitive picture of the electronic properties of a given molecular species.

Typically solid materials are crystalline and can contain millions of atoms suggesting a LCAO approach may be unnecessarily complicated. Fortunately a crystalline solid can be described by a repeating lattice of atoms. In actuality, only a single atom and the vector describing the repeat distance is needed (i.e. the unit cell). We will consider the case of an infinite 1D chain of s-orbitals, the wavefunctions for the different electronic states can be described as a linear combination of basis functions ϕ_n .

$$\psi_k = \sum e^{ikna} \phi_n \quad (1.1)$$

In this case the phase factor e^{ikna} determines whether a given pair of orbitals add in-phase or out of phase. k , the wave-vector describes how "in-phase" the given state is. An example of $k = 0$ is shown in Figure 1.1A, this results in the lowest energy configuration. The case of $k = \pi/a$ (Figure 1.1B) results in the out of phase addition of the orbitals which is the highest energy configuration. The wave-vectors allowed within a single unit cell describe all the wave-vectors possible for a given unit cell size and shape, this is known as the first Brillouin zone.³ Points at the edges of the Brillouin zone represent certain points of high symmetry and are often where energy minimum or maximum occur. Depending on the symmetry they are given specific labels, in this case Γ represents the $k = 0$ case and X represents the $k = \pi/a$ wave-vector.

In the intermediate cases of k , a dispersion relation describes how the energy varies as the wave-vector is increased. In the case of a 1D chain of s-orbitals, the energy as a function of wave-vector is described by

$$E(k) = \alpha + 2\beta \cos(ka) \quad (1.2)$$

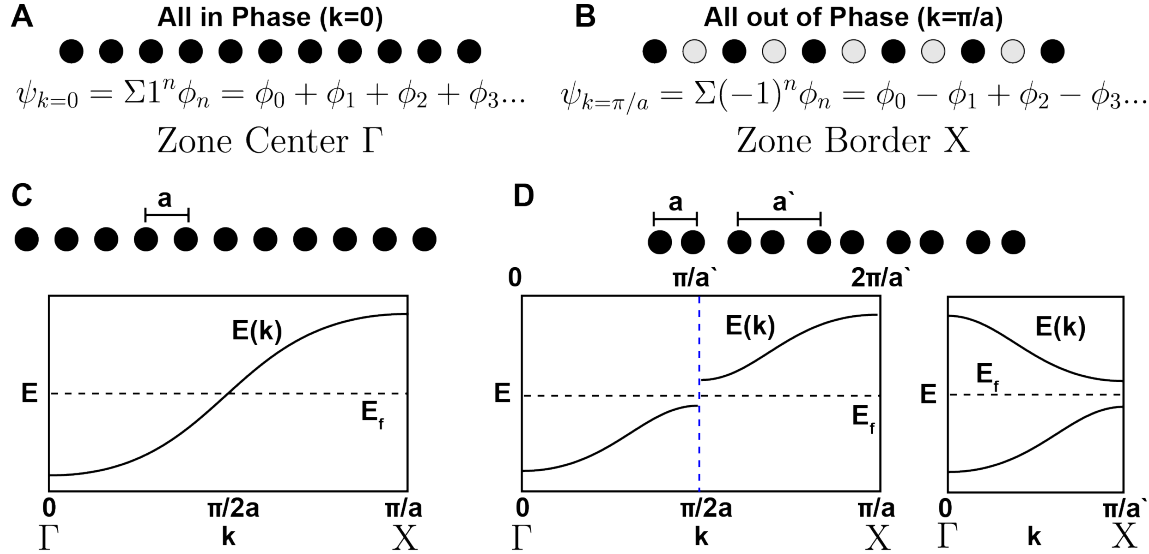


Figure 1.1: Tight binding of a 1D linear chain. (A) s-orbitals all in phase for $k = 0$, representing the Γ -point. (B) s-orbitals all out of phase for $k = \pi/a$, representing the X -point. (C) Dispersion for a uniform 1D chain of s-orbitals. (D) Dispersion of a 1D chain of s-orbitals with a Peierls (Jahn-Teller) distortion.

where α represents an orbital energy term, and β represents a nearest neighbor coupling of the atomic sites, $\langle \phi^*(r) | H | \phi(r - R) \rangle$, where R is the lattice vector. We choose to use the notation analogous to Hückel theory which is more familiar to those with a chemistry background. Figure 1.1C shows the resulting dispersion relation for a 1D chain of s-orbitals. Based on this simple extension of LCAO with a periodic lattice, we see how a single atomic basis can give rise to an energy band in a linear chain of atomic orbitals. This picture builds an intuitive understanding of how modulating structural parameters such as the lattice parameter (which will modulate β) or the type of orbital (p_z orbitals intrinsically have a phase change) will change the dispersion.

If we consider a single electron in each s-orbital, 50% filling of the band states would result. The energy separating filled and unfilled states is called the Fermi level (E_f), analogous to the energy level halfway between the HOMO and LUMO state in a molecule. The lower filled band is known as the valence band and the upper unfilled band is the conduction band. In the current configuration, every electron would be paired, preventing net electronic flow in this lattice. At finite temperature, thermal excitation of electrons to unpaired states would allow current to flow in this material making the 1D chain of s-orbitals metallic. Due to the infinitesimal spacing between states, there are differential occupation of degenerate states, which is energetically unfavorable. The system would prefer to reorganize to stabilize filled electron states, and destabilize unfilled states. This results in what is known as a Peierls or Jahn-Teller distortion.⁴ In the case of a 1D chain of s-orbitals, the result is the bond length of every other bond is decreased, which effectively stabilizes the bonding

interactions. The result is a gap in the energy opens up around E_f at $k = \pi/2a$. Due to the bond length variation, the lattice parameter of the original lattice, a , is effectively doubled to a' . This effectively halves the size of k -space and folds the bands over into a smaller Brillouin zone (Figure 1.1D right). Giving rise to a valence band of filled orbitals and a conduction band on un-filled orbitals. Addition of extra electrons to the conduction band or removal of electrons from the valence band (creating holes) can make the material conductive. A real word example of this are the p_z -orbitals of polyacetylene, which upon doping become highly conductive.⁵

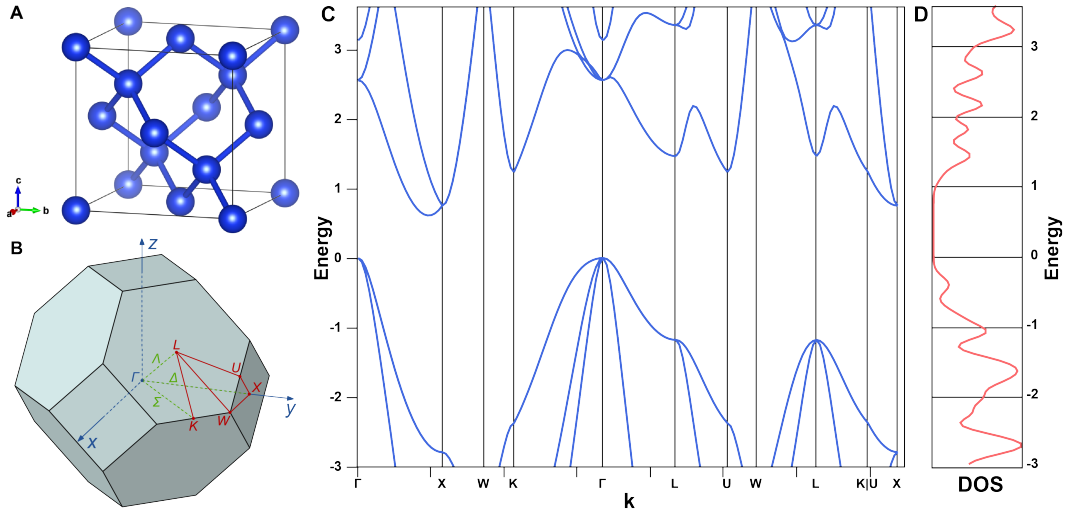


Figure 1.2: Band structure and density of states for silicon. (A) Diamond cubic crystal structure of silicon. (B) First Brillouin zone for the FCC lattice showing symmetry labels for the high symmetry points. (C) Calculated band structure for Silicon (Reference [6]). (D) Calculated density of states (DOS) for silicon.

The ideas presented for the 1D chain of atoms can be extended to 2 and 3 dimensions. As an example we show the 3D crystal structure of silicon in Figure 1.2A which crystallizes in the diamond cubic crystal structure. Next the Brillouin zone (Figure 1.2B) of the FCC Bravais lattice is used to describe the wave-vector along different crystal directions. A band structure of silicon is shown in Figure 1.2C where the dispersion in the silicon lattice is plotted along different directions. For example, the $\Gamma - X$ line represents the dispersion of the energy states along the $\langle 100 \rangle$ directions. Ultimately starting from a single atomic orbital and periodic symmetry, an intuitive understanding of the electronic properties can be built.

Several important properties of a material can be understood from the band structure of a solid. For example the density of states (DOS) is a measure of the number of states in a given energy interval is defined as

$$D(E) = \frac{1}{V} \sum_{i=1}^N \delta(E - E(k_i)) \quad (1.3)$$

which can be determined directly from the band structure. The density of states determines how many electrons can reside in a given energy range, and determines properties such as optical absorption and emission. An example of the DOS for silicon is seen in Figure 1.2D.

As a second example, the ability for current to flow in a (semi)conducting material depends on the response of an electron (or hole) to an external electric field however the mass of the electron is modified by the host giving rise to the effective mass m^* .

$$m^* = \frac{\hbar^2}{\left(\frac{d^2E}{dk^2}\right)} \quad (1.4)$$

We see that the effective mass depends on the curvature to the band. The effective mass is one parameter which determines electrical transport properties of a semiconductor. The examples of density of states and effective mass both properties which depend on both the atomic species and the structure of the lattice. Structural changes to the crystal lattices can be used to engineer properties in semiconductors. For example, compressive strain in silicon can decrease the effective mass. This can be understood by considering the strain leads to increased overlap of atoms (β), and thus more curved bands, thus decreasing the effective mass and making it easier for current to flow. Thus having control over atomic positions allows for the modulation of electronic properties of a given material. Ultimately atomic systems are limited by the crystal structures available to the constituent elements.

1.3 Crystal Structures of Common Semiconductors

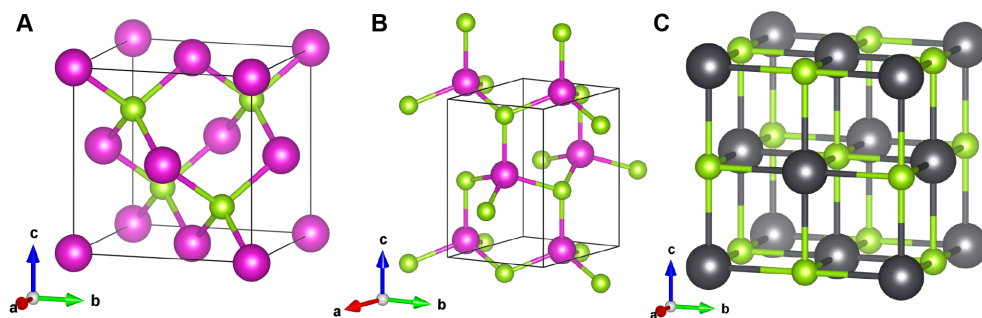


Figure 1.3: Common binary semiconductor crystal structures. (A) zinc blende, (B) wurtzite, and (C) rock salt

While silicon is the material of choice for the microelectronics industry, we will focus on compound semiconductors since they are more accessible to colloidal nanocrystal synthesis. Compound semiconductors are typically composed of binary compounds of group III and group V elements, II-VI or IV-VI compounds. Typically the III-V and II-VI semiconductors adopt a tetrahedral bonding geometry in either the cubic zinc blende phase (Figure 1.3A) or

the hexagonal wurtzite phase (Figure 1.3B). While they appear quite different, they differ only in the second nearest neighbor bonding resulting in an AaBbCc stacking sequence along the $\langle 111 \rangle$ directions for zinc blende and an AaBbAaBb stacking sequence along the $\langle 0001 \rangle$ direction for the wurtzite structure. Small modifications of synthetic conditions can control the phase of many semiconductor materials commonly grown.⁷ Importantly the atomic structure of the lattice modulates the electronic properties of a semiconducting material and as we will later see provides an important handle for controlling the shape of nanocrystals.

We will also consider IV-VI materials typical of the PbX chalcogenides. These materials adopt the rock salt crystal structure (Figure 1.3C) which is also a face centered cubic lattice with the octahedral holes filled. As a result of the change in the bonding geometry compared to zinc blende (octahedral vs. tetrahedral respectively), the two material classes have distinct band structures and the band gap occurs at different zone edges.

1.4 Miller and Miller-Bravais Indices

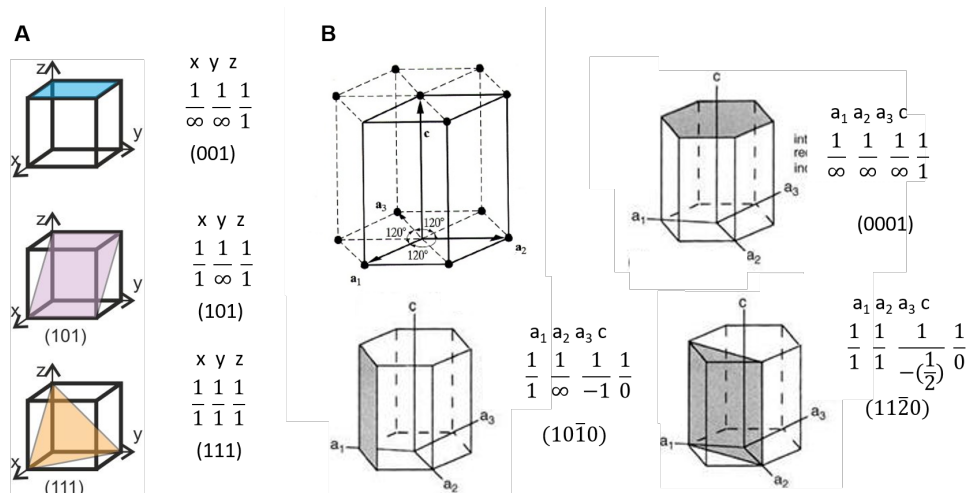


Figure 1.4: Miller and Miller-Bravais indices. (A) To describe planes in a cubic crystal system we use the Miller index system. In this system, the inverse of the intercept of a given plane with the three a_1 , a_2 , and a_3 vectors which are calculated. These three numbers thus describe a unique plane in 3D space. Examples for the (001), (101), and (111) are shown here. (hkl) are used to denote a specific plane. Over-line notation is used to indicate negative intercepts. A direction in a crystal lattice is described by projecting the direction vector onto the a_1 , a_2 , and a_3 vectors is denoted with square $[hkl]$ brackets. (i.e. the $[001]$ points co-linear with the Z axis). (B) To describe planes in a hexagonal system, we use the Miller-Bravais index system. In this system, three vectors (a_1, a_2, a_3) in the basal plane are used to describe the vertical component of the planes, and a single vector (c) is use to describe the inclination. Again the inverse of the intercept is taken for all the planes. Examples of the (0001), (10-10), and (11-20) lattice planes are shown.

Throughout this work we will need to rationally refer to crystal lattice planes and directions. To do this, the Miller index system is used.⁸ In this system, the three lattice vectors a_1 , a_2 , and a_3 bound the unit cell of the crystal (see Figure 1.4A). To describe a given plane in the crystal, we determine the fractional intercept of the plane with the three lattice vectors. Next the reciprocal of that value is calculated and the three resulting values are denoted h , k , and l . A specific plane is denoted with (hkl) . In crystals with high symmetry, there are often several planes that are related by symmetry which are identical, these belong to a family of planes. All planes in a family are denoted with $\{hkl\}$ (see Figure 1.5A). As an example the (001) plane is a facet bounding the top of the cube in 1.4A whereas $\{100\}$ refers to all the planes which are the cube faces. Further to refer to a direction in the crystal we project onto the a_1 , a_2 , and a_3 lattice vectors and use the $[hkl]$ notation to refer to a specific direction and $\langle hkl \rangle$ to refer to the family of directions related by symmetry. In the unique case of the cubic lattice, a direction $[hkl]$ is the surface normal to the plane (hkl) , however this is not general.

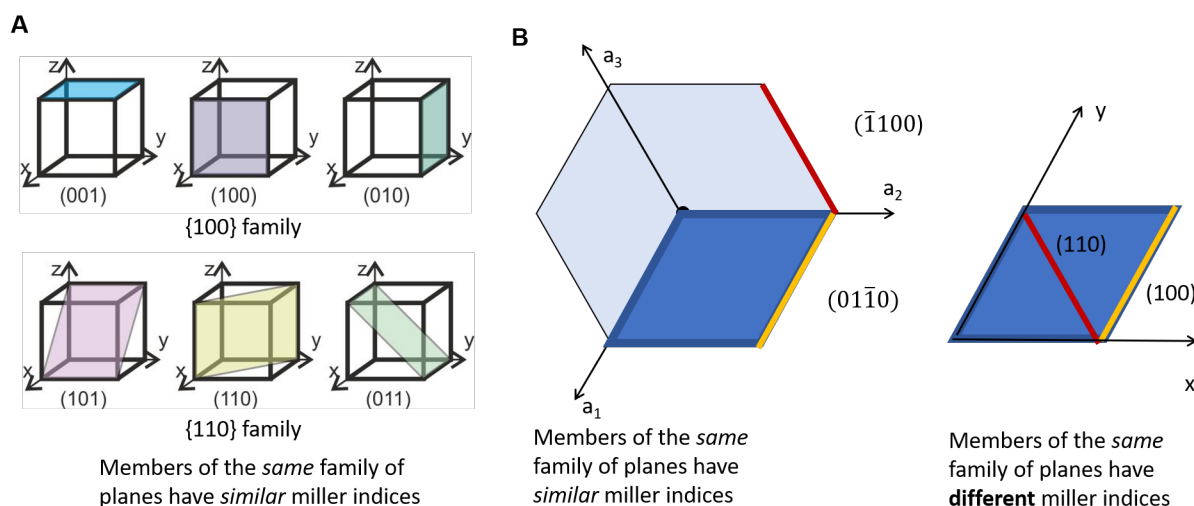


Figure 1.5: Importance of Miller-Bravais Indices for Hexagonal Crystals. (A) In a cubic crystal, Lattice planes which are related by symmetry have miller indices which are a permutation of the possible numeric index. To denote a set of symmetry related planes, curly brackets are used $\{hkl\}$ referring to all planes in that family. (B) In the Miller-Bravais system, the 6 facets terminating the hexagon have are from the $\{1\bar{1}00\}$ family of planes. To highlight the importance of the 4-index Miller-Bravais system, we use the 3-index Miller index to describe the $(01\bar{1}0)$ and $(\bar{1}100)$ planes, which would be labeled (100) and (110) respectively. The confusion of symmetry related planes having different miller indexes is avoided with the Miller-Bravais system.

For hexagonal crystals (e.g. wurtzite), a similar Miller index system is possible, but typically the Miller-Bravais index system is used. In this system, (a_1, a_2, a_3) are three vectors 120° from each other in the basal plane of the hexagonal lattice, and a c vector normal to this. Similar to the Miller index system, we take the reciprocal of the plane intercepts with

the basis vectors to determine the Miller-Bravais index (see Figure 1.4B). To understand the reason for using the Miller-Bravais system with hexagonal crystal systems we consider the notation of two planes which are related by symmetry in a hexagonal crystal system.⁹ In Figure 1.5B we denote two related planes in red and yellow respectively. Using the Miller-Bravais system, the two planes are denoted by $(\bar{1}100)$ and $(01\bar{1}0)$ respectively, ensuring that planes which belong to the same family have *similar* Miller-Bravais indices and the 6 planes which terminate a hexagonal crystal all belong to the $\langle\bar{1}100\rangle$ family of planes. If we attempted to use the 3-index Miller indices, the yellow and red plane would be denoted by (100) and (110) even though these planes belong to the same family. This confusion is completely eliminated by using the Miller-Bravais system.

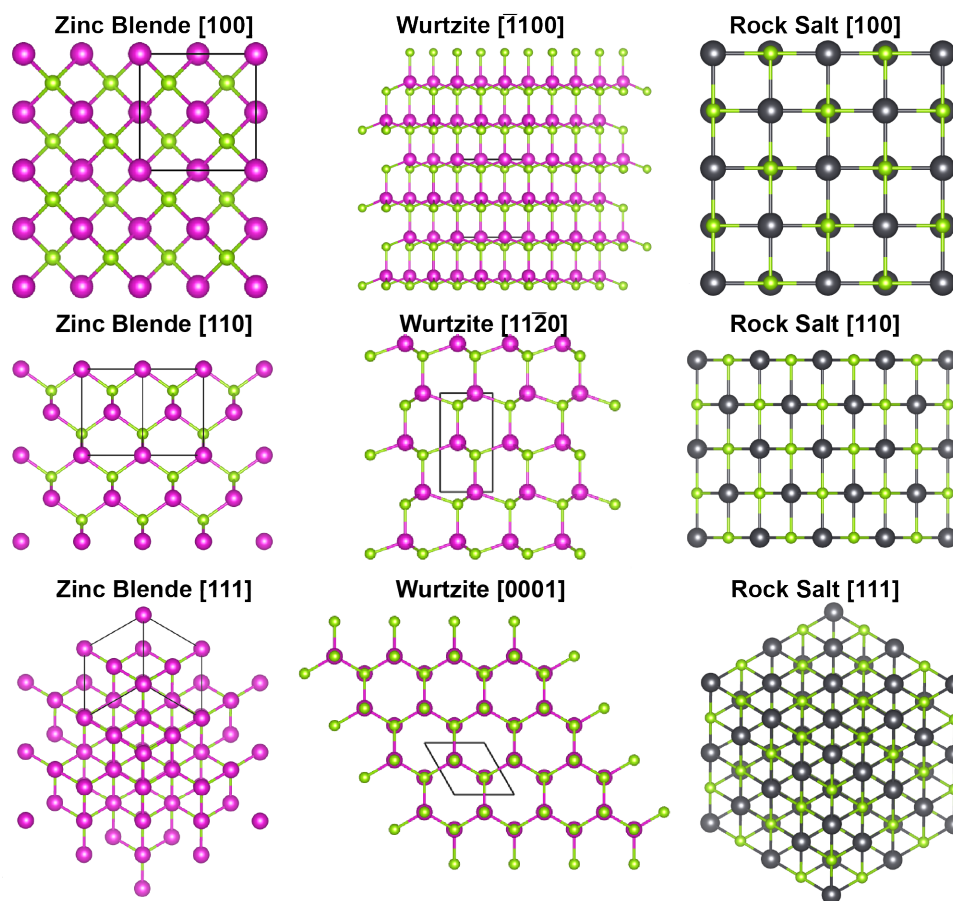


Figure 1.6: Zone axis configurations for common semiconductors.

Now that we have the language of describing crystal geometry, we consider the structure of the three prototypical binary semiconductors. Viewing crystals oriented along specific high index directions (e.g. $[001]$), all the atoms line up presenting a simple 2-D projection of the crystal structure (Figure 1.6). These orientations are important since many microscopy

techniques only allow the view of a 2D projection image of a 3D crystal to be obtained. Certain zone axis images allows for the visualization of important crystal features. For example the stacking sequence of zinc blende and wurtzite can be observed down the $[110]$ and $[11\bar{2}0]$ respectively. Ultimately choosing the correct zone axis orientation will be an important for viewing different defect structures which may be present in semiconductors.

1.5 Spatially Confined Semiconductor Heterostructures

In Section 1.2 we considered the case where we have an infinite array of orbitals, which gives rise to a band structure in a material. Now we consider what happens when the array of atomic orbitals is no longer infinite. In Figure 1.1C, we see that the lowest energy state in the band results from the all in-phase addition of the s-orbitals. Without the infinite number of orbitals, the energy of the all in-phase state is higher with fewer atoms. In essence there are certain parts of the band structure where states cannot exist because that wave-vector is not possible. This results in quantum confinement of the energy states available to a material.

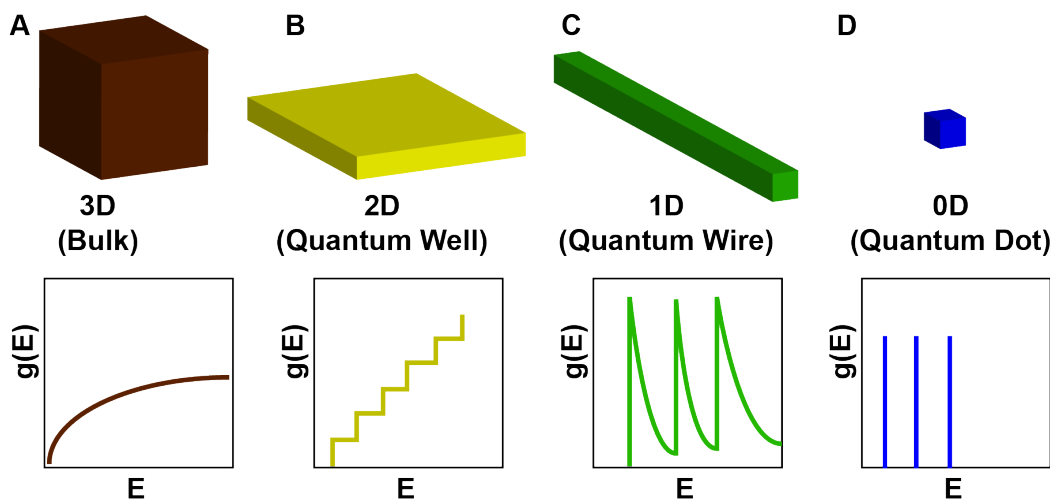


Figure 1.7: Dimensionally confined semiconductors and their density of states. (A) A bulk 3D semiconductor displaying a parabolic dispersion for the density of states. (B) A quantum well 2D semiconductor with a step-function density of states. (C) A quantum wire 1D semiconductor with a sharp density of states, and finally (D) a quantum dot 0D semiconductor with Delta function density of states similar to a molecule.

Depending on the dimensionality of the confinement, different effects are seen on the properties of a semiconductor.¹⁰ In Figure 1.7A, a 3-D bulk semiconductor typically has a $DOS \propto \sqrt{E}$ and it is continuous. With one dimension confined, a quantum well is formed

(Figure 1.7B), and a step function DOS is observed corresponding to the quantization of the energy in the confined direction. In Figure 1.7C, confinement in 2 dimensions results in a quantum wire, which has a sharp density of states with a decay after the maximum. Finally in Figure 1.7 the case of complete confinement in 3 dimensions, a quantum dot is formed which has a sharp, well-defined states similar to a molecule. As such, control of the semiconductor dimensions provides an additional powerful tool for modifying the DOS and thus properties of these materials. In addition to modifying the DOS, spatial confinement also increases the band gap of many materials as schematically indicated by the red-to-blue progression of the different structures in Figure 1.7.

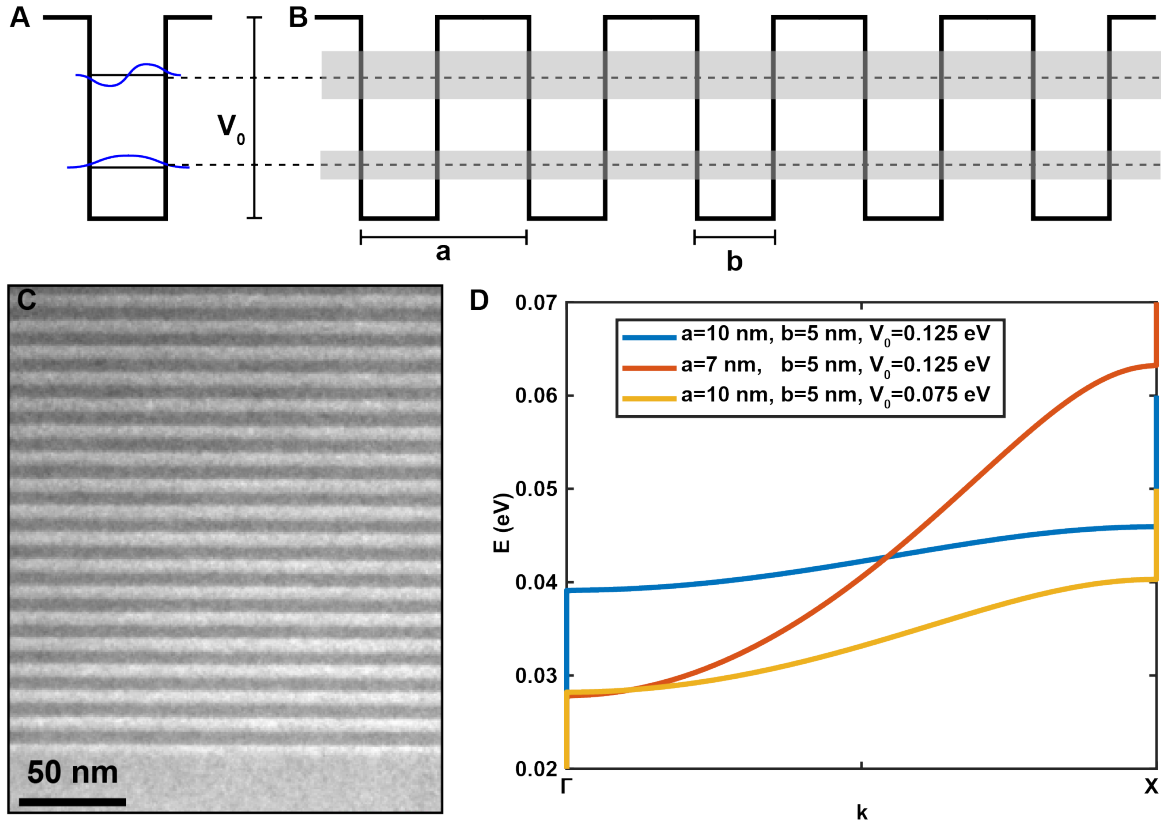


Figure 1.8: Band structure of a quantum well superlattice. (A) A single quantum well with the first two bound states. (B) A quantum well superlattice with resulting coupled quantum well states in grey. (C) Example of a multi-quantum well superlattice (Reproduced with permission from reference [11], Copyright 2017 Nature Publishing Group). (D) Band dispersion of a quantum well superlattice using a Kronig-Penney model. In the orange and blue case the superlattice parameter is modulated, and the band alignments used were for the valence band of a CdSe/CdS superlattice ($m^* = 0.15m_0$). Yellow is to illustrates the effect of V_0 on the band dispersion.

The electronic states of the discrete energy levels in spatially confined semiconductors are often similar to atomic-like states but with a larger spatial extent. For example, in

Figure 1.8A, the electronic states of a quantum well are illustrated. These states are the familiar result of a particle in a 1D square potential (particle in a box). Next we consider an array of quantum wells in Figure 1.8B. Based on our intuition, these states may couple and a dispersion of the energy levels may occur if the barriers are low enough and the wells are close enough. Synthetically these structures are achievable by molecular beam epitaxy techniques as seen in Figure 1.8C.

One way to consider the electronic structure of a quantum well superlattice is through a Kronig-Penney model which solves the plane wave solution for a periodic potential.¹² The resulting transcendental equation

$$\cos(k_z d) = \cos(\alpha a) \cos(\beta b) - \frac{1}{2} \left(\xi + \frac{1}{\xi} \right) \sin(\alpha a) \sin(\beta b) \quad (1.5)$$

where $\xi = \frac{m_{\text{well}} \beta}{m_{\text{barr}} \alpha}$, $\alpha = \sqrt{2m_{\text{well}} E / \hbar^2}$, and $\beta = \sqrt{2m_{\text{barr}} (E - V) / \hbar^2}$ can be solved numerically to get the dispersion. Figure 1.8D shows the mini-band dispersion for an example of a quantum well superlattice with $V_0 = 0.125$ meV, and $(m^* = 0.15m_0)$ for both the barrier and well. These parameters were chosen to correspond approximately to the conduction band of a CdSe/CdS superlattice. Indeed we observe in the case of a 2 nm barrier there is a band width of ~ 30 meV. Slight adjustments to the structural parameters or the offsets can tune the band structure.

Alternatively this problem can be formulated using a tight binding approach.¹³ In this case, the dispersion is

$$E_n(k) = \epsilon_n + \frac{\Delta_n}{2} (1 \pm \cos k_z d) + \frac{\hbar^2 (k_x^2 + k_y^2)}{2m} \quad (1.6)$$

which is identical in form to the 1D chain of atomic orbitals. Thus we can see an artificial band structure can be engineered from an artificial system. Indeed in the case of quantum well superlattices, mini-band structures have been experimentally confirmed.¹⁴ It is important to point out that models like this do not account for the underlying atomic lattice explicitly, and as we will see, errors in the underlying lattice will have a profound effect on nanocrystal derived superlattices.

1.6 Colloidal Semiconductor Nanocrystals

As we have seen, there is a potential to build an entire artificial chemistry around semiconductor heterostructures. However thus far, the example of quantum well superlattices is relatively contrived because the planar geometry is hardly analogous to nearly spherical atomic potentials. Standard semiconductor growth strategies are well suited to creating 1D confined materials by simply depositing different layers of the materials of interest on a substrate. Achieving well controlled spatial confinement in all three directions is much more difficult by traditional methods. Instead wet chemical approaches are well suited for preparing small semiconductor quantum dots.

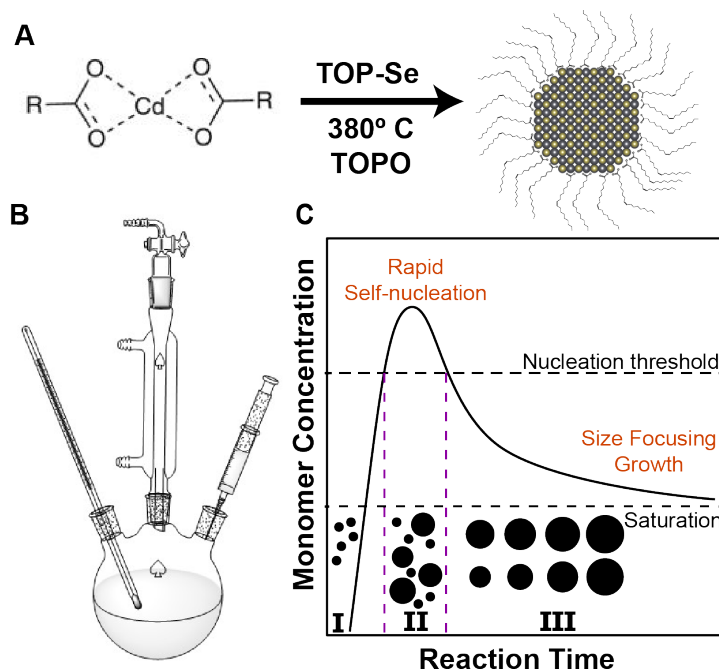


Figure 1.9: Colloidal synthesis of semiconductor nanocrystals. (A) Simplified reaction scheme for preparing CdSe nanocrystals by reacting a cadmium carboxylate with trioctylphosphine-selenium at elevated temperatures in a high boiling solvent (trioctylphosphine oxide). (B) Schematic setup for a hot injection synthesis of colloidal nanocrystals. (C) Simplified reaction scheme for synthesizing narrow size distribution colloidal nanocrystals.

The prototypical materials system for colloidal semiconductor nanocrystals is CdSe. Typically these materials are grown (see Figure 1.9A) by reacting a cadmium carboxylate salt with a soluble selenium precursor (TOP-Se) in high boiling organic solvents (TOPO).^{15,16} This is known as the “hot injection” method typically performed using a reaction setup shown in Figure 1.9B. Over the years, these growth methods have been perfected to yield samples with narrow size distributions and the phase can be reliably controlled to produce nearly phase pure wurtzite and zinc blende samples.¹⁷ A simplified picture of the growth kinetics which yield narrow size distribution semiconductor nanocrystals is shown in Figure 1.9C. The monomer concentration is rapidly increased (II) to create a burst of nucleation, which subsequently consumes monomers such that no more nucleation is possible. In III, where the monomer concentration is below the nucleation threshold, due to the higher surface energy of the smaller particles, they grow faster, allowing them to “catch up” resulting in a uniform size distribution in the final sample.

The quantum confinement in colloidal semiconductor nanocrystals leads to strongly size dependent electronic properties.¹⁸ For example the photoluminescence of CdSe nanocrystals can be tuned from blue to red by increasing the size of the CdSe nanocrystal from ~ 2 nm

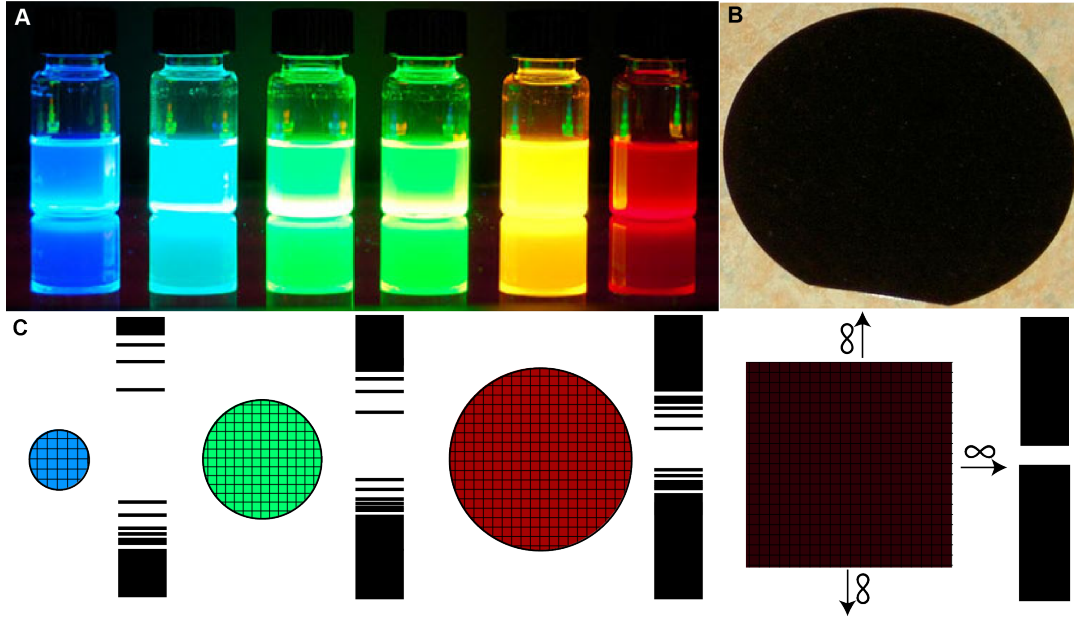


Figure 1.10: Quantum confinement in 0D semiconductor nanocrystals. (A) Photoluminescence from CdSe nanocrystals with increasing size from left to right. (B) Photograph of a bulk wafer of a semiconductor. (C) Schematic illustration of the size and density of states for increasingly large semiconductor nanocrystals and finally a bulk crystal.

to ~ 6 nm diameter (Figure 1.10A). Compared to a bulk semiconductor of the same material (Figure 1.10B) the emission is significantly red shifted.

In a semiconductor material, when a photon is absorbed a bound electron hole pair can be formed. The structure of this exciton is analogous to the hydrogen atom, but with modified masses and dielectric constants. Thus the wavefunctions and energies can be described by a Bohr model with modified masses and dielectric constants

$$E_n = 13.6eV \times \frac{\mu}{\epsilon^2 m_e} \quad (1.7)$$

Where $\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$ is the reduced mass. Further there is a characteristic radius of an exciton, the exciton Bohr radius

$$r_{ex} = 0.529 \frac{\epsilon m_e}{\mu} \quad (1.8)$$

and thus in many semiconductors the exciton can be thought of a a large hydrogen atom. For example CdSe has an exciton Bohr radius of 5.2 nm and for GaAs, 11.3 nm.

In a semiconductor nanocrystal with sizes comparable to the exciton radius, the energy is increased by a particle-in-a-box term

$$E_{conf} = \frac{h^2}{8R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) \quad (1.9)$$

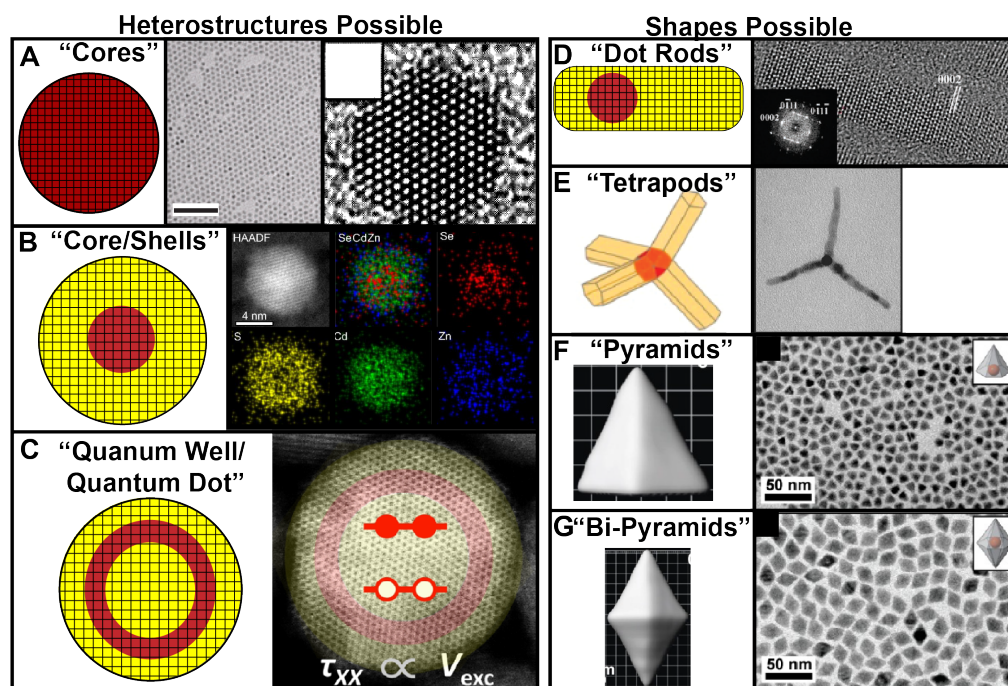


Figure 1.11: Examples of complex shapes and heterostructures of colloidal nanocrystals. (A) CdSe core nanocrystals, image adopted from reference [10] copyright 1996 AAAS. (B) CdSe/CdS core shell nanocrystals, image adopted from reference [19] Copyright 2018 American Chemical Society. (C) CdS/CdSe/CdS quantum well quantum dot, image adopted from reference [20] Copyright 2019 American Chemical Society (D) CdSe/CdS dot-in-rod, image adopted from reference [21] Copyright 2007 American Chemical Society (E) CdSe/CdS tetrapods, image adopted from reference [22] Copyright 2010 American Chemical Society (F) CdSe/CdS pyramids, and (G) CdSe/CdS bi-pyramids. Images adopted from reference [23] Copyright 2017 American Chemical Society

where R is the radius of the quantum dot. Refinement of this approach leads to a progression of hydrogenic orbitals for an exciton which are size dependent as illustrated in Figure 1.10C. In the case of 3D confined quantum dots, the artificial atoms strongly resemble simple atomic species. Importantly unlike atoms, by changing the size of the nanocrystals, the energy and level spacing can be continuously tuned.¹⁰

Beyond changing the size of the nanocrystals, many other structures can be achieved expanding the “modifications” to atoms which are possible. Beyond the simple quantum dot “core” in Figure 1.11A, radial composition variation can be engineered as shown for “core/shell” nanocrystals and “quantum well/quantum dot” structures in Figure 1.11B and C. Further the shapes of these particles can be modified beyond spherical geometries to prepare anisotropic shapes (Figure 1.11D-G). The colloidal route to semiconductor nanostructures offers considerably more diversity than the traditional vacuum deposition routes. The diversity of structures allows for more complex electronic structures to be engineered.

Further the availability of polyhedral shapes beyond spheres has many implications for the self-assembly of these materials as we will see in the next section.

Beyond the synthetic methods available to prepare heterostructures of these materials, they have impressive optical and electronic quality.²⁴ In the early days, difficulties passivating the surface and growing high quality crystals made them inferior to traditionally grown semiconductors. Surface passivation strategies and synthetic methods have evolved to the point that crystal quality and luminescence efficiency of the best colloidal quantum dots is comparable to the best vacuum deposited nanostructures.²⁴

1.7 Nanocrystal Self Assembly and Oriented Attachment

With the narrow size distribution of the colloidal nanocrystals, they can be successfully assembled into highly ordered superlattices *via* self assembly.^{25,26} Many strategies are used to self assemble nanocrystals including solvent evaporation, anti-solvent addition, and depletion assembly. Nanocrystal superlattices can be quasi 2D films or fully 3D faceted super-crystals. Multiple types of nanocrystals can be co-assembled resulting in binary and ternary superlattices which display incredibly rich structural diversity. Much of this self assembly is enabled by the high colloidal stability of nanocrystals with their long organic ligands. These enable reversible interactions *via* Van der Waals forces. As such, large area ordered superlattices can be formed since the particles can find their optimal position. See Figure 1.12A for an example.

Unfortunately the long ligands are large barriers, both in terms of distance and barrier height to coupling.^{29,30} The organic ligands can be replaced by much shorter ligands, but the transport in these materials is dominated by a hopping mechanism rather than band transport. Unfortunately the coupling between the nanocrystals is too low with organic ligands separating the nanocrystals to realize coherent band transport (Figure 1.12A). One way around this is to remove the organic ligands entirely and fuse the nanocrystals with an inorganic bridge as seen in Figure 1.12B. In this case, the electronic states of the individual nanocrystals are strongly coupled. However, the irreversible nature of the attachment makes it much more difficult to find their optimal superlattice positions and structural defects such as dislocations and stacking faults are often trapped in attached materials.

By carefully controlling the ligand removal kinetics and self assembly, large area superlattices of attached nanocrystals with square and honeycomb geometries have been fabricated from truncated octahedron shaped PbSe nanocrystals.^{31,32} These materials display long-range nanocrystal and atomic alignment.³³ While these materials appear to have all the necessary structural parameters to realize an artificial 2D band structure, these materials still display hopping based transport.³⁴ It has been shown that disorder in the nanocrystal positions and the thickness of the necks (which modulates the coupling) cause too much disorder in the material for delocalized states. Likely there are also many defects in these

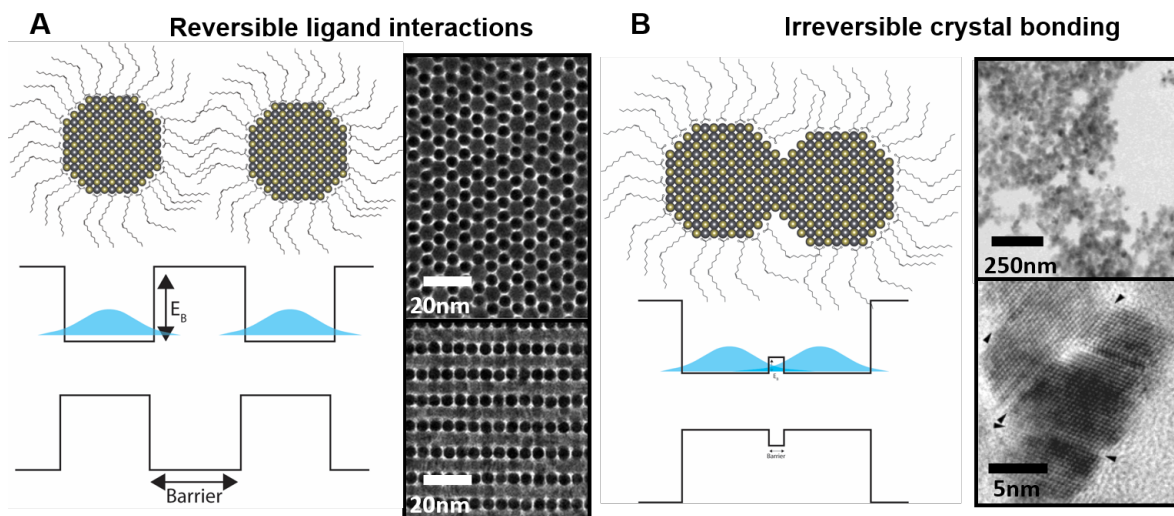


Figure 1.12: Comparison of ligand separated nanocrystals and atomic attachment. (A) Oleate ligand separated nanocrystals, a schematic potential energy diagram, and an example binary nanocrystal superlattice (TEM image adapted from reference [27] Copyright 2015 American Chemical Society). (B) Atomic attached nanocrystals, a schematic potential energy diagram, and example low mag (top) and high mag (bottom) TEM image of attached ZnS nanocrystals (TEM image adapted from reference [28] Copyright 2003 American Chemical Society).

materials due to the stochastic attachment process which may trap or scatter carriers. These atomic scale defects are not accounted for in simple models for understanding the transport in attached nanocrystal samples. Thus there is a need to understand what types of defects are present in these materials, how to remove them or prevent their formation, and their effects on the electronic properties.

1.8 Imperfections in Crystals

Unfortunately the ideal view of crystals, either atomic or super-atomic, is not reality. There are many types of faults in a crystal which break up the perfect order in a crystal.^{35–37} For example, there can be missing atoms (Figure 1.13A), an extra half plane of atoms inserted resulting in a dislocation (Figure 1.13B), or misoriented crystallites which are fused, resulting in a grain boundry (Figure 1.13C). In any case, these types of defects result in atoms which do not have the proper number of nearest neighbors which they can couple to. These dangling bonds can result in states within the band gap (which trap carriers), or the strain can scatter carriers.

While all of these defect types are present in semiconductors and in some semiconductor nanocrystals, we will focus our attention on dislocations. There are many ways dislocations can be formed in materials, but in the case of nanocrystals and oriented attachment, there

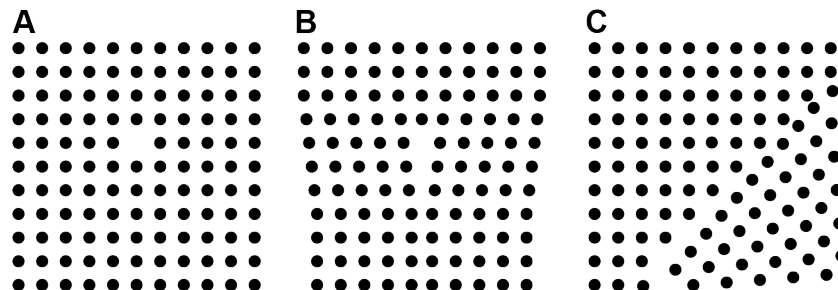


Figure 1.13: Common atomic-scale imperfections in crystals. (A) A vacancy, (B) a dislocation, and (C) a grain boundary.

is only one known mechanism: imperfect oriented attachment.³⁸ Initially nanocrystals are often thought of as small chunks of perfect single crystals which are too small to accommodate structural defects from the synthesis. In the case of two atomically flat surface facets attaching, the crystal perfection will be maintained. However if one of the surfaces contains a surface step, the extra half-plane of atoms is incorporated at the interface between the particles. This results in a dislocation in otherwise defect free nanocrystals.³⁸

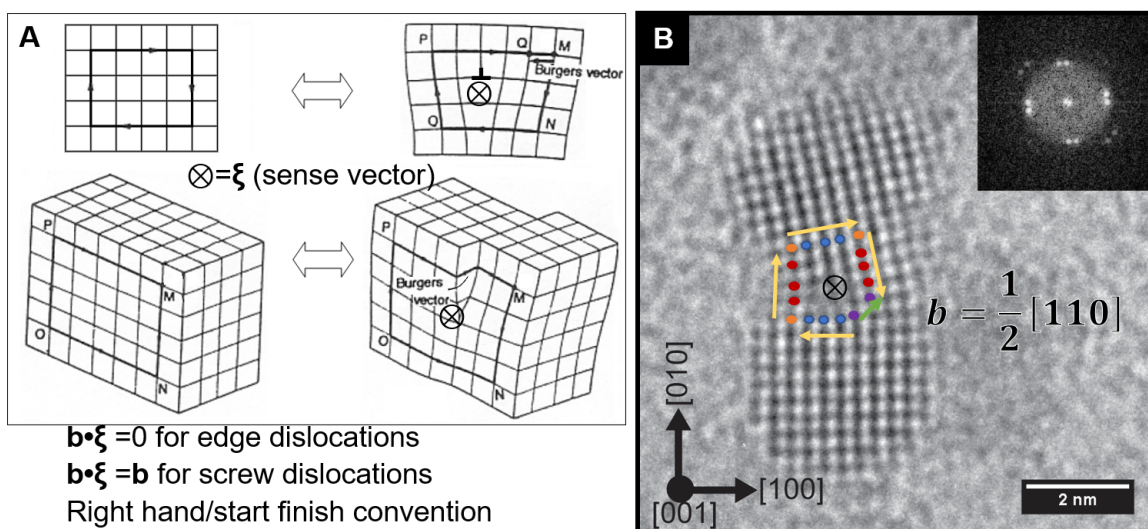


Figure 1.14: The Burgers vector of a dislocation in a crystal. (A) The relationship of the Burgers vector and sense vector for an edge dislocation (top) and a screw dislocation (bottom) (images adapted from reference [39]) (B) Example of burgers vector determination of a dislocation at the interface between two PbTe nanocrystals seen by HRTEM. Atom positions around a burgers circuit are denoted with dots. The Burgers circuit is denoted with yellow arrows, and the Burgers vector is in green.

To rationally describe dislocations in materials, we leverage the language of crystallog-

raphy. A perfect crystal can be defined by drawing a rectangle with edges that are integer multiples of a lattice vector.^{35–37} If the rectangle forms a closed circuit, the crystal is perfect, and does not contain a dislocation. The circuit MNOP in the left of Figure 1.14A is an example of a perfect crystal lattice. Attempting the same circuit for a defective crystal in Figure 1.14A right, the rectangle no longer forms a closed loop. The vector needed to close the loop is defined as the Burgers vector. The circuit drawn to determine the Burgers vector is known as a Burgers circuit. A second important vector is the sense vector which runs parallel with the dislocation line as denoted by $\otimes$ and often referred to as ξ . An important distinction results for dislocations based on the relationship of the Burgers vector and sense vector. In the case where $b \cdot \xi = 0$ (i.e. perpendicular), an edge dislocation results, which can be easily visualized in Figure 1.14A (top right) as an extra half-plane inserted in the lattice. In the case of $b \cdot \xi = b$, a screw dislocation results which can be thought of as a cutting a crystal along a plane and slipping one half across the other by a lattice vector resulting in a helical spiral of the planes around the dislocation (Figure 1.14A bottom right). An example of a Burgers circuit around a dislocation in PbTe observed by HRTEM. The dark points correspond to atomic columns. In this case, we observe a $b = \frac{1}{2}[110]$ edge dislocation.

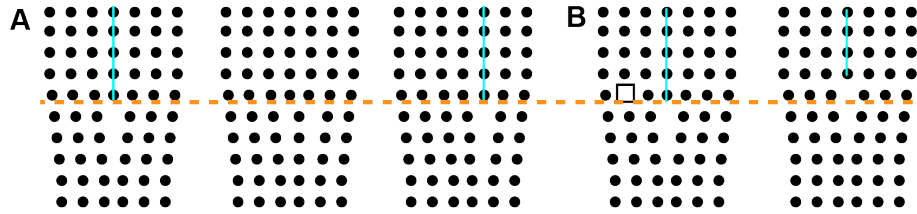


Figure 1.15: Glide and climb of dislocations. (A) Glide of a dislocation where bonds are broken and reformed to allow the dislocation to move in its glide plane (B) Climb of a dislocation where a vacancy (boxed) must coalesce with a dislocation to produce motion. The glide plane is denoted with the orange dotted line. The extra half plane of atoms are denoted in blue

Finally we consider how a dislocation can move in a material and eventually be removed from the material. There are two ways for a dislocation to move in a material. The first is dislocation glide shown in Figure 1.15A. In this mechanism, bonds are broken and remade at the terminus of the extra plane, and this can result in movement of the dislocation (to the right in this case) which can eventually lead to the removal of the dislocation if it glides to a free surface. The second case of dislocation movement is though climb as depicted in Figure 1.15B. In this case, a crystal vacancy coalesces with the terminus of the extra half-plane resulting in the dislocation moving upward. Dislocation glide is a "conservative" process since there is no need for vacancies for movement. Importantly since climb is vacancy mediated, it requires thermally produced vacancies to be present in a crystal, and as such climb is typically much slower than glide at a given temperature.[36]

As we can see, the glide of a dislocation depends on the dislocation geometry. To determine the glide plane of a given dislocation, all we need is the glide plane and sense vector.

The glide plane is defined by $b \times \xi$ where the resulting vector is the plane normal for the glide plane. For edge dislocations, there is a well-defined glide plane for the dislocation. However for screw dislocations there is no single glide plane, and all slip systems can be available for dislocation movement. As we can see, the glide plane defines specific directions which a dislocation may be easily removed, and the goal will be to understand how to ensure these easy removal pathways are possible in defective nanocrystals which are attached.

1.9 Putting it all Together

The underlying motivation for this work is to understand nanocrystal attachment chemistry since it is a route to preparing strongly coupled nanocrystals which may exhibit delocalized states.³⁴ To to this in Chapter 2 we understand the oriented attachment of PbTe nanocrystal pairs to understand, in the context of dislocation theory, the defects present and how they may be removed. Next in Chapter 3 we build on the understanding and study the oriented attachment of CdSe nano-hexagons and the defects which result from imperfect oriented attachment. The insights from understanding the attachment and defects point to several design rules for preparing attached nanocrystal assemblies. Using those insights, in Chapter 4 we design a new approach to nanocrystal assembly and attachment which has design elements to minimize various sources of disorder. The concepts presented in this introduction were are all taken into account during the design of the nanocrystal attachment, since for such a complicated material many competing requirements are needed. Finally in Chapter 5, we will discuss the outlook for nanocrystal assembly and attachment as a route to high quality semiconductor heterostructures.

Chapter 2

Dynamics and Removal Pathways of Edge Dislocations in Imperfectly Attached Lead Telluride Nanocrystal Pairs

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Using *in-situ* high resolution TEM, we study the structure and dynamics of well-defined edge dislocations in imperfectly attached PbTe nanocrystals. We identify that attachment of PbTe nanocrystals on both $\{100\}$ and $\{110\}$ facets give rise to $b = \frac{a}{2}\langle 110 \rangle$ edge dislocations. Based on the Burgers vector of individual dislocations, we can identify the glide plane of the dislocations. We observe that defects in particles attached on $\{100\}$ facets have glide planes that quickly intersect the surface, and HRTEM movies show that the defects follow the glide plane to the surface. For $\{110\}$ attached particles, the glide plane is collinear with the attachment direction which does not provide an easy path for the dislocation to reach the surface. Indeed, HRTEM movies of dislocations for $\{110\}$ attached particles show that defect removal is much slower. Further, we observe conversion from pure edge dislocations in imperfectly attached particles to dislocations with mixed edge and screw character which has important implications for crystal growth. Finally, we observe that dislocations initially closer to the surface have a higher speed of removal, consistent with the strong dislocation free surface attractive force. Our results provide important design rules for defect-free attachment of preformed nanocrystals into epitaxial assemblies

2.1 Introduction

Nanocrystals are sometimes considered perfect pieces of a single crystal because they are often free of non-equilibrium crystal defects such as dislocations and impurities. It is often thought that short diffusion lengths to surfaces where these defects can be removed facilitates the preparation of defect free nanocrystals,^{40–42} however, this is a topic of considerable debate.^{43,44} There is little direct experimental evidence showing the mechanisms for defect removal in nanocrystals. Nonetheless, it would be desirable to leverage this lack of defects in individual particles as building blocks to make larger assemblies of epitaxially connected nanocrystals while maintaining low defect densities. The tunable atomic-like electronic states of individual semiconductor quantum dots behave like that of an artificial atom, and if strongly coupled by placing the quantum dots in an ordered array, the individual states could disperse into a band potentially leading to emergent properties which may not be exhibited by a natural material. Unfortunately, as synthesized, the nanocrystals have long organic ligands on the surface which prevent the necessary coupling. However, there has been progress getting around this by creating epitaxially connected arrays of nanocrystals through oriented attachment with a variety of structures.^{45–50} These structures are theorized to have exotic electronic properties, but they have not been realized experimentally.^{51–54} Defects that arise from the attachment process may be preventing the realization of these exotic electronic structures.^{33,55} Without a microscopic understanding of defect removal mechanisms and the size dependence of these mechanisms in nanocrystals, it will be difficult to realize the goal of creating perfect epitaxial connected assemblies of nanocrystals.

Oriented attachment is the proposed mechanism through which nanocrystals are epitaxially joined.^{56–62} In this process, particles first spontaneously organize so that they share a common crystallographic orientation, then the particles fuse to create a crystallographically coherent interface. The shape of the nanocrystals, faceting, and the ligand coverage all can mediate the attachment process.⁶³ It is believed that this process plays an important role in some mineralization processes,⁶⁴ and the growth of certain types of anisotropic nanostructures.^{60,61,65} Oriented attachment of a pair of nanocrystals provides a starting point for understanding the basic unit of non-classical aggregative crystal growth^{66,67} that is active in oriented attachment growth of materials with 0, 1, 2, and 3 dimensional structures (dots,^{68,69} rods,^{60,61,65} sheets,^{70–72} and bulk solids⁶⁴ respectively). In the ideal case, oriented attachment produces perfect interfaces. However, it is well known that when nanocrystals undergo oriented attachment, if a step edge exists on the surface of one of the particles, it can create an edge dislocation in the attached structure^{56,73} and attachment of multiple particles can give rise to screw dislocations.³⁸ These dislocations have several implications for classical crystal growth and semiconductor properties. Screw dislocations for example, provide self-propagating step edges on the surface allowing crystals to grow by monomer attachments at much lower supersaturations than expected for perfect surfaces.^{74–77} In addition, dislocations in semiconductors are scattering centers for charge carriers, and they can introduce mid-gap trap states which can cause carriers to localize and recombine.^{78,79} By understanding the necessary conditions (time, temperature, nanocrystal size, etc.) required

for removal of dislocations from a single imperfect oriented attachment event, we can begin to design syntheses such that a defect that arises from an imperfect oriented attachment event is removed before subsequent attachment events occur, thus preventing the accretion and trapping of defects deep in the material. Further, there is likely a strong size dependence for defect mobility and by understanding this we can determine upper limits for size of attaching particles, where defect removal is still achieved in a reasonable amount of time.

The close proximity of any given point in a nanocrystal to the surface further complicates understanding the size scaling of defect motion since it is known there is a strong dislocation surface interaction.³⁶ From a continuum elasticity standpoint, this can be understood through the image force construction of dislocation free-surface interactions in semi-infinite crystals. Forces on a dislocation at a free surface is modeled as that between the dislocation in the material and a mirror dislocation of opposite sign placed in the vacuum opposite the interface.³⁶ In this model, the force pulling a dislocation to the surface depends strongly on the distance that dislocation is from the surface and is given, for an edge dislocation, by:

$$\frac{F}{L} = \frac{\mu b^2}{4\pi(1 - \nu)l} \quad (2.1)$$

Where $\frac{F}{L}$ is the force per unit length on the dislocation, μ is the shear modulus, ν is the Poisson ratio, and l is the distance between the dislocation and free surface. Based on equation 2.1, dislocation surface interactions should play a large role in driving dislocations out of nanocrystals faster than expected from a purely diffusion based argument. In nanocrystals, this is somewhat more complicated because there are several surfaces near the dislocation, and thus several superimposed forces act on a dislocation. Finite element methods have been used to more accurately account for this and other complications such as surface and shape relaxations expected in nanocrystals.⁸⁰ Even with these considerations, the highly non-linear distance dependent force on dislocations only cancels out for the exact center of a symmetrically shaped nanocrystal (e.g. cube, sphere) and is an unstable mechanical equilibrium.⁸¹ The barrier to removal of a dislocation in this case is now limited by the Peierls barrier, which is the activation barrier the dislocation must surmount in order to glide.⁸² If the image forces experienced by a dislocation are larger than the Peierls stress of the dislocation, which is the shear stress necessary to overcome the Peierls barrier, it will be driven to the surface resulting in a dislocation free nanocrystal.^{83,84} While the importance of dislocation surface interactions in nanocrystals and nanograins have been explored theoretically, only *ex post facto* TEM images of structurally perfect nanocrystals and nanograins below a critical size provide indirect experimental evidence in support these ideas.⁸⁵

Understanding size dependent defect stability is important for the preparation of epitaxially connected superlattices of nanocrystals through oriented attachment since it puts an upper limit on the size of particles that can likely be attached while maintaining perfect fidelity. There are many pathways to defects in these materials, for example it has been shown that the inherent size distribution of the nanocrystals used for attachment leads to places where nanocrystals in the epitaxial superlattices are not connected³³ and that improving the

connectivity is necessary for realizing delocalized carriers.³⁴ Another potential defect that may be limiting the performance of these materials are dislocations introduced during the stochastic attachment process (see for example the SI of reference [86]). Understanding how these defects can be removed from attached nanocrystals will likely be necessary to create high quality materials. There are examples of *in-situ* TEM observations where defects from imperfect oriented attachment are removed from the attached particles either thermally⁸⁷ or with electron beam stimulation.⁵⁶ However, in these examples, the experiments were not performed with the particles perfectly aligned on a zone axis which prevented identification of important parameters describing the dislocations such as the Burgers vector. Without the knowledge of the Burgers vector, the behavior of a dislocation in a nanocrystal cannot be compared to dislocation theory³⁶ to determine if these well-established ideas apply to nanomaterials.

Dislocation theory provides geometric rules which govern how a defect can move in a material and may give insight for designing defect free attachment of nanocrystals. Most examples of epitaxial superlattices use materials which have the rock salt crystal structure (PbS, PbSe, and PbTe). In the following, we introduce dislocation theory considerations for attaching rock salt nanocrystals. It is commonly understood that oriented attachment typically occurs on nonpolar facets of crystals, thus for the rock salt crystal structure both the $\{100\}$ and $\{110\}$ facets can be used for attachment. Indeed, epitaxial superlattices have been made by attaching PbX (X=S,Se) particles on either the $\{100\}$ and $\{110\}$ facets, suggesting that both routes are viable for preparing these epitaxial superlattices.⁸⁶ However, this does not consider the potential for crystalline defect formation and removal. In the rock salt crystal system, the lowest energy edge dislocation that can be formed has a Burgers vector $b = \frac{a}{2}\langle 110 \rangle$. The glide plane, which is the plane that it is easiest for a dislocation to move in, is defined by the plane normal given by $b \times \xi$ where ξ is the sense vector collinear with the dislocation line.³⁶ For a dislocation to be glissile (able to move), the glide plane of the dislocation must coincide with one of the slip planes of the crystal system hosting the dislocation.³⁶ In the case of PbS, PbSe, and PbTe, in bulk the observed slip planes are $\{100\}$, however this is likely from two sets of $\langle 110 \rangle$ dislocations whose shear sums to $\langle 002 \rangle$,³⁶ and TEM studies on PbS indicate both $\{100\}$ and $\{110\}$ slip planes are active for $b = \frac{a}{2}\langle 110 \rangle$ dislocations.⁸⁸ Thus $\{110\}$ planes are possible slip planes in these crystals and $b = \frac{a}{2}\langle 110 \rangle$ dislocations are glissile. If a $b = \frac{a}{2}\langle 110 \rangle$ edge dislocation was formed at the interface between two PbX particles attaching on $\{100\}$ facets, no matter the exact relationship between the attachment direction and Burgers vector, the glide plane will always intersect the surface of the particles even in the case of attaching multiple particles into a lattice. Figure 2.1 shows all possible Burgers vector and glide plane permutations for $\{100\}$ and $\{110\}$ attachment. Instead, if they are attached on $\{110\}$ facets, for certain configurations of the Burgers vector and attachment direction, the glide plane is collinear with attachment direction meaning the dislocation has a large distance to travel before reaching the surface. In this case, attaching multiple particles into a lattice would require the dislocation traverse a quasi-infinite distance in the glide plane before it is annihilated at the surface. These simple geometric arguments suggest that, for the rock salt crystal system, it should be far easier to

remove edge dislocations when the particles are attached on $\{100\}$ facets compared to those attached on the $\{110\}$ facets.

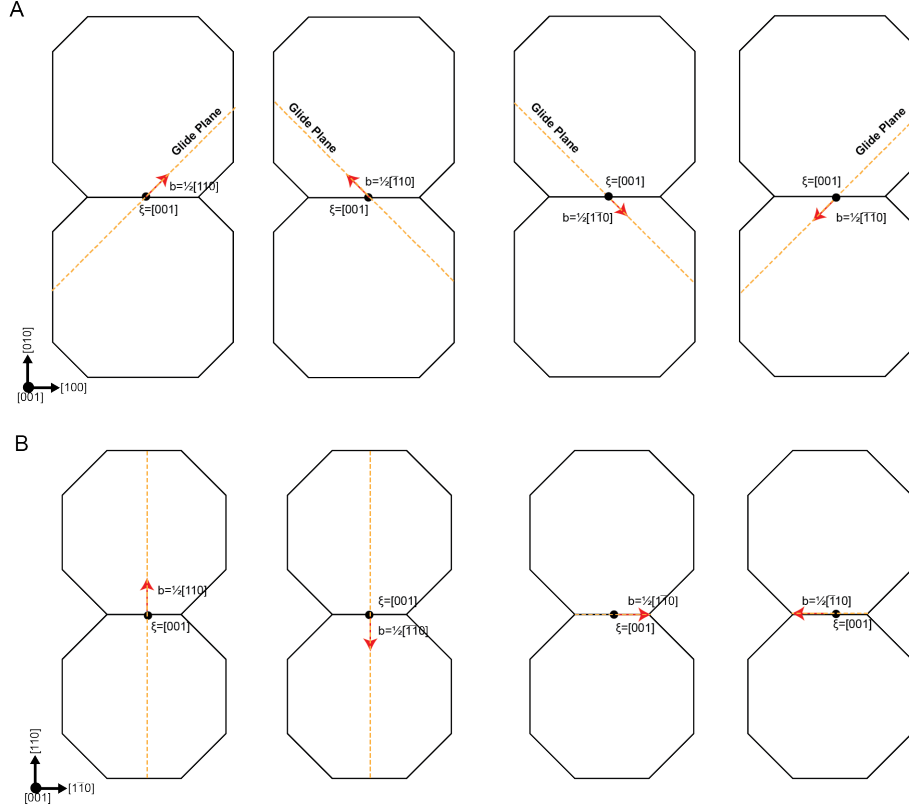


Figure 2.1: Analysis of all the possible Burgers vectors and glide planes for $b = \frac{a}{2}\langle 110 \rangle$ edge dislocations for $\{100\}$ (A) and $\{110\}$ (B) attachment of rock salt crystals. The right two examples of $\{110\}$ attachment are very unlikely because they do not involve step edges, instead it would require the shearing of the crystal by $a[1\bar{1}0]$

In this work, we show using high resolution transmission electron microscopy (HRTEM) that PbTe nanocrystals attached on either $\{100\}$ or $\{110\}$ facets produce $b = \frac{a}{2}\langle 110 \rangle$ edge dislocations. Further, we show using *in-situ* HRTEM that with electron beam stimulation, the $b = \frac{a}{2}\langle 110 \rangle$ edge dislocation in $\{100\}$ attached particles quickly glides to the surface easily producing a defect free interface between the particles. Whereas, the $b = \frac{a}{2}\langle 110 \rangle$ edge dislocation in a $\{110\}$ attached particle undergoes a complex trajectory involving dislocation glide, climb, and conversion to a screw dislocation all while not reaching the surface even after an order of magnitude longer time exposed to the same electron dose rate. Further we analyze the misorientation angle between the two imperfectly attached crystallites and find it is consistent with the continuum elastic solution to an edge dislocation in a thin plate. In addition, we provide evidence that the speed of dislocation removal depends on the initial distance of that dislocation from the surface, which is qualitatively consistent with the image

force description of dislocations at free surfaces. Finally, we discuss how our results indicate two points that should be considered when epitaxially attaching nanocrystals: (1) Once anisotropy has been introduced into a nanostructure, the relationship of the glide plane of possible dislocations and the attachment direction becomes an important consideration for removing dislocations from nanomaterials. (2) Smaller attachment interfaces are more easily made defect free because of strong image forces pulling potential defects out of the material.

2.2 Results

Atomic Attachment of PbTe Nanocrystals on $\{100\}$ and $\{110\}$ Facets

Epitaxial attachment between individual PbX nanocrystals can be induced through several methods such as heating nanocrystal superlattices on a liquid subphase,⁸⁶ chemically treating them to remove surface ligands^{34,46} or simply diluting the particles sufficiently to desorb bound surface ligands. We found that dilution of the nanocrystal surface ligands during solvent processing with toluene or ortho-dichlorobenzene to sandwich ~ 4.0 nm oleate capped PbTe nanocrystals (synthesis, TEM and size distribution shown in Figure A.2.1) between sheets of graphene was sufficient to induce significant attachment of particles on both $\{100\}$ and $\{110\}$ facets (Figure 2.2 A-D and Figure A.2.2). We found that it was important to maintain rigorous oxygen and moisture free conditions during purification and handling of the PbTe nanocrystals to observe epitaxial nanocrystal attachment. Synthesis was performed on a Schlenk line with ultrapure argon (< 5 ppm O_2) which was further purified to < 1 ppb O_2 by a nupure III pre-purifier. Nanocrystals were cleaned in an argon glovebox (< 1 ppm O_2 and H_2O) using anhydrous acetone and dissolved in anhydrous toluene. TEM samples were prepared in a N_2 filled glovebox (< 1 ppm and H_2O) and quickly (~ 3 min air exposure) transferred to the TEM column. Lead chalcogenide nanocrystal surfaces are easily oxidized likely to PbX/PbO or PbX/PbXO₃ (X=Se,Te) surfaces^{89,90} which even a small amount would be sufficient to prevent epitaxial attachment. Due to the low temperature and somewhat uncontrolled nature of the oriented attachment with this sample preparation strategy, we could observe nanocrystals that had undergone both perfect and imperfect oriented attachment. In addition, the nearly cubic shapes of the starting nanocrystals lead to preferential orientation of the particles on $\langle 100 \rangle$ zone axes which is ideal for HRTEM observation due to the large lattice spacing in that direction and the ability of observe $b = \frac{a}{2} \langle 110 \rangle$ edge dislocations.

Figure 2.2 overviews different attachment processes that can give rise to perfect and imperfect attachment on either $\{100\}$ and $\{110\}$ facets. Schematic representation of the attachment process of PbTe nanocrystals that do not contain step edges on $\{100\}$ facets is shown in Figure 2.2A. We experimentally observed the perfect attachment of PbTe nanocrystals on $\{100\}$ facets (Figure 2.2B) by HRTEM imaging with dark atom contrast. The inset fast Fourier transform (FFT) shows sharp spots consistent with a single crystalline domain

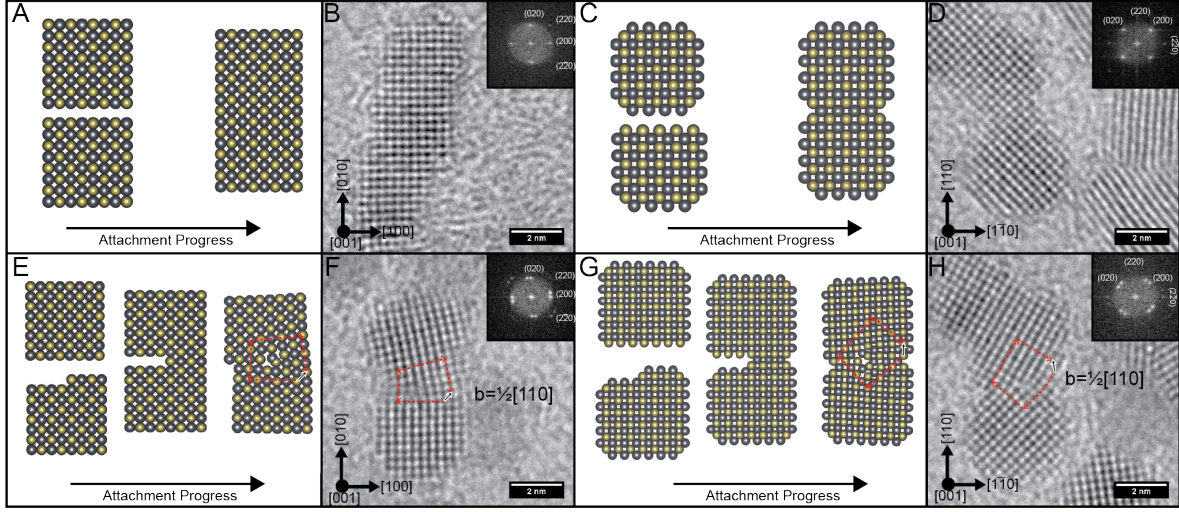


Figure 2.2: (A) Schematic representation of the process leading to perfect attachment of PbTe nanocrystals on $\{100\}$ facets and (B) experimental HRTEM image and corresponding FFT of 3 PbTe nanocrystals that have attached perfectly on the $\{100\}$ facets. (C) Schematic representation of the process leading to perfect attachment of PbTe nanocrystals on $\{110\}$ facets and (D) experimental HRTEM image and corresponding FFT of two PbTe nanocrystals that have attached perfectly on the $\{110\}$ facets. (E) Schematic representation of a step edge leading to a $b = \frac{a}{2}[110]$ edge dislocation during the attachment of PbTe nanocrystals on $\{100\}$ facets. Red dotted arrows outline the Burgers circuit with the Burgers vector shown with a white outlined black arrow. (F) Experimental HRTEM image and corresponding FFT of PbTe nanocrystals attached imperfectly on $\{100\}$ facets with a $b = \frac{a}{2}[110]$ Burgers vector. (G) Schematic representation of a step edge leading to a $b = \frac{a}{2}[110]$ edge dislocation during the attachment of PbTe nanocrystals on $\{110\}$ facets. (H) Experimental HRTEM image and corresponding FFT of PbTe nanocrystals attached imperfectly on $\{110\}$ facets with a $b = \frac{a}{2}[110]$ Burgers vector.

and no crystal misorientation. Figure 2.2C shows a process that can lead to perfect attachment of PbTe nanocrystals on $\{110\}$ facets. We note in the model when viewed as a projection down the $\langle 001 \rangle$ zone axis, it appears that a Te rich facet is reacting with a Pb rich facet, but $\{110\}$ facets are indeed nonpolar and consist of alternating layers of the two elements. We experimentally observed the perfect attachment of PbTe nanocrystals on $\{110\}$ facets (Figure 2.2D) and the inset FFT shows a single crystal pattern consistent with no misorientation. In these experiments, attachment of particles on $\{100\}$ facets was observed much more frequently than $\{110\}$ facets (Figure A.2.2). We suspect that the higher ratio of $\{100\}$ faceting of our nanocrystals, observed by HRTEM of the particles before attachment (Figure A.2.1C), could lead to a greater probability of this attachment pathway however other effects such as ligand binding strength to the different facets may have an effect.

Most of the time, perfect attachment between particles was observed. In surveying our samples across $33\mu\text{m}^2$ and 258 attachment events, $\sim 80\%$ of the particles had perfect inter-

faces. The rest were attached with a mixture of high angle tilt boundaries and imperfect oriented attachment. Imperfect oriented attachment that generated edge dislocations were observed for particles attached on both $\{100\}$ and $\{110\}$ facets. Figure 2.2E shows schematically how a step edge on a $\{100\}$ facet can yield a $b = \frac{a}{2}\langle 110 \rangle$ edge dislocation. Red dotted arrows outline a Burgers circuit around dislocation with a white outlined black arrow for the Burgers vector following the right-hand start finish convention with a dislocation sense going into the page. We experimentally observed similar edge dislocations with Burgers vectors of $b = \frac{a}{2}\langle 110 \rangle$ at the interface between 2 PbTe nanocrystals (Figure 2.2F). The formation of this dislocation is unsurprising since this is the lowest energy dislocation for the rock salt crystal structure.³⁶ In addition, the step edge necessary for the particles to imperfectly attach and yield a $b = \frac{a}{2}\langle 110 \rangle$ edge dislocation is relatively common in the particles used for attachment (Figure A.2.1C). The inset FFT shows two distinct spots for the $\{100\}$ spacing coming from the two distinct nanocrystal domains that are misoriented by the dislocation.

We also observed dislocations form at the interface where particles attached on $\{110\}$ facets. Figure 2.2G shows a schematic process for the generation of a $b = \frac{a}{2}\langle 110 \rangle$ edge dislocation due to a step edge on a $\{110\}$ facet of one of the particles. We experimentally observed a $b = \frac{a}{2}\langle 110 \rangle$ edge dislocation at the interface of two particles that attached on $\{110\}$ facets. The inset FFT shows two distinct spots that correspond to the two misoriented nanoparticle domains. It is interesting that dislocations with the same Burgers vector are formed from attachment of different facets, although this is unsurprising since the $b = \frac{a}{2}\langle 110 \rangle$ edge dislocation is the lowest energy, and there are reasonable surface faceting that can give rise to the same dislocation for both facets. The data suggests that the energetics of the dislocation formation dictates the type of dislocation formed, rather than the facet that is attaching for this material. We observed the formation of $b = \frac{a}{2}\langle 110 \rangle$ edge dislocations on both $\{100\}$ and $\{110\}$ attached particles on multiple occasions (Figure A.2.3) indicating this type of defect formation is common. Another common defect in the rock salt crystal structure is a dislocation with a Burgers vector $b = a\langle 100 \rangle$. We did not observe any instance of this dislocation. This dislocation has a higher elastic energy, which goes as b^2 , and thus we suspect this makes it less favorable to form. Further the formation of a $b = a\langle 100 \rangle$ edge dislocation would require a two atomic layer $\{100\}$ step edge, which we observe few of in the original PbTe nanoparticle sample (Fig A.2.1C).

Removal of $b = \frac{a}{2}\langle 110 \rangle$ Edge Dislocation From a $\{100\}$ Interface

Next, we wanted to understand if $b = \frac{a}{2}\langle 110 \rangle$ edge dislocations are more easily removed from particles attached on $\{100\}$ facets compared to $\{110\}$ facets, which is what would be predicted based on the simple geometric arguments in the introduction. To this end, we collected HRTEM movies of the imperfectly attached particles under $\sim 4000 \frac{e^-}{\text{\AA}^2 \text{s}}$ electron beam irradiation. Recent experimental and theoretical studies have indicated that electron beam irradiation can induce sample excitations similar to thermal excitation,^{91–93} thus performing our experiments at the same dose rate should allow us to compare dislocation dynamics in different samples. Under these conditions we could collect movies with sufficient resolution

to track the dislocation as it evolved (Movie B.2.1). Figure 2.3A shows selected frames from the TEM movie of $\{100\}$ imperfectly attached particles showing the dislocation moves in its glide plane to the surface of the particle where it is annihilated within 24 seconds. The overlaid blue and yellow lines correspond to the (100) and (010) planes which show the extra (100) and (010) plane that is expected for a $b = \frac{a}{2}\langle 110 \rangle$ edge dislocation. At $t=12.2$ s and $t=17.1$ s, we could not distinguish the (010) planes definitively; we suspect the bottom crystal is rotating so quickly during the collection of these frames (1s) that the atom columns are getting blurred. To objectively track the dislocation position as a function of time, we performed geometric phase analysis on each frame of the movie to measure the experimental strain field in the attached particles. Then, the position of the discontinuity in the strain field was taken to be the position of the dislocation for that frame (Details in Figure A.2.4). The position of the dislocation is plotted in Figure 2.3B where the color of each dot corresponds to the time. The edge of the nanocrystal is outlined in black. Overlaid on the plot is the glide plane for the dislocation determined from the Burgers vector clearly showing the dislocation following the $\{110\}$ glide plane directly to the surface of the particle. In addition, we determined the average misorientation angle between the two particles by taking the difference of the average value of the rotation image from geometric phase analysis for each of the two particles (Figure A.2.5). The error bars were determined by measuring standard deviation of the rotation value, determined by GPA, for each crystallite and adding the standard deviations in quadrature. These error bars are both a metric for the intrinsic error in the measurement and to variations in the orientation across individual crystallites due to strains imposed by the dislocation or quick rotation of the lattice during image acquisition. The misorientation angle as a function of time is plotted in Figure 2.3C where the color of each point corresponds to the colorbar in 2B to facilitate comparison. We observe that the misorientation angle between the particles decreases as the dislocation approaches the surface. Further, in frames where one of the crystallites is rapidly changing and shows spatial variation of orientation, such as the bottom crystallite at the $t=12.2$ s timepoint, a larger standard deviation in the misorientation angle is measured.

Removal of $b = \frac{a}{2}\langle 110 \rangle$ Edge Dislocation From a $\{110\}$ Interface

To test our hypothesis that $b = \frac{a}{2}\langle 110 \rangle$ edge dislocations would be more difficult to remove from $\{110\}$ attached particles, we performed the same experiment as above (with the same electron dose rate) on $\{110\}$ imperfectly attached particles (Movie B.2.2). Snapshots from this movie are shown in Figure 2.4A. Initially, the dislocation moves in the glide plane ($t=0$ -87s), but this movement does not bring it any closer to the surface of the particle. This is further highlighted in the dislocation position map determined by geometric phase analysis (Figure 2.4B). In addition to glide, we briefly observe the dislocation move closer to the particle surface ($t=122$ s) seen both in the dislocation position map and in the HRTEM image (Figure 2.4A $t=122.0$ s). While this appears to be progress towards removing the dislocation from the material, it is happening on a much slower timescale than we observed for $\{100\}$ attachment. The slower rate is consistent with dislocation climb,³⁶ where a dislocation

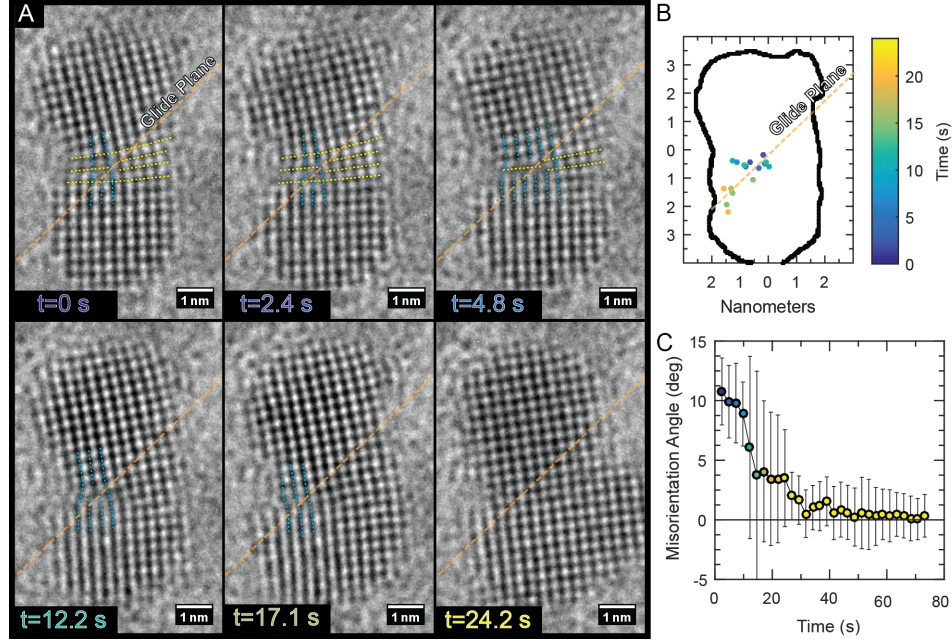


Figure 2.3: (A) Evolution of the $b = \frac{a}{2}[110]$ edge dislocation position during $\sim 4000 \frac{e^-}{\text{\AA}^2 s}$ electron beam irradiation of the two PbTe nanocrystals attached imperfectly on $\{100\}$ facets. Selected HRTEM images with dark atom contrast from the timeseries showing the dislocation removal process. Blue and yellow lines are overlaid on the (100) and (010) planes respectively as guides to the eye. The color of each timestamp corresponds to the colorbar in (B). (B) The dislocation position was determined from geometric phase analysis of a timeseries of HRTEM images. The color of each dot corresponds to the time. Overlaid is the glide plane of the dislocation determined from the Burgers vector. (C) The misorientation angle of the two crystallites as a function of time. The color of each point corresponds to colorbar in (B). Error bars represent the standard deviation of the rotation value difference across the two crystallites determined by geometric phase analysis.

moves out of its glide plane to an adjacent one. However, in dislocation climb, vacancies must coalesce with the dislocation to move it out of the current glide plane, meaning the speed of this process depends on the vacancy concentration in the material and is typically much slower than dislocation glide. Further we observe a small, $\sim 3^\circ$, decrease in the misorientation angle (Figure 2.4C) after the dislocation undergoes dislocation climb moving it closer to the surface ($t=122s$) and the source of the angle change will be discussed later. After the dislocation climb event, the dislocation undergoes a complex trajectory which will be discussed later, but importantly even after $217s$ of $\sim 4000 \frac{e^-}{\text{\AA}^2 s}$ the particle still contains a defective interface (Figure 2.4A). This is consistent with our hypothesis that the collinear glide plane and attachment direction would lead to more difficult dislocation removal.

In addition to dislocation climb, we observe other types of dislocation dynamics later in this defect's trajectory. In two subsequent frames (Figure 2.4A $t=144.0s$ to $146.4 s$),

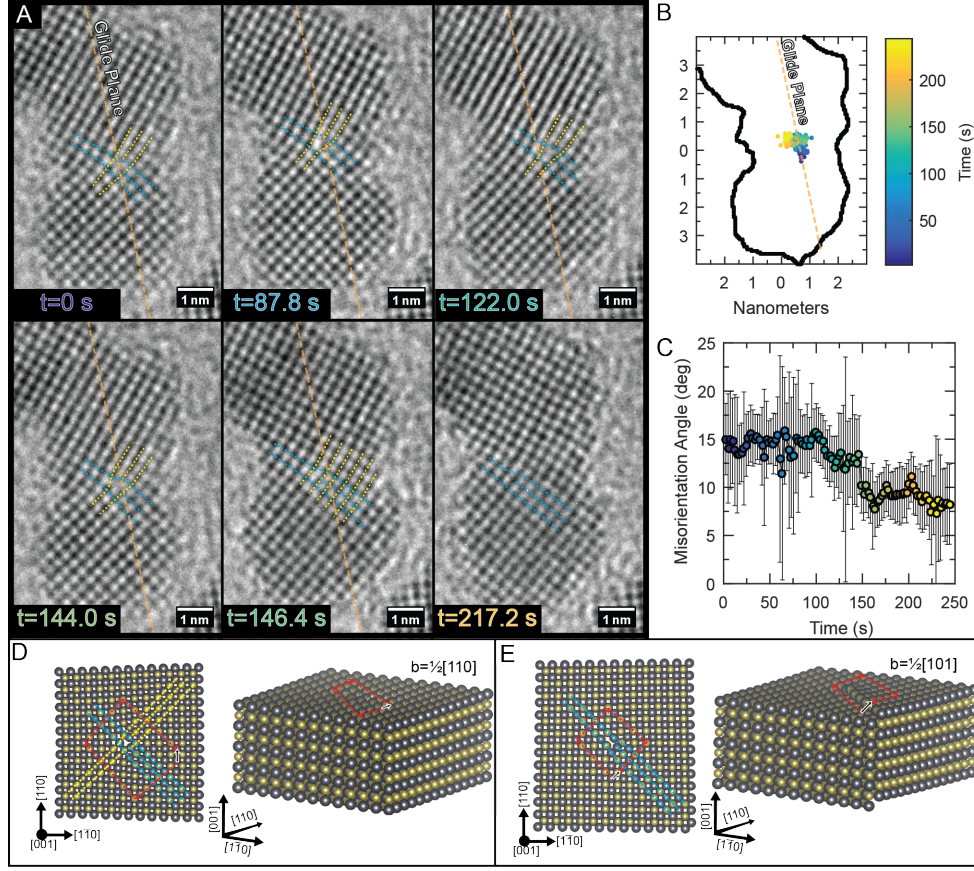


Figure 2.4: (A) Evolution of the $b = \frac{a}{2}[110]$ edge dislocation position during $\sim 4000 \frac{e^-}{\text{\AA}^2 s}$ electron beam irradiation of the two PbTe nanocrystals attached imperfectly on $\{100\}$ facets. Selected HRTEM images with dark atom contrast from the timeseries showing the dislocation removal process. Blue and yellow lines are overlaid on the (100) and (010) planes respectively as guides to the eye. The color of each timestamp corresponds to the colorbar in (B). (B) The dislocation position was determined from geometric phase analysis of a timeseries of HRTEM images. The color of each dot corresponds to the time. Overlaid is the glide plane of the dislocation determined from the Burgers vector. (C) The misorientation angle of the two crystallites as a function of time. The color of each point corresponds to colorbar in (B). Error bars represent the standard deviation of the rotation value difference across the two crystallites determined by geometric phase analysis.

we first observe the defect with orthogonal (100) and (010) extra half planes, consistent with a $b = \frac{a}{2}[110]$ edge dislocation. In the subsequent frame, only the extra (100) plane is present. Based on this projection it would appear that the system now has a $b = \frac{a}{2}[100]$ edge dislocation, yet that Burgers vector is not allowed in the rock salt crystal system and does not make physical sense because it would result in Pb-Pb and Te-Te bonds (Figure 2.5). However, if we consider out of plane, $b = \frac{a}{2}[001]$, character to the Burgers vector of the new dislocation, a sensible structure can be deduced. In this case, the dislocation now has partial

screw character. Figure 2.4D and E shows a crystal model of a dislocation with pure edge ($b = \frac{a}{2}[110]$) character and with partial screw character ($b = \frac{a}{2}[101]$) respectively. It is clear based on the structural model in Figure 2.4E that when viewed along the $[001]$ zone axis, only the (100) extra half plane would be observed. We performed multislice HRTEM image simulations of a $b = \frac{a}{2}[101]$ mixed dislocation and the simulated image is consistent with the experimental image (Figure A.2.6). We note that we cannot determine the handedness of the screw dislocation based on TEM, and the equivalent $b = \frac{a}{2}[10\bar{1}]$ is also possible. The tilted models and overlaid Burgers circuit on the right of each panel highlight the out of plane character that in the proposed screw dislocation. In addition, we observe a $\sim 5^\circ$ decrease in in-plane misorientation angle when the dislocation converts to partial screw character, consistent with a decrease in edge character of the dislocation, which is what gives rise to the in-plane misorientation. Furthermore, we would expect a tilt around the attachment $[110]$ axis of the crystallites if a screw dislocation was present. This can be thought of as a small slice of a twist boundary between two grains which has a characteristic twist angle given by $\theta = \frac{b_{screw}}{D}$ where D is the spacing between screw dislocations.⁹⁴ In this case, the spacing of screw dislocations can be approximated at the neck thickness, and thus we would expect a twist of approximately $\sim 5^\circ$ between the two crystallites. This twist could be manifested as a decrease in contrast due to one of the particles rotating off the $\langle 001 \rangle$ zone axis. Indeed, we observed several cases of screw dislocations (Fig A.2.7) where one of the particles appears to be rotated off zone axis while the other remains on the $\langle 001 \rangle$ zone axis. To corroborate this, we performed multislice TEM image simulations of tilted 3.8nm PbTe cuboctahedra shaped nanocrystals (Fig A.2.8) which showed that a 5° rotation off the $\langle 001 \rangle$

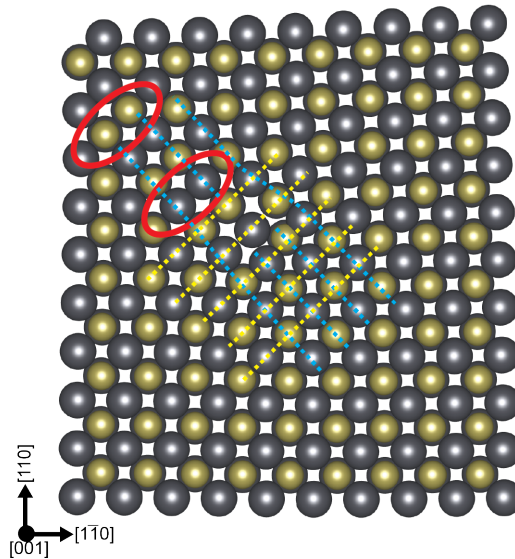


Figure 2.5: Model of a $b = \frac{a}{2}\langle 100 \rangle$ edge dislocation with improper bonding circled indicating this is likely not the true structure.

zone axis was sufficient to result in reduced contrast in the planes whose surface normal is perpendicular to the rotation axis. This evidence further supports the conversion from edge to mixed dislocations in imperfectly attached nanocrystals. Finally, we observe edge to mixed conversion multiple times (Figure A.2.9) indicating that this process is common in imperfectly attached PbTe nanocrystals where the defect takes a significant amount of time to anneal out.

Understanding the Misorientation Angle in Imperfectly Attached Nanocrystals

Based on our data, there is a strong interplay between the misorientation of the two crystallites, the dislocation distance from the surface and the dislocation character. The misorientation angle between the crystallites on both $\{100\}$ and $\{110\}$ attachment is much larger than expected for an isolated dislocation in an infinite crystal. However, we realized the geometry of these attached particles is the same as an edge dislocation in a thin plate.^{95,96} The isotropic continuum elasticity solution for this dislocation geometry has been solved and it predicts that the misorientation angle of the crystal on either side of the crystal depends on the magnitude of the Burgers vector, dislocation distance from surface, and crystal thickness according to equation 2.2 (adopted and rearranged from references⁹⁵ and⁹⁶).

$$\beta = \frac{6by(t-y)}{t^3} \quad (2.2)$$

Where β is the misorientation angle in radians, b is the magnitude of the Burgers vector in Å, y is the dislocation distance from the surface in Å, and t is the crystal thickness in Å. Figure 2.6A shows the geometry and variables described in this equation. This equation provided reasonable predictions for 160 nm thick SnS₂ foils with edge dislocations by careful angle measurements using convergent beam electron diffraction⁹⁵, and recently modern synchrotron based μ -Laue diffraction experiments of misorientation in GaAs thin foil with a single dislocation showed that a continuum model accurately predicted misorientation angles.⁹⁷ Using the dislocation position and misorientation angle that we have determined from the geometric phase analysis, we plotted the misorientation angle as a function of dislocation distance from the surface for the $\{100\}$ attached particles in Figure 2.6B. We observe that the misorientation angle decreases as the dislocation approaches the surface. Further, we measured the crystal thickness at the dislocation position and plotted Eq. 2.2 for that thickness. We can see particularly when the dislocation is far from the surface, Eq. 2.2 provides a good prediction for the misorientation angle. We performed the same analysis for the $\{110\}$ attached particles. In this case, we separated the analysis into the regime before conversion to a mixed dislocation (Figure 2.6C) and after conversion to a mixed dislocation (Figure 2.6D). In the mixed case, only the magnitude of the edge component ($b_{edge} = \frac{a}{2}[100]$) is input to Eq. 2.2 for the Burgers vector since the screw component does not contribute to the in-plane misorientation. In both cases, the agreement between Eq. 2.2 and the experimental data is quite good. Unfortunately for the $\{110\}$ trajectory,

the dislocations did not approach the surface, thus the validity of the equation could not be evaluated as the dislocation approached the surface. Furthermore, the $\{100\}$ attached particles (Figure 2.3 and 2.6B) had a larger contact area between the two crystals and thus a smaller misorientation angle than the $\{110\}$ attached crystals (Figure 2.4 and 2.6C), which is consistent with the inverse relationship between misorientation angle and thickness in Eq. 2.2. Taken together, misorientation angles observed in imperfectly attached particles are consistent with the predictions from a simple continuum elasticity model.

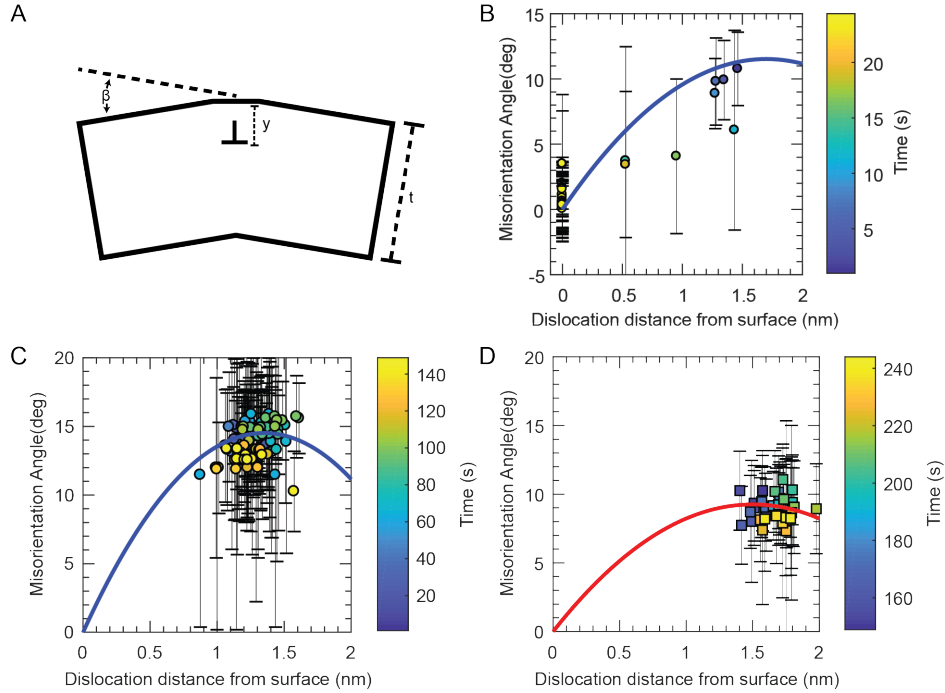


Figure 2.6: (A) Schematic representation of a dislocation in a thin plate described in Eq. 2.2. (B) Misorientation angle a function 2.3. (C) Misorientation angle a function dislocation distance from the surface for the of $b = \frac{a}{2}[110]$ edge dislocation in the $\{110\}$ attached particles shown in Figure 2.4. In both cases, the line is a plot of Eq. 2.2 using the measured thickness of the crystal at the defect and a $b = \frac{a}{2}[110]$ Burgers vector. (D) Misorientation angle a function dislocation distance from the surface for the mixed dislocation from Figure 2.4 observed after conversion to partial screw character. The line is a plot of Eq. 2.2 for the $b = \frac{a}{2}[100]$ edge component of the dislocation. We note that upon conversion to screw character, the dislocation moved towards the opposite surface of the particle, Eq. 2.2 is defined across the whole thickness of the particle and is simply a maximum at the exact middle.

Analysis of Dislocation Removal Speed Across Several Attachment Events

Thus far we have carefully analyzed the trajectories of two dislocations, however we wanted to determine if our hypothesis that dislocation removal is easier for $\{100\}$ attached particles was significant across multiple particles. To do this, we evaluated the dynamics for several particles attached on both facets to determine the average removal speed for those dislocations and understand the generality of our observation. We defined the average removal speed by first measuring the shortest distance between the initial position of the dislocation and the surface, then we determined how long it took the particle to achieve a perfect interface. The dislocation removal speeds at the same electron dose rate for 5 different particles (movies B.2.1-B.2.5) are shown in Figure 2.7. We observe that for particles attached on $\{100\}$ facets, the dislocation is removed more quickly than for those attached on $\{110\}$ facets. In addition, we observe that the initial distance the dislocation is from the surface has a strong effect on the average removal speed. This indicates that the closer a dislocation is to the surface, the faster it moves towards the surface. This is qualitatively consistent with the attractive force expected between a dislocation and a surface based on the image force representation of dislocation surface interactions.³⁶ Indeed, across several attachment events, $\{100\}$ attachment provides much easier dislocation removal compared to $\{110\}$ attachment in the rock salt crystal system.

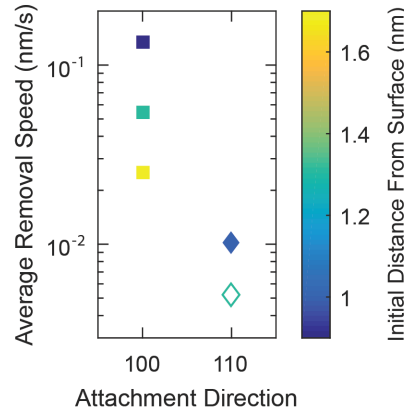


Figure 2.7: Average dislocation removal speed for particles attached on the $\{100\}$ (squares) and $\{110\}$ (diamonds) facets. The speed was determined by measuring the shortest distance between dislocation and the surface and dividing it by the total time needed to achieve a perfect particle. The color of each point shows the initial distance of the dislocation from the surface. All data points were taken at an electron dose rate of $\sim 4000 \frac{e^-}{\text{\AA}^2 s}$. Solid points correspond to particles that achieved perfect interfaces within the observation time, open points did not.

2.3 Discussion

On the importance of attachment direction and size for dislocation removal from nanocrystals

We observe that $b = \frac{a}{2}\langle 110 \rangle$ edge dislocations that result from $\{100\}$ attachment are much easier to remove than $\{110\}$ attachment for the rock salt crystal structure. This is consistent with our hypothesis that the collinear glide plane and attachment direction would lead to more difficult dislocation removal. Our results indicate that care must be taken when attaching nanoparticles to ensure that the glide plane of the dislocation formed intersects a surface. More generally, once anisotropy is induced in a nanoparticle, defects cannot be ignored since it is possible for a dislocation to have a glide plane that does not intersect the surface of the particle. Further, since different materials have different slip systems and low energy dislocations, the attachment directions that are ideal will depend on the crystal structure of the material. In addition, our results imply that many of these undesirable dislocations can be avoided if the starting nanocrystals were free of step edges on the surface. Currently, there is a lack of methods to characterize this parameter in ensembles of nanocrystals, and thus it is unclear which synthetic parameters must be tuned to make smooth nanocrystal surfaces. Careful consideration of these dislocation removal design rules will be important for preparing defect free epitaxial nanoparticle assemblies.

The image force representation of the dislocation surface interactions provides an additional consideration for attachment. A dislocation near the surface is far easier to remove because the distance the dislocation must diffuse to reach the surface is less and because the force pulling the dislocation to the surface increases as the dislocation approaches the surface. The first takeaway is that oriented attachment of small particles is much more likely to produce defect free interfaces because potential interfacial defects are much easier to heal. In support of this, there are several examples in the literature of the preparation of single crystal extended nanostructures which appear to be free of dislocations though the attachment of small (<3 nm) particles.⁹⁸⁻¹⁰¹ Further, these considerations indicate that when attaching larger particles, controlling the shapes such that smaller epitaxial necks form may be better because the small necks will be much easier to heal if imperfectly attached. In the context of epitaxial superlattice assembly, this result indicates that the shape of the starting particles should be controlled such that small necks form initially, and then the necks can be thickened using post synthetic reactions.¹⁰² In the specific case for lead chalcogenide nanocrystals, the ideal shape for epitaxial attachment would be truncated cuboctahedra where the small $\{100\}$ terminating facets are induced to attach, and any defects which may form are easily removed. However, as the desired attachment facet is made smaller, it may increase the likelihood of attachment happening on different facets. Thus, a balance will need to be found between smaller attachment facets needed to minimize defects and larger facets to ensure facet selective epitaxial connections. The limited diffusion length and surface image force, where the importance of the latter has not been fully appreciated until now, combine to greatly facilitate defect removal from colloidal nanomaterials. This explains the ease of preparation

of defect free colloidal nanocrystals of many materials at modest temperatures compared to their bulk melting temperatures. These ideas can be extended to provide guidelines for attaching nanocrystals while maintaining their perfect crystal lattices.

Conversion from edge to mixed dislocations and its implications for classical crystal growth and nanocrystal synthesis

Understanding how a pure edge converts to a screw dislocation is important because the latter are difficult to remove and serve as spots for monomer attachment. From a continuum elasticity standpoint, a screw dislocation has a lower strain energy than a pure edge dislocation with the same magnitude of Burgers vector; thus it is not unexpected that the dislocation converts to partial screw character.³⁶ The timescale of the conversion is intriguing because it happens within 1 frame in our HRTEM movie (1.4s readout time between frames). In addition, there is essentially a discontinuity in the misorientation angle between the two particles when the conversion occurs, which further highlights the speed of the conversion. One possible mechanism for this conversion is the collective shearing in the $\langle 011 \rangle$ direction in the (010) slip plane. Considering the finite number of atomic planes that this occurs over, this mechanism is only reasonable and possible in the smallest nanocrystals. On the other hand, a kink in the dislocation with screw character could also nucleate and propagate rapidly to convert the dislocation to partial screw character. With this mechanism, screw conversion could occur regardless of nanocrystal size since the kink nucleation activation barrier is not as strongly size dependent. Future studies on the size dependent dislocation dynamics in nanocrystals with better time resolution should be able to answer this question.

It was previously hypothesized that imperfect orientated attachment between two particles would likely only give rise to edge dislocations because there is a significant driving force for crystals to achieve full coherence around an axis normal to the attachment direction. Thus imperfect oriented attachment of two particles would not give rise to screw dislocations.³⁸ The only confirmed mechanism for generating screw dislocations in nanocrystals is imperfect oriented attachment of 3 or more particles where one particle lays across a low angle tilt boundary between the two other particles.³⁸ Our results show that it is possible for a pure edge dislocation in two attached particles to convert to a dislocation with partial screw character. This shows there are alternative ways to form screw dislocations during imperfect particle attachment. We observed conversion to mixed dislocations in many instances of two attached particles with either $\{100\}$ and $\{110\}$ attachment (Figure A.2.9), and some already had mixed character initially (Figure A.2.7). It is unclear if they contained mixed character initially, or if they converted during the electron beam exposure while searching and focusing. Importantly, once a screw dislocation is formed, it provides a self-propagating step edge for monomer attachment based crystal growth.^{74,77} Screw dislocations are often cited as the source of step edges that allows for crystal growth to occur at far lower supersaturations than expected if the surface of crystals were perfect. Our results show an additional path-

way for the formation of those defects which could have important implications for further understanding of crystal growth and mineralization processes.

Further, from the standpoint of removing dislocations from imperfectly attached nanocrystals, the character of the dislocation has important consequences. Typically screw dislocations are less mobile than edge dislocations because of larger Peierls barriers^{36,103}, and this is the case for rock salt crystals.^{104,105} Thus, once the screw dislocation forms, it will be even harder to remove. In addition, the image force experienced by a screw dislocation at a free surface is smaller than an edge dislocation with the same magnitude of burgers vector,³⁶ meaning the critical size for defect free nanocrystals is smaller for screw dislocation free materials.⁸³ The combination of larger Peierls barriers and smaller image forces make screw dislocations the most difficult to remove from a nanocrystal. This is observed experimentally in Figure 2.4A where over the course of almost 100 seconds, the mixed dislocation remains in essentially the same location in the crystal. This further highlights the importance of removing the dislocations from nanocrystals quickly to minimize the likelihood of making dislocations with screw character which are harder to remove.

Understanding the misorientation between imperfectly attached nanocrystals

It is interesting to consider the mechanisms giving rise to the misorientation angle between the two crystallites. The ability of individual nanocrystal domains to freely misorient without needing to strain the surrounding crystal causes them to misorient more than expected compared a dislocation cut from a bulk crystal. Further, we observe the misorientation angle between the crystallites decreases as the dislocation approaches the surface. We can understand this by considering the same dislocation geometry as Figure 2.2A. If the dislocation moves upward, the interface below the dislocation increases in length, and it becomes less favorable for a large misorientation angle to be present because a larger number of bonds are highly strained if the angle remains large. Likewise, as the misorientation angle decreases, fewer atomic bonds are highly strained above of the dislocation and thus are not as great of an energy penalty for the misorientation angle to decrease. This behavior is quantitatively captured in a continuum elasticity model by equation 2.2. It is surprising that an isotropic continuum model can predict the misorientation angles measured in the nanocrystals considering the size and discreteness of the bonding at these length scales. We can understand this by considering how the discrete lattice will affect the energy of the system. The continuum model neglects the dislocation core energy, which corresponds to the nonelastic energy at the center where the atom displacements are large. Typically, the dislocation core energy is much smaller than the elastic contributions. Further, changes in misorientation angle may only have a small effect on the magnitude of the core energy. Thus, we suspect the core energy change with misorientation angle will have a small effect on the overall energy of the system compared to the elastic energy reduction that results from misorienting the crystals. Further understanding of the details of the misorientation angle in imperfectly attached

nanocrystals will require more detailed size dependent studies and comparison with results from continuum elastic theories, molecular dynamics simulations, and ab-initio calculations.

2.4 Conclusion

We have studied the dynamics of $b = \frac{a}{2}\langle 110 \rangle$ edge dislocations in PbTe nanocrystals which have imperfectly attached on $\{100\}$ and $\{110\}$ facets. For particles attached on the $\{100\}$ facets, the dislocation follows its glide plane, which lies 45° to the surface, and quickly yields a perfect interface. For particles attached on the $\{110\}$ facets, the glide plane is collinear with the attachment direction. In this case, the dislocation moves in its glide plane initially, but this does not bring the particle any closer to the surface. Instead, the dislocation undergoes a complex trajectory including dislocation climb and conversion to a screw dislocation. These trends were realized across multiple particles by measuring the dislocation removal speed which showed that particles attached on $\{100\}$ facets became perfect an order of magnitude more quickly than for those attached on $\{110\}$ facets. We believe that our results reveal several important considerations regarding crystalline defects in nanocrystals. First, once anisotropy is introduced in a structure, the relationship between the glide plane of the dislocation and the anisotropy direction becomes important. In addition, the observation of pure edge dislocations converting to screw dislocations provides a source of self-propagating step edges which are important growth sites for monomer attachment driven crystal growth. Relating to epitaxially connected superlattices of nanocrystals our results suggest that attachment of PbX particles on the $\{100\}$ facets will make it easier to remove defects than those attached on $\{110\}$ facets. Further we provide direct experimental evidence for dislocation surface attractive interactions in nanocrystals which highlights the highly nonlinear scaling of defect removal kinetics in nanocrystals. To put this in context, II-VI and IV-VI nanocrystals have been successfully prepared with high material quality. However, the development of colloidal nanocrystals of more covalent materials (III-V and IV materials), which have higher Peierls barriers and thus smaller defect free critical sizes, with high material quality lags. Higher temperatures, which are limited in colloidal synthesis, are thus needed to anneal out defects in a reasonable amount of time. With a fundamental understanding of size dependent defect stability and dynamics in nanocrystals, it may be possible to design colloidal syntheses that may prevent defect formation or facilitate removal thus realizing high quality III-V and IV materials colloiddally. The behavior of defects in nanocrystals and how well-developed dislocation theory can describe extended defects in small ($<5\text{nm}$) volumes is a relatively underexplored field and further understanding will be needed to continue the drive to synthesize nanomaterials with ever increasing material quality.

2.5 Materials and Methods

Materials: PbO Lead (II) Oxide 99.9% Sigma; Oleic Acid (OA) 90% Technical grade Aldrich; Octadecene 90% Technical grade Aldrich; *n*-trioctylphosphine 97% Strem; Tellurium Shot 99.9999% Alfa Aesar; CVD graphene on copper 3-5 layer ACS materials; Quantifoil R1.2/1.3 300 mesh Au Holey carbon SPI supplies. All solvents used were purchased as anhydrous with sure seal lids and sparged with argon prior to bringing into an argon filled glovebox.

Nanocrystal synthesis: PbTe nanocrystals were synthesized based on modified methods from Zhu *et al.*¹⁰⁶ 1.0 M TOP-Te was prepared by dissolving tellurium shot in TOP in an argon glovebox (<1 ppm O₂ and H₂O) at room temperature for 36 hours. Next, 900 mg PbO, 7.56 g OA, 16 g ODE were loaded in a 3-neck round bottom flask and heated under vacuum on a Schlenk line at 100°C for 1 hour to complex lead oleate and dry the solution. The flask was refilled with argon (ultrapure <1ppm O₂) 3× and heated to 120°C. 2 ml of the 1.0 M TOP-Te solution was injected and the nanocrystals were allowed to grow for 10 min at 120°C. The reaction was quenched by quickly cooling to room temperature using a water bath. The nanocrystals were cannula transferred to a Schlenk flask and transferred to an argon glovebox. The nanocrystals were washed 3× by precipitating them with excess acetone, centrifuging and dissolving the resulting pellet in toluene. The sample were stored in an argon glovebox. It was found that pristine unoxidized surfaces were necessary for ligand displacement mediated attachment.

TEM sample preparation: Graphene coated TEM grids were prepared by direct transfer of 3-5 layer graphene onto holey quatifoil TEM grids.¹⁰⁷ PbTe particles sandwiched between graphene sheets where prepared based on modified methods for making graphene veils and sandwiches.¹⁰⁸ Briefly, in a glovebox a small droplet of dilute PbTe nanocrystals in toluene was dropped on a graphene coated TEM grid and the droplet was allowed to dry. A second graphene coated TEM grid was placed on top and a droplet of toluene or orthodichlobenzene (ODCB) was placed on the sandwich. This assembly was covered with a glass dish and the solvent was allowed to slowly evaporate for several hours to seal the sample between the graphene. The sample was taken out of the glovebox and quickly (~3min) transferred to the TEM column.

TEM imaging: TEM imaging was performed on a FEI Tecnai T20 S-TWIN TEM operating at 200kV with a LaB₆ filament. Images were taken near Scherzer focus which resulted in dark atom contrast for this crystal thickness. Timeseries of TEM images were collected with a Gatan Orius SC200 using a custom digital micrograph script with full 2048×2048 pixel readout, at a nominal magnification of 400k× resulting in a pixel resolution of $0.13 \frac{\text{\AA}}{\text{pixel}}$, an exposure time of 1s, and a readout time of 1.4s yielding a framerate of 0.4 fps. Since the defect dynamics were beam initiated, care was taken to minimize electron dose prior to imaging. Searching was performed with a spread beam, then once a suitable defective nanoparticle was found, a custom Digital Micrograph script was used to condense the beam to reproducibly return to the same dose rate within a session for each movie acquisition. We estimate a dose rate of $\sim 4000 \frac{e^-}{\text{\AA}^2_s}$ was used for all data collected.

Chapter 3

Design Principles for Atomic Attachment of Wurtzite CdSe Nanocrystals

Reproduced in part with permission from: Ondry, J. C.; Philbin, J. P.; Lostica, M.; Rabani, E.; Alivisatos, A. P. “Resilient Pathways to Atomic Attachment of Quantum Dot Dimers and Artificial Solids from Faceted CdSe Quantum Dot Building Blocks” *ACS Nano* **2019**, 13, 12322–12344. Copyright 2019 American Chemical Society

The goal of this work is to identify favored pathways for preparation of defect resilient attached wurtzite CdX ($X = \text{S}, \text{Se}, \text{Te}$) nanocrystals. We seek guidelines for oriented attachment of faceted nanocrystals that are most likely to yield pairs of nanocrystals with either few or no electronic defects, or electronic defects that are in and of themselves desirable and stable. Using a combination of *in-situ* high resolution transmission electron microscopy (HRTEM) and electronic structure calculations, we evaluate the relative merits of atomic attachment of wurtzite CdSe nanocrystals on the $\{1\bar{1}00\}$ or $\{11\bar{2}0\}$ family of facets. Pairwise attachment on either facet can lead to perfect interfaces, provided the nanocrystal facets are perfectly flat and the angles between the nanocrystals can adjust during the assembly. Considering defective attachment, we observe for $\{1\bar{1}00\}$ facet attachment that only one type of edge dislocation forms, creating deep hole traps. For $\{11\bar{2}0\}$ facet attachment, we observe that four distinct types of extended defects form, some of which lead to deep hole traps while others only to shallow hole traps. HRTEM movies of the dislocation dynamics show that dislocations at $\{1\bar{1}00\}$ interfaces can be removed, albeit slowly. Whereas only some extended defects at $\{11\bar{2}0\}$ interfaces could be removed, others were trapped at the interface. Based on these insights, we identify the most resilient pathways to atomic attachment of pairs of wurtzite CdX nanocrystals and consider how these insights can translate to creation of electronically useful materials from quantum dots with other crystal structures.

3.1 Introduction

Self-assembly of colloidal nanocrystals (NCs) into superlattices is a tunable strategy with great potential to prepare materials with rationally designed properties.²⁶ Much of the tunability comes from the separation of the synthesis of individual NC building blocks from the assembly process. The ability to systematically control factors such as NC size,²⁷ surface ligands,^{109–112} assembly solvent,¹¹¹ NC faceting,¹¹³ assembly method,^{114–117} and other factors have allowed the preparation of superlattices with impressive 2D¹¹⁸ and 3D¹¹⁹ ordering, multicomponent diversity,¹²⁰ substitutional doping,¹²¹ quasicrystalline order,^{122–124} and long-range crystallographic orientation,¹²⁵ among others.

One significant limitation of this strategy for the preparation of optoelectronic materials is the insulating nature of the organic surface ligands used to synthetically control the size and shape of the NCs. The organic surface ligands also appear necessary to achieve highly ordered NC assemblies.¹²⁶ This requirement is limiting, however, because the ligands present a significant barrier to coupling of electronic states between individual NCs, hampering collective phenomena such as carrier transport, miniband formation, or superradiance. Their insulating nature can be partially mitigated by replacing them with short chain bidentate ligands^{29,30,127} or amorphous inorganic material,^{128–130} however, these still prevent the strong coupling necessary for some of the most interesting emergent optoelectronic phenomena.

One way to circumvent the coupling barriers introduced by surface ligands is to eliminate them entirely and chemically fuse the NCs,¹³¹ which if the NCs share the same crystal orientation, can lead to crystallographically coherent NC arrays.^{34,46,49} Fusing the NCs can dramatically increase the conductivity of the arrays indicating strong NC coupling.^{49,132} One complication of this strategy is the irreversible nature of the chemical attachment of NCs which can trap structural defects such as dislocations at the interface of imperfectly attached NCs.^{38,73,86} Much like their bulk counterparts, dislocations in imperfectly attached NCs likely introduce undesirable mid-gap trap states.^{78,79} Furthermore, disorder in the attached NC superlattice structure, which can prevent carrier delocalization,¹³³ may also be introduced by dislocations. Thus, the realization of many of the theorized collective properties of attached NC arrays^{51,54} will remain elusive until strategies to sufficiently reduce the density of electronically deleterious defects are developed.

Throughout the maturation of the traditional semiconductor industry, deleterious defects have been eliminated to an acceptable level for specific applications.^{35,134} Defect elimination was achieved through an unrelenting cycle where “harmful” defects were identified, their formation mechanism understood, and, finally, appropriate changes to the process were developed which lead to their elimination.^{135–137} A similar virtuous cycle over the last 25 years has led to the development of semiconductor CdSe/CdS NCs with exceptionally high photoluminescence quantum yields.²⁴ Without an understanding of the defects present, their electronic and structural consequences, and their formation pathways, it is difficult to devise procedures that prevent defect formation or remove defects from chemically fused NC arrays.

In addition, there are many examples where crystal imperfections have desirable properties and are purposely engineered into materials. One example in semiconductors is the

intentional doping of grain boundaries of polycrystalline CdX solar cells or photodetectors with chlorine to engineer p-n junctions at the grain boundaries.^{138–142} Another example is the preparation of stacking fault and twin boundary superlattices for quantum well structures.^{143–146} Preceding structural defect engineered materials is an understanding of the defect formation mechanisms, their properties and their stability, however in this case the motivation is to identify defects with desirable properties, the process to form them, and the conditions under which they are stable.

To begin to address dislocation formation and stability in imperfect oriented attachment, Ondry *et. al.* used transmission electron microscopy (TEM) to study the removal pathways of well-defined edge dislocations at the interface of two rock salt PbTe NCs attached on $\{100\}$ and $\{110\}$ facets.¹⁴⁷ They found that attachment on $\{100\}$ facets lead to dislocations with an easy pathway for dislocation removal. On the other hand, attachment on $\{110\}$ facets resulted in a dislocation that had no easy path to the surface. Two important takeaways, in the context of preparing defect-free materials, from this work are as follows: the primary NCs should be prepared to avoid stepped surfaces as they lead to dislocation formation, and through careful analysis of *in-situ* TEM observing dislocation trajectories, optimal attachment geometries which facilitate dislocation removal can be identified. In a different context, the considerably retarded removal kinetics for imperfect $\{110\}$ attachment compared to $\{100\}$ attachment provides an opportunity to engineer stable dislocations in materials which may have desirable properties. While this work provided a framework for how to approach the preparation of dislocation free pairs of NCs, it did not consider the electronic consequences of the attachment or whether and resulting defects will be deleterious to materials performance.

Wurtzite CdSe and CdSe/CdS core/shell NCs are by far the most well-developed semiconductor NC building blocks in terms of material quality,²⁴ shape control,¹⁴⁸ optical properties,¹⁴⁹ and theoretical understanding.¹⁵⁰ With these considerations in mind, it is desirable to build more complex assemblies out of these prototypical materials. Thus, there is good reason to develop defect resilient oriented attachment strategies for CdX materials. However, the wurtzite lattice is considerably more complex than the rock salt PbX lattice. In terms of dislocations (1D defects), there are 13 distinct perfect dislocations¹⁵¹ and 18 distinct partial dislocations possible.¹⁵² In addition, there are two distinct classes of stacking faults (2D defects) possible: basal plane stacking faults (which alter the AaBbAaBb stacking sequence)¹⁵³ and prismatic stacking faults (PSFs) (which result in a 4/8 member ring structure),¹⁵⁴ both of which can modify electronic structures in these materials.^{155,156} Stacking faults present good candidates for preparing metastable defect engineered materials due to their small formation energy, especially for II-VI materials.^{157,158} Further complications arise due to the non-centrosymmetry of the wurtzite lattice which can lead to other planar defects such as inversion domain boundaries.¹⁵⁹ The plethora of possible defects in wurtzite compared to rock salt is a result of the lower symmetry of the lattice and the tetrahedral bonding geometry and thus considerably complicates the considerations for engineering oriented attachment. To begin to consider the attachment of wurtzite NCs, we focus on the nonpolar prismatic facets: the $\{1\bar{1}00\}$ facet and the $\{11\bar{2}0\}$ facet. These arise through cutting the wurtzite

lattice with hexagons rotated 30° relative to each other. Synthetically, the $\{1\bar{1}00\}$ facet is typically seen for colloidal CdX NCs,^{148,149,160–164} and investigation of the $\{11\bar{2}0\}$ facet and its attachment possibilities has been considerably hampered by the difficulty in preparing $\{11\bar{2}0\}$ facet terminated CdX NCs.

In this section, we work to develop a detailed understanding of the defects that are formed when colloidal CdSe NCs are chemically attached into crystallographically coherent arrays. Specifically, we characterized the defects that form, their electronic consequences and how easily they can be removed once formed. We successfully prepared well-faceted CdSe NCs terminated with either the $\{1\bar{1}00\}$ or $\{11\bar{2}0\}$ (throughout this work, we use the 4 index Miller-Bravais notation⁹ for hexagonal crystals) prismatic facets, and we demonstrated that a methanolic Na₂Se solution can be used to remove the ligands and chemically fuse the NCs. Using HRTEM, we identified $b = \frac{a}{3}\langle 2\bar{1}\bar{1}0 \rangle$ edge dislocations in the case of attachment on $\{1\bar{1}00\}$ facets. In the case of attachment on $\{11\bar{2}0\}$ facets, we observed prismatic stacking faults (PSFs), $b = \frac{a}{2}\langle 10\bar{1}1 \rangle$ partial dislocations bound by a PSF, and $b = \frac{a}{3}\langle 2\bar{1}\bar{1}0 \rangle$ edge dislocations at the interface. Next, we evaluated the electronic consequences of the identified defects by performing electronic structure calculations within the semiempirical pseudopotential model. These calculations show the formation of deep hole trap states for $b = \frac{a}{3}\langle 2\bar{1}\bar{1}0 \rangle$ edge dislocations and shallow hole trap states in the case of PSFs. Using *in-situ* HRTEM imaging, we identified the pathways these different defects follow as they are annealed out of the NC arrays, and we observed that the dislocations with glide planes leading directly to the surface are much easier to remove. Additionally, we found that interfaces with multiple dislocations are considerably more difficult to remove compared to single dislocations. From this, we propose guidelines for the preparation of attached CdX NCs such as optimal attachment facets, NC assembly tolerances, and superlattice geometry. Altogether, this work constitutes a step towards understanding the defect formation mechanisms, the electronic consequences of defects and the defect healing pathways in attached NCs that is needed to engineer defect resilient materials.

3.2 Results

Synthesis of $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ Terminated Wurtzite CdSe

One goal in this work was to determine the ideal facets for attachment of wurtzite CdX (X = S, Se, Te) NCs. In the wurtzite crystal structure, the two most prevalent non-polar low index (energy) prismatic facets which can terminate the crystal are the $\{1\bar{1}00\}$ or the $\{11\bar{2}0\}$ family of facets. To experimentally consider the attachment on these facets, we needed to prepare samples of NCs terminated with the different facets, but still having comparable sizes, crystalline quality, and surface chemistry. Most strategies for preparing wurtzite CdX NCs result in predominately $\{1\bar{1}00\}$ facet termination.^{148,149,160–164} To prepare $\{11\bar{2}0\}$ terminated CdSe NCs, we built off the results of Teranishi and co-workers,¹⁶⁵ which showed one of the few examples of $\{11\bar{2}0\}$ terminated colloidal CdX NCs.¹⁶⁶ Using modifications of their

chemistry, we were able to synthesize both $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ terminated CdSe NCs of similar size, crystalline quality, and surface chemistry (see methods section for details). Figure 3.1A, E show low magnification TEM images of $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ terminated CdSe NCs, respectively, which show well-defined hexagonal shapes. Both samples had similar size and relatively narrow size distributions, 15.5 ± 2 nm pseudo-diameter for $\{1\bar{1}00\}$ termination and 16 ± 2 nm for the $\{11\bar{2}0\}$ termination, allowing them to readily assemble into hexagonal close packed monolayers with long range orientational order (Figure A.3.4). Figure 3.1B shows a HRTEM image of a particle viewed down the $[0001]$ zone axis clearly showing the 6 $\{1\bar{1}00\}$ planes terminating the particle – resulting in a well-defined hexagonal shape. Figure 3.1C shows a ball and stick model of a wurtzite CdSe NC with $\{1\bar{1}00\}$ termination viewed down the $[0001]$ zone axis. The inset Fourier transform (FT) shows 6 spots corresponding to the $\{1\bar{1}00\}$ planes of the wurtzite lattice. These images were taken under dark-atom contrast conditions, thus the bright dots observed in the HRTEM images correspond to the open channels in the wurtzite lattice. In Figure 3.1F, we show a HRTEM image of the $\{11\bar{2}0\}$ terminated sample viewed down the $[0001]$ zone axis where the underlying wurtzite crystal has the same orientation relative to Figure 3.1B. The inset FT of both Figures are aligned confirming the same wurtzite lattice orientation for both images. In the $\{11\bar{2}0\}$ case, the sample still adopts a hexagonal shape however it is rotated 30° relative to the hexagonal shape of the $\{1\bar{1}00\}$ terminated sample indicating it is terminated with $\{11\bar{2}0\}$ facets. We note that the $\{11\bar{2}0\}$ terminated samples are truncated by $\{1\bar{1}00\}$ facets to a small extent resulting in a truncated hexagonal shape. Figure 3.1G shows a ball and stick model of a $\{11\bar{2}0\}$ terminated wurtzite CdSe NC viewed down the $[0001]$ zone axis. Another way to consider the different termination of the two samples is that the $\{1\bar{1}00\}$ facet has a “zig-zag” like termination and the $\{11\bar{2}0\}$ has an “armchair” like termination. Importantly, both the $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ terminated samples are slightly elongated along the c-axis (Figure A.3.1) leading to a cylindrical shape, which can facilitate the vertical assembly since the ordered vertical alignment maximizes favorable ligand/ligand interactions forcing facets to adopt a face-to-face geometry.¹⁶⁷

In order to demonstrate the high crystalline quality of the NCs, Figure 3.1D, H show wide-angle X-ray diffraction patterns for the $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ terminated samples, respectively, which were carefully prepared as powders to ensure random orientation distribution. Both diffraction patterns contain all the peaks characteristic of wurtzite CdSe (stick pattern) – indicating their similar crystalline quality. We note that the intensity distributions of the $\{10\bar{1}0\}$, $\{0002\}$, and $\{10\bar{1}1\}$ peaks are different from what is expected for phase pure wurtzite, which can be indicative of stacking disorder, but also from shape effects.^{15,168} To confirm the presence of stacking faults, we collected HRTEM images of both the $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ terminated samples down the $[11\bar{2}0]$ zone axis (Figure A.3.1 A, C). These images confirmed that both samples have basal plane stacking disorder in the form of stacking faults and zinc blende inclusions; however, the samples are still primarily wurtzite with the shape expected for that structure. This is supported by the fact that viewing the samples down the $[11\bar{2}0]$ zone axis reveals that the samples are clearly elongated along the $[0001]$ direction, consistent with the anisotropic reactivity known for wurtzite CdSe.^{56,78^{21,148}} Im-

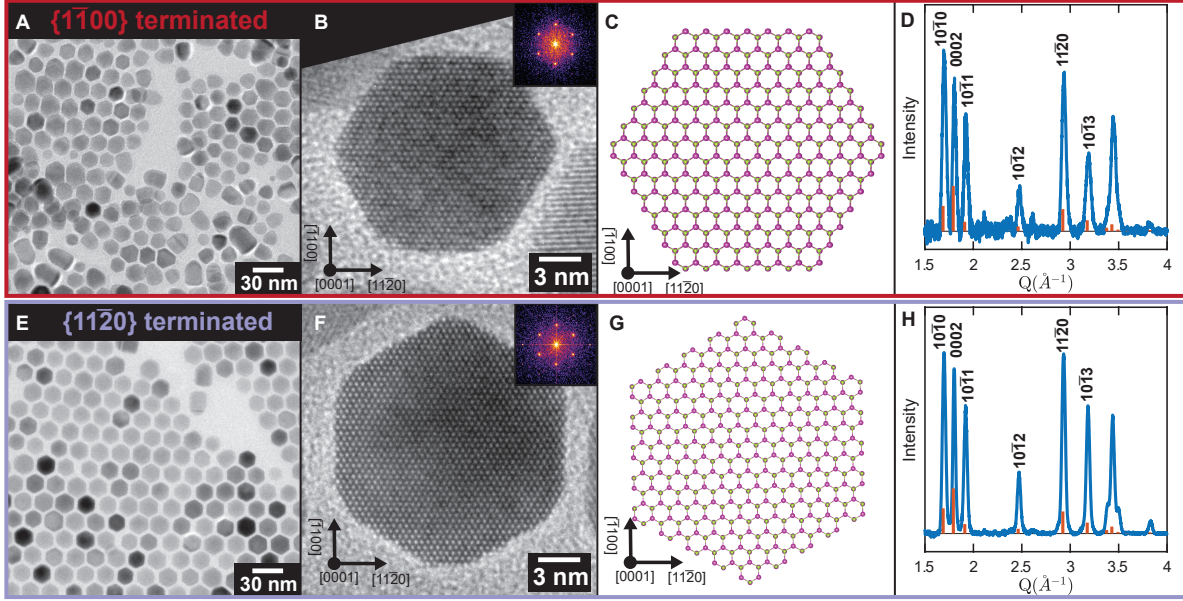


Figure 3.1: (A)TEM image of $\{1\bar{1}00\}$ terminated CdSe NCs. (B) HRTEM image of a $\{1\bar{1}00\}$ terminated CdSe NC taken down the $\langle 0001 \rangle$ zone axis and (C) a model of $\{1\bar{1}00\}$ terminated wz-CdSe shown down the $\langle 0001 \rangle$ zone axis. (D) Wide angle XRD from a carefully prepared powder of $\{1\bar{1}00\}$ terminated CdSe NCs with a wurtzite stick pattern (ICSD collection code 415786). (E)TEM image of $\{11\bar{2}0\}$ terminated CdSe NCs. (F) HRTEM image of a $\{11\bar{2}0\}$ terminated CdSe NC taken down the $\langle 0001 \rangle$ zone axis and (G) a model of $\{11\bar{2}0\}$ terminated wz-CdSe shown down the $\langle 0001 \rangle$ zone axis. (H) Wide angle XRD from a carefully prepared powder of $\{11\bar{2}0\}$ terminated CdSe NCs with a wurtzite stick pattern.

portantly, the samples have similar length distributions, 20 ± 3 nm for the $\{1\bar{1}00\}$ terminated sample and 24 ± 3 nm for the $\{11\bar{2}0\}$ terminated sample. We also collected wide angle powder electron diffraction patterns for samples deposited on carbon TEM grids (Figure A.3.2) to understand the ensemble level crystallographic orientation effects. For the $\{1\bar{1}00\}$ terminated sample, we observed preferential alignment with the $[0001]$ parallel to the substrate, but with a significant portion with the $[0001]$ perpendicular to the substrate. For the $\{11\bar{2}0\}$ terminated sample we see significant alignment with the $[0001]$ perpendicular to the substrate. This alignment is consistent with the orientation preference observed in TEM images of the diffraction area (Figure A.3.3). Based on the detailed structural characterization of these two materials, we have successfully prepared wurtzite CdSe NCs with nearly identical parameters except for the prismatic facets terminating the sample.

Perfect Atomic Attachment Scenarios for Prismatic Facets in Wurtzite CdSe

Having successfully prepared comparable $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ terminated CdSe samples, we developed a strategy to induce epitaxial attachment between CdSe NCs. There are many documented approaches for doing this with IV-VI NCs, particularly the PbX (X=S,Se,Te) systems. In these materials, attachment can be induced by heating NC superlattices on a liquid subphase,⁸⁶ heating in high vacuum,⁸⁷ chemical treatments to remove the organic ligands,^{34,46,47} or diluting the particles to desorb surface bound ligands.¹⁴⁷ Ondry *et. al.* used ligand dilution as an effective means to induce atomically coherent attachment in PbTe NCs for *in-situ*-TEM studies.¹⁴⁷ Because the organic ligands are typically more difficult to remove from the surface of CdX and other II-VI materials compared to IV-VI materials,¹⁶⁹ it is harder to induce atomically coherent attachment of CdX NCs. One strategy that has been effective for attaching II-IV materials has been treatment of NC films with dilute methanolic solutions of ammonium sulfide.¹⁷⁰ In this strategy, it is proposed that the S^{2-} ion cleaves the M(oleate)₂ bond that tethers the ligands to the surface. This bond cleavage allows the oleate (or other carboxylate ligands) to leave as soluble NH_4 -Oleate species. The excess sulfur is incorporated into the inorganic bridge between two adjacent NCs. To circumvent the additional complexity of having multiple chalcogens present, we treated our samples of shape controlled CdSe NCs deposited on carbon or graphene coated gold TEM grids with methanolic solutions of Na_2S in a glovebox. This treatment successfully led to the atomically coherent attachment of both $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ terminated CdSe NCs (Figure 3.2A, E respectively). In both cases, the inset FTs in Figure 3.2A and 2E show distinct spots indicating atomic coherence across the field of view in the images. Figure 3.2B and 2F show ball and stick models of the interface that would result between two merged $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ terminated NCs, respectively. This strategy successfully yielded large arrays of connected NCs with atomic coherence resulting in large (200×200 nm) crystals of CdSe (Figure A.3.4). While we cannot directly observe the attachment mechanism during the ligand removal process in our experimental design, some information on the attachment mechanism can be inferred by comparing the structure of the assembled nanocrystals before and after the Na_2S treatment. Initially the nanocrystals are separated by ~ 2 nm by the organic ligands (Figure 3.1E for example), and after attachment, we see the films have contracted into relatively large ($\sim 200 \times 200$ nm) dense arrays of attached nanocrystals (Figure A.3.4) with large cracks separating the attached domains. This indicates the nanocrystals are briefly mobile on the substrate during attachment, which allows relatively small domains to uniformly contract and attach where the overall volume change is accommodated by significant cracking. Cracking and other volume change issues may be mitigated by performing assembly and attachment at liquid/liquid interfaces,¹²⁷ however implementing this with CdSe attachment is beyond the scope of this work.

With a strategy in place to attach wurtzite CdSe on both prismatic facets, we wanted to understand how attachment on the different facets would affect the strength of electronic coupling between quantum confined CdSe NCs. Thus far, the experimental NCs we have shown

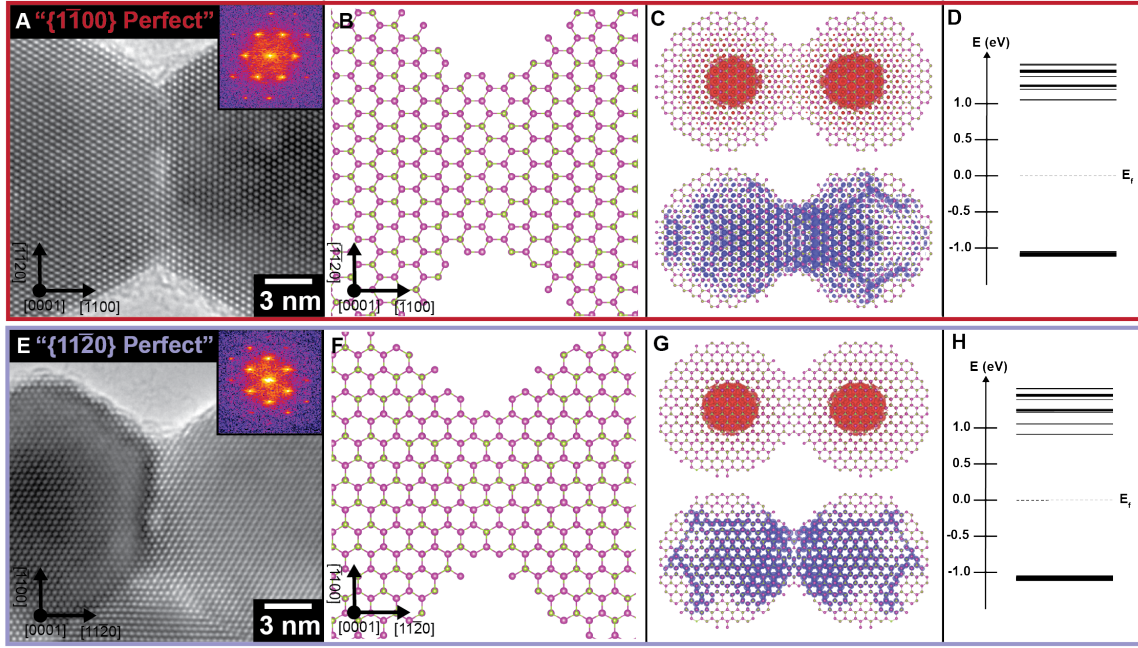


Figure 3.2: (A, E) HRTEM images and (B, F) models of two wurtzite CdSe NCs attached on $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ facets, respectively. (C, G) Electron (red) and hole (blue) probability densities including e^- and h^+ interactions for two wurtzite CdSe NCs attached on $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ facets, respectively. (D, H) Energy level diagrams for the single-particle states attached NCs in C and G, respectively. (computations performed by Michael Lostica and John Philbin)

are too large to exhibit strong quantum confinement effects. Large NCs were used because clear faceting only develops at larger edge lengths, further it facilitates HRTEM investigations and finally, we have been unable thus far to develop a synthetic method to prepare small (<5 nm) $\{11\bar{2}0\}$ terminated CdSe NCs. Nonetheless, it is interesting to consider how the attachment facet may affect the coupling strength between wurtzite CdSe quantum dots. To do this, we performed atomistic electronic structure calculations using the semi-empirical pseudopotential model¹⁷¹ on two merged NCs attached on either the $\{1\bar{1}00\}$ or $\{11\bar{2}0\}$ facet. Structures were created with a comparable number of planes at their interface and relaxed using molecular dynamics using the Stillinger-Weber interaction potentials for CdSe.¹⁷² We employed the filter-diagonalization technique^{158,173} to obtain the noninteracting charge carrier (*i.e.* electron and hole) eigenstates near the band edge. These noninteracting eigenstates allowed us to compute carrier densities as well as the excitonic (*i.e.* correlated electron-hole) states by using them as input to the Bethe-Salpeter equation.^{174,175} See the Methods section for more details on the molecular dynamics and electronic structure calculations. Figure 3.2B, F show the interface of the two attached NCs which are attached on the $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ facets, respectively. Their respective charge carrier probability densities are shown in Figure 3.2C, G, and their corresponding single-particle energy diagrams are shown in Figure

3.2D, H. Both perfectly attached NCs have fundamental gaps of ~ 2.1 eV, and no mid-gap trapped states are seen in the energy level diagrams. The charge carrier densities, Figure 3.2C, G, are Boltzmann weighted averages over the lowest energy electron and hole states and show that both carriers are delocalized in both NCs. The electron energy levels and densities can be understood by noting that the two lowest lying electron states exhibit the expected bonding and antibonding level splitting that result from the linear combination of the 1Se electron states of the individual NCs.¹⁷⁶ The hole energy levels and densities are more complicated because of the large hole effective mass in CdSe and large number of hole states that are thermally accessible at room temperature. One consequence of the large hole effective mass relative to the electron mass is that the hole densities (Figure 3.2C, G) show that the hole has much greater probability of being in the center of the fused NCs compared to the electron. A more detailed analysis of the energy levels and carrier densities will be given later in comparison to the imperfectly attached NCs.

Imperfect Atomic Attachment Scenarios for Prismatic Facets in Wurtzite CdSe

While perfect attachment of NCs is the ideal scenario, it is well known that step edges on the surface of NCs can lead to the formation of dislocations when otherwise perfect NCs undergo oriented attachment.^{38,56,73} Recently we showed that the dislocations in imperfectly attached rock salt PbTe NC pairs can be rationally described using dislocation theory.¹⁴⁷ Furthermore, we found that the dislocation dynamics in PbTe NCs were consistent with how dislocations are known to glide in the rock salt lattice. We wanted to test the translatability of dislocation theory to NCs with different lattices. To do this, first we identified the types of dislocations present in the samples of attached wurtzite CdSe NCs. Figure 3.3A-B shows how a step edge on a $\{1\bar{1}00\}$ facet can give rise to a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ NCs dislocation. This dislocation has a glide plane that requires the dislocation to glide through the entire NC to be removed from the interface. Figure 3.3C shows an overview HRTEM image viewed down the $[0001]$ zone axis of an imperfect interface between two $\{1\bar{1}00\}$ terminated CdSe NCs displaying a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation with an overlaid Burgers circuit and glide plane. A zoomed in HRTEM image of the dislocation core is shown in Figure 3.3D with an overlaid Burgers circuit. The extra $(1\bar{1}00)$ and $(10\bar{1}0)$ planes indicative of a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation are highlighted in blue and yellow, respectively. In Figure 3.3B, we show the so-called “full core” structure of the dislocation core which is consistent with what is unambiguously observed in GaN¹⁷⁷ and supported by HRTEM image simulations for CdSe here (Figure A.3.5). For the rest of this section, we will refer to this dislocation scenario as the “ $\{1\bar{1}00\}$ Edge” since the attachment is on the $\{1\bar{1}00\}$ family of facets and it results in an edge dislocation. For $\{1\bar{1}00\}$ terminated CdSe, this was the only type of edge dislocation observed in the case of single dislocations at the interface of the NCs.

In the case of attachment on the $\{11\bar{2}0\}$ facets, four distinct extended defect scenarios were observed. In Figure 3.3E, we consider the attachment of two pristine $\{11\bar{2}0\}$ terminated

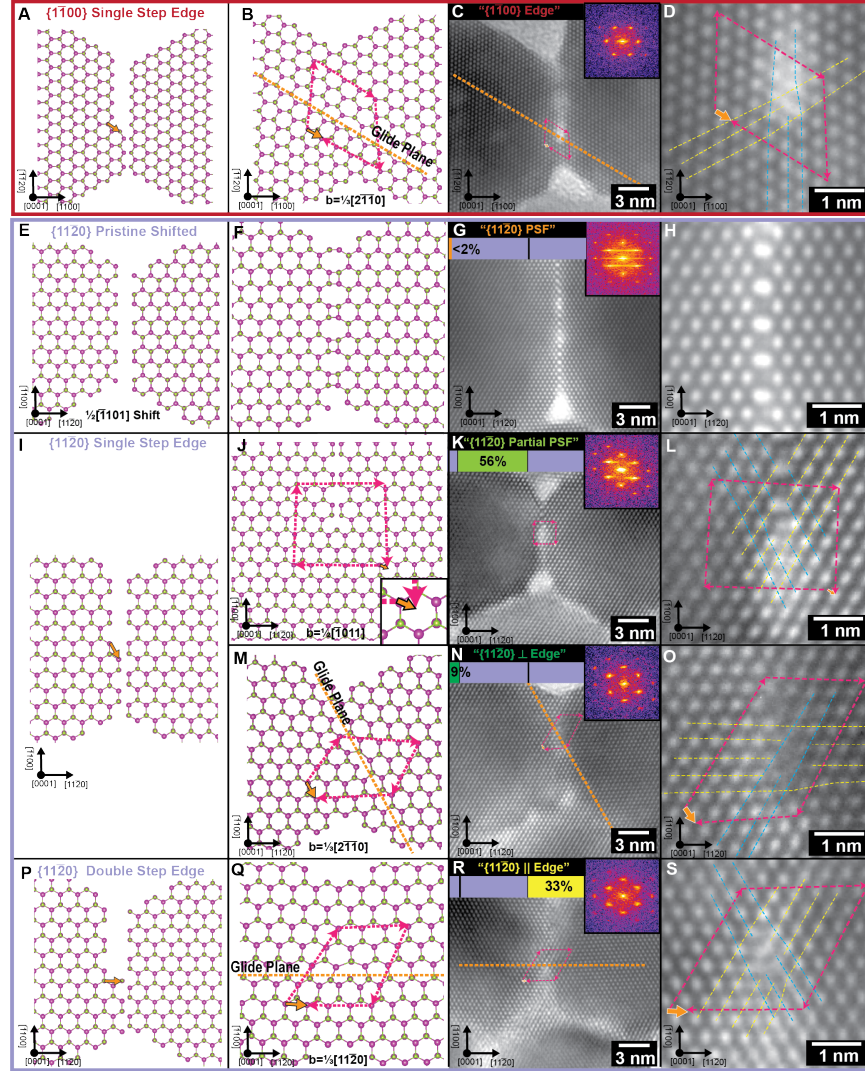


Figure 3.3: (A) Model of a single step edge on the $(1\bar{1}00)$ facet of wz-CdSe and (B) after attaching to a second NC giving rise to a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation. (C, D) HRTEM image with inset FT of imperfectly attached $\{1\bar{1}00\}$ terminated wz-CdSe particles displaying a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation. (E) Model of 2 pristine $\{11\bar{2}0\}$ terminated wz-CdSe particles with a $\frac{1}{2}[1\bar{1}01]$ shift between the particles and (F) after attaching to create a prismatic stacking fault (PSF) with the $\frac{1}{2}(10\bar{1}1)\{1\bar{2}10\}$ configuration. (G, H) HRTEM with inset FT of imperfectly attached $\{11\bar{2}0\}$ terminated wz-CdSe particles displaying a PSF (I) Model of a single step edge on a $(11\bar{2}0)$ facet which after attachment can give rise to either (J) a $b = \frac{a}{2}[\bar{1}011]$ partial dislocation bound by a prismatic stacking fault or (M) a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation which has a glide plane nearly perpendicular to the attachment direction. (K, L) $b = \frac{a}{2}[\bar{1}011]$ partial dislocation bound by a prismatic stacking fault and (N, O) HRTEM image with inset FT of imperfectly attached $\{11\bar{2}0\}$ terminated wz-CdSe showing a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation. (P) Model of a double step edge on a $(11\bar{2}0)$ facet which after attachment can give rise to (Q) a $b = \frac{a}{3}[11\bar{2}0]$ edge dislocation which has a glide plane parallel to the attachment direction. (R, S) HRTEM image with inset FT of imperfectly attached $\{11\bar{2}0\}$ terminated wz-CdSe showing a $b = \frac{a}{3}[11\bar{2}0]$.

NCs, but with a $\frac{1}{2}[\bar{1}\bar{1}01]$ shift between the two particles. This shift gives rise to a prismatic stacking fault (PSF) between the two NCs. PSFs are well-documented in many wurtzite materials^{178–181} and have been reported to adopt two configurations, the Amelinkx model with a $\frac{1}{6}\langle 20\bar{2}3 \rangle$ displacement¹⁸² and the Drum model with a $\frac{1}{2}\langle \bar{1}101 \rangle$ displacement.¹⁷⁸ The latter configuration is more common in wurtzite semiconductors.¹⁸⁰ Drum model PSFs are characterized by the alternating 8- and 4-member rings in the lattice (Figure 3.3F) which is qualitatively consistent with the HRTEM images shown in Figure 3.3G, H. In Figure 3.3G, we show an overview HRTEM image viewed down the $[0001]$ zone axis showing a PSF that extends across the entire interface between two $\{11\bar{2}0\}$ terminated NCs. The inset FT shows significant streaking of the $(10\bar{1}0)$ and $(01\bar{1}0)$ spots. Streaking in electron diffraction patterns and FT's of HRTEM images are indicative of a stacking error present in a sample.¹⁸³ We note that FTs were carefully processed with a Hanning window to avoid streaking artefacts from image edge effects (see methods section). Figure 3.3H shows a zoomed in HRTEM image of the PSF; the large white dots correspond to the 8-member rings, and the 4-member rings are unresolved in the dark voids. Multislice HRTEM image simulations of the Drum model (Figure A.3.6) compared with the experimental images confirm the Drum structure is observed in our samples. For the remainder of this section, we will refer to this as the “ $\{11\bar{2}0\}$ PSF” extended defect. When considering all the fault errors for $\{11\bar{2}0\}$ attachment, we observe the “ $\{11\bar{2}0\}$ PSF” case less than 2% of the time.

Next, we consider structures that can arise from a single step edge on one of the $\{11\bar{2}0\}$ facets (Figure 3.3I), for which two different extended defect scenarios were observed. First, we discuss the scenario where the stepped surface forms a proper interface, and the recessed surface attaches with a PSF (Figure 3.3J). This will lead to the formation of a $b = \frac{a}{2}[10\bar{1}0]$ partial dislocation which separates the perfect stacking and the PSF. Partial dislocations are characterized by Burgers vectors that do not correspond to a translation vector of the lattice. This can be seen by the $[0001]$ projection of the Burgers circuit where the Burgers vector does not connect two atomic positions (see Figure 3.3J inset). An example of two joined $\{11\bar{2}0\}$ terminated particles with a PSF across part of the interface is shown in Figure 3.3K. The streaking of the $(10\bar{1}0)$ and $(01\bar{1}0)$ spots in the FT is also observed indicating the presence of a PSF in the image. Figure 3.3L shows a zoomed in HRTEM image of the dislocation core showing how the $(01\bar{1}0)$ and $(10\bar{1}0)$ planes (blue and yellow, respectively) merge perfectly at the bottom of the image and have a stacking error at the top of the image. In Figure 3.3J, we show the “full core” structure of the partial dislocation, however an open core structure is also possible (Figure A.3.7). We attempted to identify the structure by comparing with multislice HRTEM image simulations (Figure A.3.7) and the full core structure seems more plausible; however, we were unable to unambiguously determine the structure due to the limited resolution of our TEM. Unfortunately, we could not find literature reports of the core structure of this partial dislocation determined by more reliable techniques such as aberration corrected HAADF-STEM imaging. Despite this, our results clearly indicate that $b = \frac{a}{2}[10\bar{1}0]$ partial dislocations can exist at the interface between CdSe NCs attached on the $\{11\bar{2}0\}$ facet. Furthermore, we observe this dislocation scenario, which we will call the “ $\{11\bar{2}0\}$ Partial PSF”, in 56% of the defective interfaces for attachment on the $\{11\bar{2}0\}$ facet.

In the second case of $\{11\bar{2}0\}$ attachment with a single step edge, a full edge dislocation is formed at the interface again with a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ Burgers vector. This is shown in Figure 3.3M with overlaid Burgers circuit and glide plane. Figure 3.3N shows an overview HRTEM image of two joined $\{11\bar{2}0\}$ terminated CdSe particles with a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation at the interface. This dislocation has the same Burgers vector and dislocation structure as described previously for the " $\{1\bar{1}00\}$ Edge" scenario, however its relationship relative to the attachment direction is rotated by 30° . In this case, the glide plane of the dislocation quickly intersects the surface which should allow for easier dislocation removal. In Figure 3.3O we show a zoomed in image of the dislocation core and highlight the extra $(\bar{1}010)$ and $(1\bar{1}00)$ planes in blue and yellow, respectively. We will refer to this dislocation, which we observe 9% of the time, as the " $\{11\bar{2}0\} \perp$ Edge" because it results from attachment on $\{11\bar{2}0\}$ facets and has a glide plane nearly perpendicular to the attachment direction.

Finally, we consider the case of a double step edge on the $\{11\bar{2}0\}$ facet shown in Figure 3.3P. This case also leads to a $b = \frac{a}{3}\langle 2\bar{1}\bar{1}0 \rangle$ type edge dislocation that is related by symmetry to the other edge dislocations. Specifically, in this case, using the same indexing conventions as the other dislocation cases, it has a $b = \frac{a}{3}[11\bar{2}0]$ Burgers vector (Figure 3.3Q) and associated glide plane which is co-linear with the attachment direction. Figure 3.3R shows an overview HRTEM image of an interface between two particles attached on the $\{11\bar{2}0\}$ facet displaying a $b = \frac{a}{3}[11\bar{2}0]$ edge dislocation with overlaid Burgers circuit and glide plane. Figure 3.3S shows a zoomed in HRTEM image of the dislocation core with the overlaid extra $(01\bar{1}0)$ and $(10\bar{1}0)$ planes (blue and yellow, respectively) planes characteristic of the edge dislocation. This dislocation scenario, which we will call the " $\{11\bar{2}0\} \parallel$ Edge" since the glide plane is co-linear with the attachment direction, was observed 33% of the time for imperfect attachment events on the $\{11\bar{2}0\}$ facet. One interesting observation is how the step vector describing the surface step that would lead to each of the different edge dislocation scenarios (orange arrow in Figure 3.3A, I, and P) corresponds exactly with the Burgers vector of the various dislocations observed. The five extended defect cases for the two attachment facets presented here represent all those that we observed; however, it is important to remember that in this orientation, screw dislocations are not easily observed by HRTEM and may be present in our samples.

Having identified the dislocation structures present after oriented attachment, we wanted to elucidate which dislocations would have deleterious electronic consequences. To this end, we performed electronic structure calculations using the semi-empirical pseudopotential method as described above (and in detail in the Methods section) on the imperfectly attached NCs (*i.e.* fused NCs with the observed dislocations at the interface of the two NCs). The calculation results for the " $\{11\bar{2}0\}$ PSF" and the " $\{11\bar{2}0\} \parallel$ Edge" are shown in Figure 3.4. Localized mid-gap trap states were identified for both defective structures, with the energy level diagrams of the single-particle states shown in Figure 3.4B, F. We assign a deep or shallow label to such trap states (red and orange respectively), with the former only present in the $\{11\bar{2}0\} \parallel$ Edge scenario. The Fermi level (E_f) for Figure 3.4B, F were taken from the perfect attachment calculation shown in 3.2D, which is the calculated midpoint of the band gap (E_g) for two NCs that had undergone perfect oriented attachment at the $\{11\bar{2}0\}$ facet.

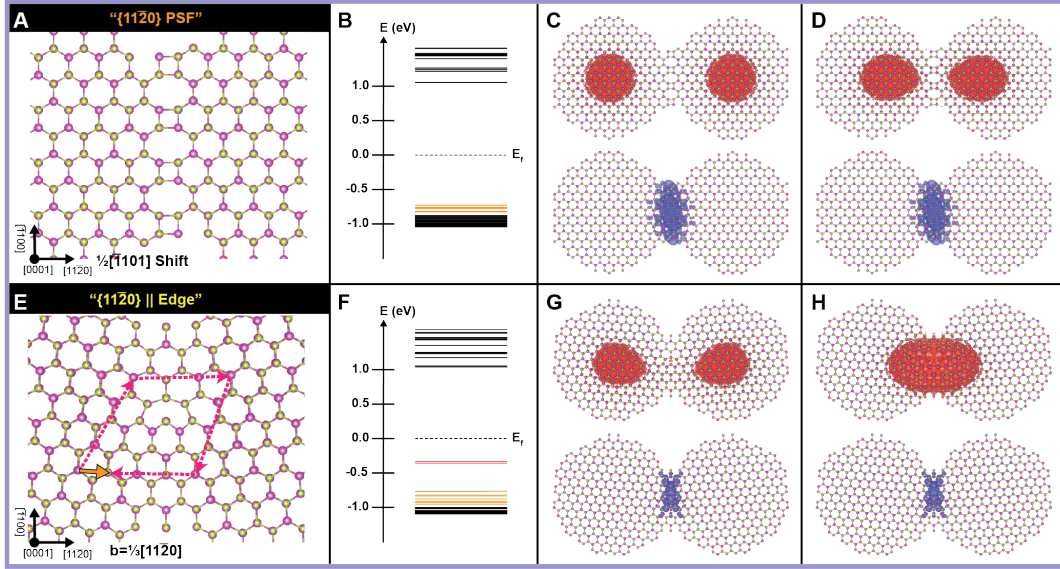


Figure 3.4: Electronic structure calculations of attached quantum dots with a (A-D) $\{11\bar{2}0\}$ PSF interfacial defect and (E-H) “ $\{11\bar{2}0\}$ || Edge” interfacial defect. (A, E) Interface of the attached particles used in electronic structure calculations, with a Burgers circuit included in (E). (B, F) Energy level diagrams (in eV) for the single-particle states. Defect related shallow and deep hole trap states are shown in orange and red, respectively. The Fermi energy, E_f , was chosen to be the midpoint of the calculated fundamental gap, E_g , for the attached quantum dots that underwent perfect oriented attachment on the $\{11\bar{2}0\}$ facet. (C, D, G, H) Electron (red) and hole (blue) probability densities for (C, G) the single-particle (i.e. noninteracting electron and hole) states and (D, H) the excitonic (i.e. correlated electron-hole) states. All probability densities are shown at the same isosurface value and are Boltzmann weighted averages over the low energy (C, G) single-particle and (D, H) excitonic states. (computations performed by Michael Lostica and John Philbin)

For both the “ $\{11\bar{2}0\}$ PSF” (Figure 3.4C, D) and “ $\{11\bar{2}0\}$ || Edge” (Figure 3.4G, H), a Boltzmann weighted average of the charge densities of the lowest energy states show localization of the hole at the crystalline interface. This is independent of whether the hole is the only charge carrier in the fused NC or if the hole is interacting with an electron, as would be the case if the hole was generated *via* photon absorption. For the PSF, localization occurs at the 4- and 8- membered ring motif at the interface and, for the “ $\{11\bar{2}0\}$ || Edge”, the deep hole trap states are restricted to the dislocation core of the “ $\{11\bar{2}0\}$ || Edge”. Interestingly, the charge probability densities for the electron states display clear differences between the charge excitation (noninteracting) picture (Figure 3.4C, G) and neutral excitation (interacting) picture (Figure 3.4D, H) charge densities. In the charged excitations, the electron probability densities are segregated: an interfacial node separates the electron density of each particle (Figure 3.4C, G). When allowed to interact with hole states in the neutral excitation case, the electron densities for both structures are brought closer to the hole (Figures

D, H). However, Figure 3.4D shows that for the “ $\{11\bar{2}0\}$ PSF”, the electron density still avoids the interface. This is contrasted by the “ $\{11\bar{2}0\} \parallel$ Edge” in Figure 3.4H, where the electron and hole probability densities of the lowest energy excitonic states are localized at the dislocation core. Similar hole localization and subsequent electron localization in the interacting case were observed for the “ $\{1\bar{1}00\}$ Edge” and “ $\{11\bar{2}0\} \perp$ Edge” cases (A.3.8). Compared to perfect attachment in 3.2, structural defects at the interface lead to mid-gap trap states which could negatively impact the performance of devices based on chemically fused NCs.

Dislocation Removal Dynamics *via in-situ* HRTEM

In the context of realizing delocalized electronic states, the extended defects have many negative consequences, and thus we consider the prospects for removal of these defects. In rock salt PbTe, we previously observed that a dislocation with a glide plane which quickly intersected the surface is much easier to remove compared to ones that do not.¹⁴⁷ In this work, we again performed electron dose rate controlled *in-situ* TEM experiments,¹⁸⁴ which can qualitatively simulate thermal annealing,^{91,92} to observe the dislocation dynamics in imperfectly attached NCs. Figure 3.5 overviews the dislocation removal pathways for the five dislocation scenarios observed. Figure 3.5A shows snapshots from a timeseries of HRTEM images (Video B.3.1) showing the pathway a “ $\{1\bar{1}00\}$ Edge” dislocation follows as it is expelled from the interface at the surface. Figure 3.5B shows the position of the dislocation, determined by image analysis techniques (see methods), in each frame as a function of time. The dislocation moves out of its glide plane generally in the $[11\bar{2}0]$ direction which has both glide (movement $\parallel$ to glide plane) and climb (movement $\perp$ to glide plane) character. The dislocation takes nearly 200 seconds to reach the surface, and the relatively slow kinetics is consistent with a process needing dislocation climb, which requires vacancies to coalesce with the dislocation for it to move out to its glide plane. We note that we do observe some sublimation of material during this annealing process, however the magnitude of sublimation (~ 1.5 nm of material in the worst case) is considerably less than the distance the dislocation traveled (~ 7 nm) and thus the dislocation dynamics in the crystal appear to dominate the removal kinetics rather than surface effects.

Next, we consider the “ $\{11\bar{2}0\}$ PSF” scenario. Snapshots from a timeseries of TEM images are shown in Figure 3.5C and the full movie is shown in Video B.3.2. In this case, even after over 245 seconds of electron beam stimulation, signatures of the PSF are still present both in the image and manifested as streaks in the FTs for each frame. Analysis of the streak intensity (see methods section for details) in the FT for each frame (Figure 3.5D), which indicates the presence of a PSF shows that the defect is not removed during the observation period. Thus, it seems that the PSF interface is very stable and difficult to remove. On the other hand, when the PSF is terminated with a partial dislocation, the “ $\{11\bar{2}0\}$ Partial PSF” case (Figure 3.5E and Video B.3.3), we observe that the PSF spontaneously and quickly heals compared to the “ $\{11\bar{2}0\}$ PSF” scenario. This can be further illuminated by plotting the FT streak intensity of each frame as a function of time

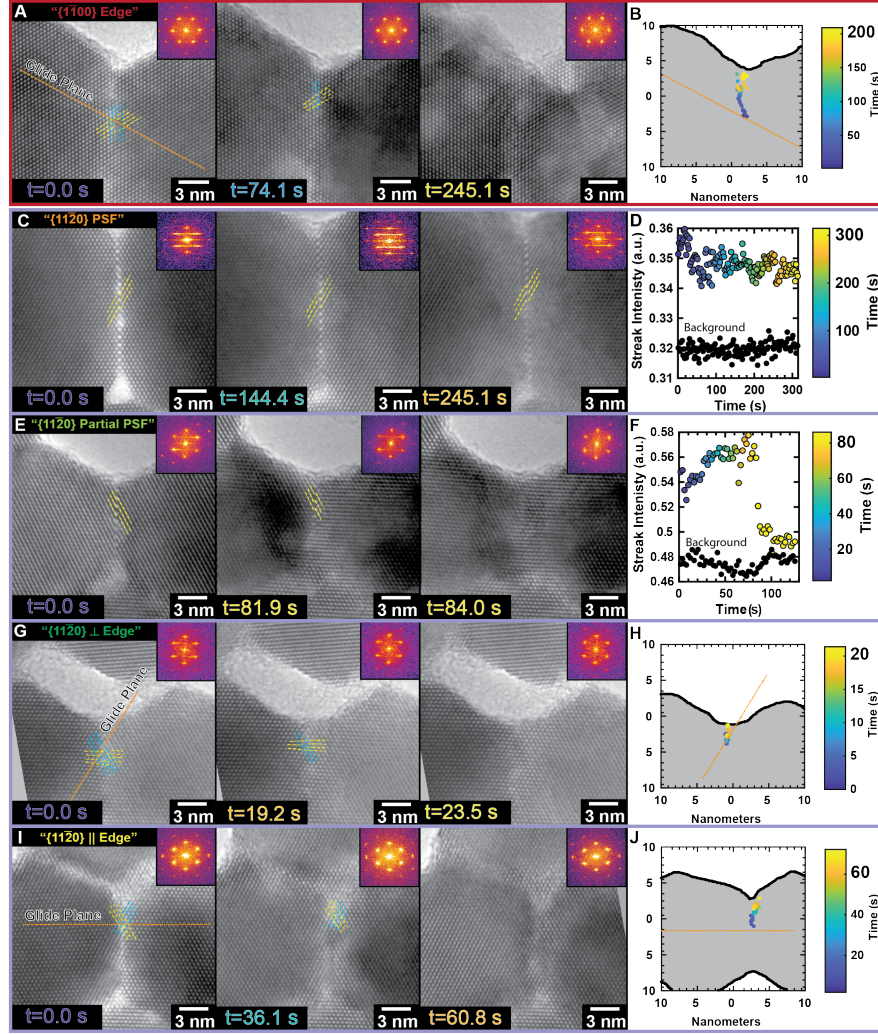


Figure 3.5: (A) Timeseries of images as a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation anneals out of the interface between two $\{1\bar{1}00\}$ terminated particles. (B) Position of the dislocation in each frame determined by the discontinuity in the strain field measured by geometric phase analysis. (C) Timeseries of images with inset FTs as a perfect PSF between two $\{11\bar{2}0\}$ terminated particles is electron beam annealed with a dose rate of $\sim 5000 \frac{e^-}{\text{\AA}^2 \text{s}}$. (D) Plot of the streak intensity in the FT of each frame, which is a characteristic of stacking errors, as a function of time while the PSF is electron beam annealed. The background intensity (black) is from a nearby part of the image without a PSF present. (E) Timeseries of images as a $b = \frac{a}{2}[\bar{1}011]$ dislocation bound by a prismatic stacking fault anneals out of the interface between two $\{11\bar{2}0\}$ terminated particles. (F) The intensity of the streak in the FT which signifies the presence of a PSF as a function of time. (G) Timeseries of images as a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation anneals out of the interface between two $\{11\bar{2}0\}$ terminated particles with the position of dislocation in each frame shown in (H). (I) Timeseries of images as a $b = \frac{a}{3}[11\bar{2}0]$ edge dislocation anneals out of the interface between two $\{11\bar{2}0\}$ terminated particles with the position of dislocation in each frame shown in (J). For all plots, the time is shown by the colorbar, but each trajectory has a different timescale. Gray shading in the plots indicates the NC outline.

(Figure 3.5F) which shows higher intensity than the background initially, then abruptly (<2 s) returns to the background levels when the defect is removed. These observations suggest that the presence of a partial dislocation facilitates the removal of PSFs from the interfaces between $\{11\bar{2}0\}$ terminated nanoparticles.

Finally, we consider the two distinct edge dislocations that form during the attachment of $\{11\bar{2}0\}$ terminated nanoparticles. In the case of the “ $\{11\bar{2}0\} \perp$ Edge”, we observe that the dislocation is removed from the material faster than all the other defects (Figure 3.5G and Video B.3.4). Tracking the dislocation position in each frame (Figure 3.5H) shows that, as expected, the dislocation follows its glide plane to the surface where it is annihilated. In the “ $\{11\bar{2}0\} \parallel$ Edge” scenario (Figure 3.5I and Video B.3.5), the dislocation does not have a glide plane that leads directly to the surface or, in this specific case, the void that exists in at the node of 3 nanoparticles. Figure 3.5J shows that the dislocation undergoes climb to move out of its glide plane and, importantly, takes approximately 3 times longer to travel an almost identical distance as the “ $\{11\bar{2}0\} \perp$ Edge” case. These findings clearly highlight the importance of the orientation of the glide plane relative to the surface for edge dislocation removal and are consistent with our previous observations in PbTe.¹⁴⁷

Multiple Dislocations at an Interface

We also observed situations where multiple dislocations formed at the interface of $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ terminated particles shown in Figure 3.6A, B and C, D, respectively. In one observed case of multiple edge dislocations resulting from $\{1\bar{1}00\}$ attachment, we see two edge dislocations with $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ (top) and $b = \frac{a}{3}[\bar{1}2\bar{1}0]$ (bottom) Burgers vectors and associated glide planes (3.6A) which show a complicated geometry. 3.6B shows the detailed structure near the dislocation cores. The dislocation cores are separated by ~ 2.5 nm. In the case of multiple dislocations at interfaces, the exact geometries of the Burgers vectors and the glide planes were distinct in each case, even for the same attachment facet. The presence of multiple dislocations resulted in larger mistilt between the two attaching quantum dots; the evidence of the mistilts is the two distinct $\{1\bar{1}00\}$ peaks in the FT which are further highlighted by the FT inset.

The case of multiple dislocations at the attachment interface of two $\{11\bar{2}0\}$ terminated particles is shown in 3.6C. In this specific case, we observe edge dislocations with $b = \frac{a}{3}[11\bar{2}0]$ (top) and $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ (bottom) Burgers vectors with their associated glide planes overlaid on 3.6C. 3.6C shows the detailed structure at the dislocation cores which are separated by ~ 3 nm in this $\{11\bar{2}0\}$ case. We also observed a variety of specific geometries for multiple dislocations at $\{11\bar{2}0\}$ interfaces.

To understand the effects on removal kinetics that multiple dislocations have, we observed the dislocation trajectories of the “Multiple Edge $\{11\bar{2}0\}$ ” scenario during electron beam annealing and found that even after 250 s of annealing time, the defects made little progress to the surface (3.6E-F and B.3.6). The position of the two dislocations was determined for each frame and their positions are plotted in 3.6G with color corresponding to the time. We observe the dislocations make little progress to the surface. The center of mass of the two

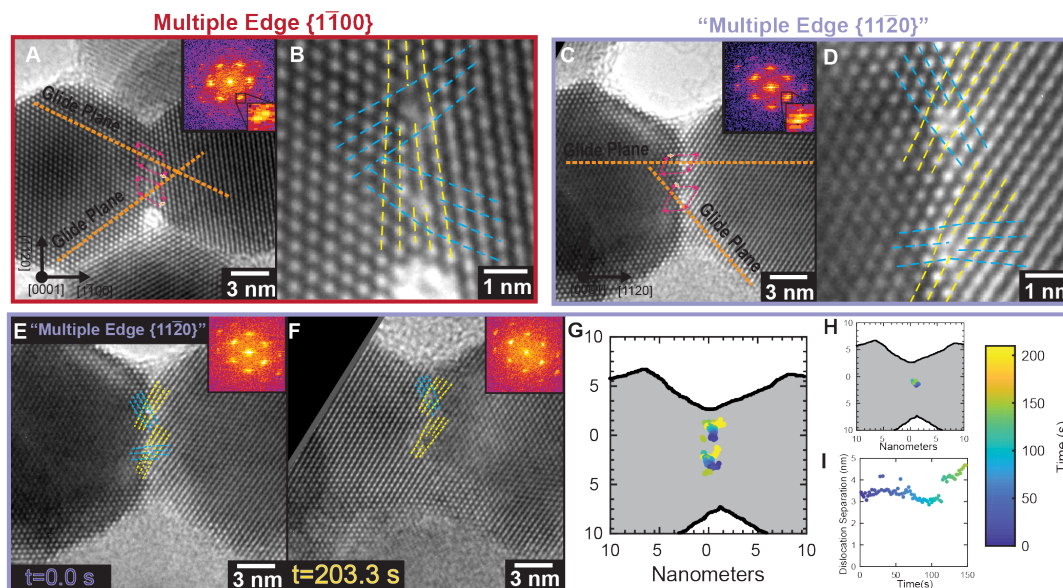


Figure 3.6: (A) Overview HRTEM image of the imperfect interface between two $\{1\bar{1}00\}$ terminated CdSe particles which has two dislocations overlaid with the Burgers circuits and glide planes. (B) Zoomed in view of the dislocation cores with the 2 extra $(10\bar{1}0)$ planes in yellow and extra $(1\bar{1}00)$ and $(01\bar{1}0)$ planes highlighted in blue. (C) Overview HRTEM image of the imperfect interface between two $\{11\bar{2}0\}$ terminated CdSe particles which has two dislocations overlaid with the Burgers circuits and glide planes. (D) Zoomed in view of the dislocation cores with the 2 extra $(10\bar{1}0)$ planes in yellow and extra $(1\bar{1}00)$ and $(01\bar{1}0)$ planes shown in blue (E) initial structure of $\{11\bar{2}0\}$ attachment with 2 edge dislocations and the same NCs (F) after considerable electron beam annealing. (G) The position of the two dislocations with time, (H) the center of mass of the two dislocations and (I) the separation between the two dislocations as a function of time.

dislocations (3.6H) also shows little movement to the surface. Furthermore, the distance between the two dislocations remains relatively constant over the first 120 seconds of the trajectory until it abruptly increases. This change happens concurrently with an abrupt decrease in the image quality; thus, it is difficult to discern if the abrupt change is real. We also saw significantly slower defect removal in the case of multiple dislocations at the interface of $\{1\bar{1}00\}$ terminated particles (B.3.7). Based on these trajectories, it is clear that the addition of a second dislocation at an interface greatly hampers the system's ability to heal those dislocations.

Average Dislocation Speeds for Multiple Attachment Scenarios

While the individual trajectories are illuminating about the mechanisms of dislocation removal, it is important to verify that the trends observed hold across multiple attachment events. In 3.7J, the dislocation removal speed, which we defined as the distance the disloca-

tion had to move to be removed divided by the time it takes for removal, is shown for many different trajectories in each defect category. Because dislocation surface attractive forces can have an effect on the kinetics,¹⁴⁷ we differentiate the initial distance the dislocation was from the surface by the color of the point on the graph. In this plot, the full circles indicate that the dislocations were removed during the observation time and the open circles indicate that the dislocations were not successfully removed from the interface, thus, giving an upper bound for the dislocation removal speed. It is important to note that all the data was collected at the same dose rate which was carefully calibrated in a self-consistent manner for each experiment (see methods). In 3.7J, we arrange the dislocation categories by increasing removal difficulty (slower removal speed) from left to right. Based on removal speed, the “ $\{11\bar{2}0\}$ Partial PSF” and “ $\{11\bar{2}0\} \perp$ Edge” provide the best prospects of removal. The “ $\{11\bar{2}0\} \parallel$ Edge” and “ $\{1\bar{1}00\}$ Edge” provide similar prospects for dislocation removal, especially when considering that the specific dislocation trajectories were a bit larger in the “ $\{1\bar{1}00\}$ Edge” case than in the “ $\{11\bar{2}0\} \parallel$ Edge” case. Finally, we observe that in either attachment facet, when more than one dislocation is at the interface, the dislocation removal was significantly slowed. In seven cases with two or more defects at the interface, all of them were stable during the observation time (>200 s), which was as long, if not longer than all the cases where successful removal was observed.

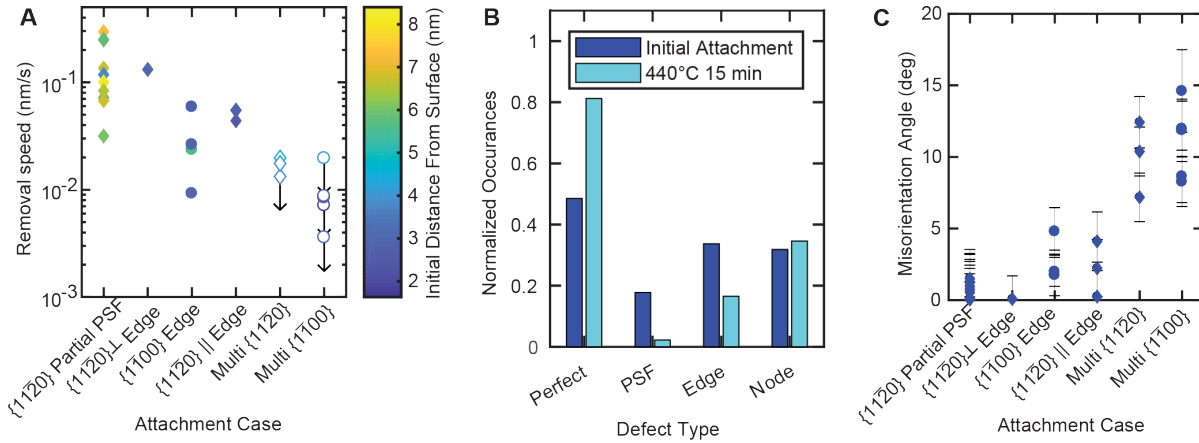


Figure 3.7: (A) Average removal speeds for the different dislocation classes of attachment. The color of each dot represents how far the dislocation was from the surface initially. Filled dots represent dislocations which annealed out in the observation time, and open circles did not, thus the removal speed is only an upper bound. (B) Number of interface types observed in a sample of $\{11\bar{2}0\}$ attached CdSe before and after annealing the sample at 440°C in vacuum for 15 min. the plot was normalized to the sum of perfect, PSF, and edge interfaces. Node refers to a defect at the node where 3 particles touch. (C) Misorientation angle between the two NCs for each attachment case in the different dislocation classes.

Thermal Annealing Effects on Dislocation Density

Thus far in this work, the dislocation dynamics were stimulated with the electron beam, yet thermal annealing would likely be used to drive dislocations out of these materials in a synthetic procedure. To determine if dislocation removal kinetics for thermal annealing are qualitatively consistent with our observations, we compared the interface dislocation densities before and after annealing a sample of NCs attached on $\{11\bar{2}0\}$ facets at 440°C for 15 min in a TEM column vacuum using a heating holder. We simplified our comparative analysis to include perfect interfaces, defects with edge character, and defects with PSF character (either partial or full). 3.7K shows the prevalence of perfect, edge, and PSF dislocations before (dark blue) and after (light blue) annealing the sample. Initially, $\sim 50\%$ of the interfaces are perfect with the rest having either a PSF (20%) or an edge dislocation (30%). After annealing, over 80% of the interfaces are perfect with $\sim 18\%$ containing an edge dislocation, and $\sim 2\%$ of the interfaces have a PSF defect. These results are qualitatively consistent with the observations in 3.7J that the partial PSF are the easiest to remove, and all the different cases of edge dislocations are more difficult to remove. Furthermore, the only remaining PSFs after the annealing were the case of the PSF across the entire interface (Figure A.3.9), consistent with our observation that full PSF are stable. Finally, we observed defects that at the confluence of three particles (labeled “Node” in 3.7K). There were a significant number of defects at the 3-particle intersection, but their concentration did not significantly change after annealing. Altogether, the dislocation and stacking fault concentration changes upon thermal annealing are consistent with our single particle kinetic observations.

Relationship Between Mistilted Nanocrystals and Low angle Tilt Boundaries

A simple metric for quantifying the degree of error in the attachment process is the misorientation angle between the two crystallites. We plot the misorientation angle for all the dislocation classes considered in the previous panel in 3.6H. Unsurprisingly, the multiple dislocation cases have the largest average misorientation angle of $\sim 11^\circ$. The single edge dislocation cases have on average a $\sim 3^\circ$ misorientation angle and the “ $\{11\bar{2}0\}$ Partial PSF” had a $\sim 1^\circ$ misorientation angle. The defective boundary between two NCs can be thought of as a small snapshot of a low angle tilt boundary. In this context, the number of dislocations per unit length is directly related to the mistilt angle.³⁶ Figure 3.8A shows a low angle tilt boundary for an idealized cubic lattice where the dislocation spacing, D , depends on the Burgers vector, b , and mistilt, θ , according to equation 3.1.

$$D \cong \frac{b}{\theta} \quad (3.1)$$

The different shades of orange outline what can be thought of as NCs of different sizes having imperfect interfaces for a fixed mistilt angle. In the case of the smallest interface, zero dislocations at the interface are expected. As the size of the NC increases, an increasing

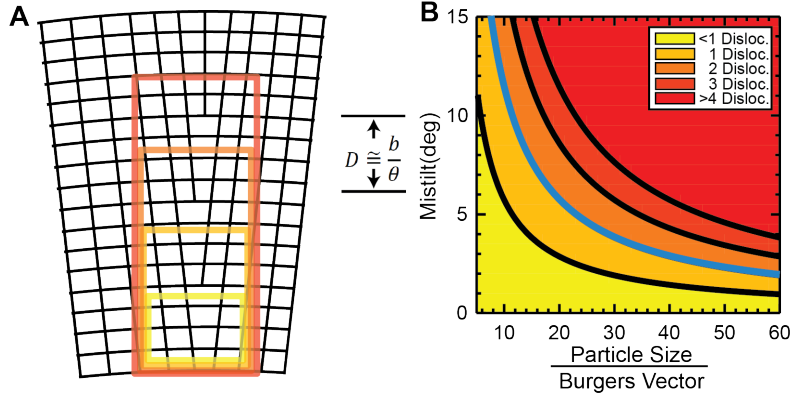


Figure 3.8: (A) A low angle tilt boundary between two crystals where for low tilt angles, the dislocation is given by the equation. The colored boxes represent different sized NCs attaching with a given mistilt, which can be thought of different sized snapshots of the low angle tilt boundary. (B) Plot showing the number of dislocations expected at a NC interface as a function of mistilt angle and particle size normalized by the Burgers vector of dislocations at that interface. Different colors represent how many edge dislocations would be expected for a given particle size and mistilt.

number of dislocations are expected along the interface. We make this more quantitative by calculating the number of dislocations at an interface for a given NC size normalized by the Burgers vector magnitude and mistilt angle. Figure 3.8B shows the results of this analysis; we immediately see that smaller NCs can tolerate larger mistilts before increasing the number of dislocations. We emphasize the cutoff between one and two dislocations at the interface with a blue line, because staying to the left of this line will avoid the formation of multiple dislocations which we observed to greatly hamper dislocation removal (Figure 3.7J). This simple analytic model provides general guidelines for the angular alignment required to achieve attached NCs for which the defects can be more easily removed.

3.3 Discussion

We consider the implications of this work for those interested in attached assemblies of nanocrystals and their electronic properties. In the first section, we discuss the removal dynamics of the dislocations themselves in CdSe. In the second section, we consider the electronic consequences of dislocations in CdSe and discuss ways to mitigate them. Next, we compare the relative merits of attaching wurtzite CdSe on the $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ facets by considering the synthesis of starting materials, dislocation formation, electronic consequences, and dislocation removal. Then, using the insights gleaned from individual NC attachment, we suggest ideal attachment geometries and assembly tolerances necessary to achieve high quality arrays of attached NCs. Finally, we generalize our results to NC attachment of arbitrary materials and connect them to other material growth mechanisms.

Understanding dislocation removal mechanisms in imperfectly attached CdSe

An improved understanding of the removal mechanisms of edge dislocations and prismatic stacking faults is important for this area to advance from strictly empirical to a more predictive approach. The mechanisms themselves vary considerably, depending on the precise local structure of any defects, the orientation of the glide lane relative to the surface, the number of dislocations at the interface, and the possible presence of chemical species at the surface that may be incorporated into the interface upon attachment. In what follows, we discuss the various cases that arise starting first with single edge dislocations, then multiple edge dislocations, followed by PSFs and finally the presence of impurities.

Starting with the simplest case of the perfect edge dislocation scenarios, even here we see that there are various outcomes, depending on the orientation of the glide plane with respect to the surface where the defect can be removed. This changes the relative amounts of climb and glide character needed to remove the dislocations. The “ $\{11\bar{2}0\} \perp \text{Edge}$ ” dislocation has a removal path with pure glide character while such a pathway does not exist for the “ $\{11\bar{2}0\} \parallel \text{Edge}$ ” dislocation. The “ $\{1\bar{1}00\} \text{Edge}$ ” dislocation is in the intermediate regime with both climb and glide character. Based on our kinetic observations, dislocations that require climb for removal are slower and, thus, should be avoided if the goal is to prepare defect free materials. This observation in wurtzite CdSe supports the generality of our previous observations in PbTe.¹⁴⁷ Later we will discuss the feasibility of avoiding dislocations which need climb for removal in the specific case of wurtzite CdSe.

One interesting observation is that the presence of two or more dislocations at the interface greatly hinders dislocation removal. We now consider why it might be that two nearby dislocations can be expected in principle to be much more difficult to remove than a single isolated one. The approach of a single dislocation to the surface can be described as arising by a force between the dislocation and an opposite sense image dislocation present in the vacuum.³⁶ Because of the highly non-linear nature of the surface image force on a single dislocation at an interface, the forces only cancel out if the dislocation is in the exact center, which is mechanically unstable.⁸¹ In the case of two real dislocations at the interface, there are now elastic interactions between both the real and image dislocations. Depending on the exact geometry of the real dislocations, they can be attracted to each other, repelled, or held at an equilibrium distance from each other.³⁶ These interaction forces can cancel out the image forces which attract the dislocation to the surface leading to hindered removal. A detailed examination of the elastic interactions and the precise dislocation geometries that can retard removal is beyond the scope of this work (and would likely require detailed finite element modeling). Nonetheless, the basic idea that the strain fields of multiple dislocations at an interface interact and can suppress removal provides a qualitative understanding for the considerably slowed defect removal of multiple interfacial dislocations.

The simple glide versus climb picture does not apply for prismatic stacking faults. We observed that when a PSF is terminated by a $b = \frac{a}{2}[10\bar{1}0]$ partial dislocation (“ $\{11\bar{2}0\}$ Partial PSF”), the PSF and corresponding partial dislocation are easily removed, whereas a “ $\{11\bar{2}0\}$

PSF” is quite stable. At first glance, this is consistent with the role partial dislocations play in facilitating basal plane stacking sequence changes during wurtzite/ zinc blende phase transitions where nucleated partial dislocations easily move across the basal planes while changing the stacking sequence.¹⁸⁵ If this mechanism were in play here, we would expect to see the partial dislocation move towards the surface and the length of the PSF would become gradually shorter. However, we observe a nearly constant length of the PSF (Figure A.3.10) throughout the annealing and, thus, no movement of the partial dislocation up until removal. Furthermore, we observe a constant streak intensity until the streak returns to the background level within a single frame (Figure 3.5F), indicating an unusually rapid (sub 2 s) defect removal. Therefore, simple partial dislocation migration to the surface is inconsistent with our observations, and we suspect the mechanism of $b = \frac{a}{2}[10\bar{1}0]$ partial dislocation/ PSF removal is more complicated. One possibility is that the PSF first folds over to become a basal plane stacking fault separated by a $b = \frac{a}{6}[10\bar{1}0]$ stair-rod dislocation. The movement of this stair rod dislocation along the $[0001]$ direction could lead to rapid removal of the PSF as it exits the top or bottom surface of the NC film, consistent with the sudden removal of the “ $\{11\bar{2}0\}$ Partial PSF” we observed. Unfortunately, direct observation of this would be difficult since it requires viewing down the $[11\bar{2}0]$ zone axis, which requires a 90° rotation of our sample in its current geometry, something infeasible at present in a TEM. Nonetheless, we speculate the presence of a $b = \frac{a}{2}[10\bar{1}0]$ partial dislocation may facilitate the movement of the stair-rod dislocation which allows the removal of “ $\{11\bar{2}0\}$ Partial PSF” dislocations and not “ $\{11\bar{2}0\}$ PSF” dislocations.

Finally, it is interesting to consider the role that surface impurities may have on dislocation motion in CdSe. It has been well established that chlorine, either from Cl terminated NCs or CdCl_2 treatments of films, is a grain growth and wurtzite/zinc blende phase transition promoter in CdX thin film processing.^{138–141,186} This indicates that Cl facilitates atom rearrangement in CdX materials, and we suspect that Cl may also influence dislocation removal kinetics. In particular, Cl may facilitate dislocation motion since the wurtzite/zinc blende phase transition proceeds *via* partial dislocation motion to alter the stacking sequence.¹⁸⁵ In our work, the NCs likely have some amount of Cl on the surface from the Cetyltrimethylammonium chloride (CTAC) used to prepare the $\{11\bar{2}0\}$ terminated samples. We were careful to ensure that NCs with both $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ facets were prepared using similar chemistry, particularly the presence of CTAC, to ensure impurities had similar effects on the dislocation dynamics for the different facets. It would be interesting to understand the role of impurities on extended defect removal in Cl terminated CdSe and non-Cl terminated CdSe. Considering the vast chemistry available for surface modification in colloidal NCs, surface impurity introduction may be an additional tool to facilitate defect removal after imperfect oriented attachment. The understanding of dislocation motion in CdSe determined by *in-situ* TEM will be used in the subsequent sections to identify ideal attachment facets for wurtzite NCs.

Understanding and mitigating electronic consequences of defects in CdSe

Given the small size and large surface to volume ratio of nanocrystals, materials produced through attachment processes are likely to produce a very high density of electronic defects, at least initially. Thus, the question of identification and if possible mitigation of attachment induced electronic defects is central to the viability of these materials for optoelectronics uses. In many crystalline inorganic semiconductors, some dislocations have negative consequences while others are electronically inactive or can be rendered inactive through appropriate doping. In the case of perfect edge dislocations (Figure 3.4 and A.3.8), we observe the formation of deep hole trap states. The observation of deep trap states for $b = \frac{a}{3}\langle 2\bar{1}\bar{1}0 \rangle$ edge dislocations is qualitatively consistent with what has been calculated for GaN,¹⁸⁷ and the observation of shallow hole traps for PSFs is also consistent with GaN.¹⁵⁵ Phenomenologically this is consistent with the ease of hole trapping in CdSe on un-passivated chalcogen atoms.¹⁸⁸ While not explicitly considered here, the stoichiometry of the dislocation core (determined by the chemical potential of the components during growth) can have a considerable impact on the electronic properties and may represent a pathway to render dislocations electronically harmless.¹⁸⁷ Further small impurities such as hydrogen have been speculated to passivate dislocations cores in GaN. Finally, modulation of the Fermi level through impurity doping can fill dislocation states rendering them inactive. All these factors could be optimized in the future to render harmful defects inactive or at least minimize their influence in attached NC-based materials.

One interesting observation in the case of the “ $\{11\bar{2}0\}$ PSF” is that the electron states avoid the 4- and 8- member ring motif of the PSF in both the noninteracting case, and the interacting case, even though the localized holes at the interface provide a strong Coulomb driving force for electron localization (see for example the edge cases Figure 3.4D). To understand the reason for this, we recall that the electron wavefunction of a state in an individual NC can be modeled as the product of the S-like envelope function and the Bloch wavefunction at the bulk semiconductor band edge.¹⁸⁹ For a carrier to delocalize across an interface, the phase relationship between the Bloch functions of the two NCs must match. Because the PSF introduces a shift of the atomic lattice that is not a lattice translation vector, the Bloch wavefunctions of the two NCs do not share the same phase and, thus, are not able to couple. This observation is similar to the “bond-sign disorder” proposed by Delerue and co-workers.¹⁹⁰ This inhibited coupling appears to be an interesting consequence of PSF formation and is further supported by our electronic structure calculation of the “ $\{11\bar{2}0\}$ Partial PSF” where we observe electron density across the perfect part of the interface and a lack of electron density along the part with the PSF (Figure A.3.11). The ability of PSFs to still create confined states even in attached materials presents interesting possibilities for strongly coupled yet confined systems.

Determining Ideal Attachment Facets for Wurtzite CdSe

One overarching goal of this section was to rationally determine the ideal attachment facet for wurtzite CdSe NCs in the context of minimizing structural defects. As is evident, there is no attachment facet in wurtzite CdSe that leads to an easy removal pathway for all dislocations. This is in contrast to PbTe, and likely more generally, the rock salt lattice where $\{100\}$ attachment provided fast dislocation removal kinetics compared to $\{110\}$ attachment.¹⁴⁷ The CdSe case is more nuanced, and we must consider many aspects, including the shape-controlled synthesis prospects, coupling strength, potential dislocations formed, electronic consequences of those defects, and dislocation removal prospects.

One aspect that must be considered is the prospect of controllably preparing prismatic facet specific NCs. In this work, we were able to prepare comparable samples of CdSe terminated with both the $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ facets. Unfortunately, we were only able to achieve this control with large (~ 15 nm) NCs and we were unable to prepare sub-15 nm $\{11\bar{2}0\}$ terminated CdSe. For CdSe and most other interesting wurtzite semiconductor NCs, this is larger than the exciton Bohr radius in those materials. One big motivator for developing atomically coherent attachment of semiconductor NCs is the goal of producing “confined but connected” solids, where the quantum confined electronic states of the individual NCs are strongly coupled. Thus, we would need to start with small CdSe NCs to contribute to this endeavor and currently only $\{1\bar{1}00\}$ terminated CdSe NCs are available in small sizes. Furthermore, heterostructured NCs such as core shell CdSe/CdS also routinely display $\{1\bar{1}00\}$ surface faceting. We believe considerable synthetic breakthroughs will be needed to prepare small, strongly quantum confined, $\{11\bar{2}0\}$ terminated CdSe, heterostructured CdSe/CdS, or other wurtzite semiconductors. There is a strong case for pursuing connected wurtzite semiconductors on $\{1\bar{1}00\}$ facets.

Attachment on different facets may modulate the strength of coupling between neighboring NCs and is an important consideration if the goal is to prepare materials with delocalized electronic states. The carrier densities shown in 3.2 show that there is little qualitative difference in the carrier delocalization between the two attachment facets in the electron or hole states in both the noninteracting or interacting picture, suggesting that the attachment facet is not the most important factor in determining the electronic coupling. This finding can be understood by considering that the attachment on the $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ facets represent extending the electronic structure along different slices of the Brillouin zone in bulk CdSe.¹⁹¹ Because carrier effective masses are predicted to modulate the resulting miniband structure in patterned electron gasses,¹⁹² the differences in the electronic couplings should be dictated by the differences in the hole effective mass in the light hole band along $\Gamma \rightarrow K$ for the $\langle 1\bar{1}00 \rangle$ direction and $\Gamma \rightarrow M$ for the $\langle 11\bar{2}0 \rangle$ direction as the electron effective masses are the same in both directions ($m_e = 0.12m_0$).¹⁹³ In CdSe, the light hole effective masses are almost identical for the two directions ($m_{lh} = 0.18m_0$ for $\langle 1\bar{1}00 \rangle$ and $m_{lh} = 0.16m_0$ for $\langle 11\bar{2}0 \rangle$).¹⁹³ In more strongly confined systems, the heavy hole properties are likely more important since heavier quasiparticles are less sensitive to confinement effects^{194,195} and, thus, will become the valence band edge state. In this case, the effective masses differ by less than a factor of

two ($m_{hh} = 0.9m_0$ for $\langle 1\bar{1}00 \rangle$ and $m_{hh} = 1.7m_0$ for $\langle 11\bar{2}0 \rangle$),¹⁹³ potentially leading to small differences. Thus, this simple analysis is in agreement with our findings of similar electronic coupling for NC attachment on the $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ facets. A quantitative measure of the electronic coupling between the two attached NCs is the energy difference between the bonding and antibonding states of the lowest energy electron states. Our calculations found splittings of 4.5 meV for $\{1\bar{1}00\}$ attachment and 3.8 meV for $\{11\bar{2}0\}$ attachment. Due to these similar splittings and the predictions of a highly non-linear dependence of the coupling strength on the epitaxial connection area,⁵⁵ we believe facet dependent coupling is of secondary importance in materials with similar direction specific charge carrier effective masses.

As discussed in the first section, avoiding edge dislocations which require climb to be expelled from the interface would greatly expedite defect removal. Here we consider the merits of attaching wurtzite CdSe on the two prismatic facets in the context of extended defect formation and removal prospects. Attachment on both the $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ facets leads to the formation of $b = \frac{a}{3}\langle 11\bar{2}0 \rangle$ edge dislocations with different relative orientations of the glide planes to the surface where they can be removed. $\{1\bar{1}00\}$ attachment leads to an unfavorable glide plane which requires climb of the dislocation for successful removal. $\{11\bar{2}0\}$ attachment leads to two scenarios, one with a favorable glide plane and one with an unfavorable glide plane. As expected, the “ $\{11\bar{2}0\} \perp$ Edge” is able to quickly glide out of the material whereas the “ $\{11\bar{2}0\} \parallel$ Edge” is forced to more slowly climb out of the material. Considering the low incidence of the “ $\{11\bar{2}0\} \perp$ Edge”, there is little difference in the edge dislocation removal, because unfavorable glide plane scenarios occur for both $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ attachment.

In the first section we identified that PSFs bound by a partial dislocation are easily removed while PSF’s across the whole interface are stable. Considering the non-negligible electronic consequences of PSFs, they should be avoided if the desire is to prepare defect free materials. In the case of $\{11\bar{2}0\}$ attachment, there is a pathway to the formation of PSFs and partial PSFs at the interface of the particles (Figure 3.3 E, I). Whereas for attachment on the $\{1\bar{1}00\}$ we did not observe PSFs. For this reason, we believe $\{11\bar{2}0\}$ attachment is less favorable if the desire is to prepare defect free interfaces between attached NCs since $\{1\bar{1}00\}$ attachment avoids the formation of PSFs.

Defects are only undesirable if they result in deleterious properties and in this case, we consider the electronic consequences of those defects. With regard to $b = \frac{a}{3}\langle 2\bar{1}\bar{1}0 \rangle$ edge dislocations, which results in deep level hole traps (Figure 3.4E-H), attachment on either facet can lead to the formation of this edge dislocation with unfavorable removal geometries. Thus, either facet leads to undesirable electronic states coming from perfect edge dislocations. Defects such as PSFs and $b = \frac{a}{2}[10\bar{1}0]$ partial dislocations, which both lead to mid-gap, shallow hole trap states (Figure 3.4A-D, and Figure A.3.11) and deep hole traps in the latter case, make the $\{11\bar{2}0\}$ facet less appealing. This preference for attaching $\{1\bar{1}00\}$ faceted NCs to avoid PSFs is exacerbated in the case of perfect PSF’s because they can’t be removed and likely these defects will persist even after considerable thermal treatment. Considering that PSFs (and associated electronic consequences) and related defects only arise from $\{11\bar{2}0\}$

attachment, the $\{1\bar{1}00\}$ facet is more desirable for attachment when considering the electronic consequences of the dislocations.

Taken together, we believe that, if the goal is to prepare defect free materials, there are fewer negative consequences for attachment on the $\{1\bar{1}00\}$ facet. The specific advantages of the $\{1\bar{1}00\}$ facet are as follows: $\{1\bar{1}00\}$ terminated CdX materials are typically easier to synthesize and $\{1\bar{1}00\}$ attachment does not lead to PSF type defects. The other considerations such as coupling strength, other defect types, and removal are all relatively equal for the different facets. Our considerations are by no means comprehensive nor do the specifics necessarily hold for materials other than CdSe. Nonetheless, we hope to have presented guidelines and the thought process for designing defect free oriented attachment of NCs.

While there is considerable desire is to prepare defect free semiconductor solids from attaching NCs, in practice it may prove too difficult to sufficiently decrease the extended defect concentration. Instead we discuss devices which take advantage of the extended defect electronic levels. In one mode of operation, semiconductor photodetectors operate by trapping the minority carrier for a long time.^{196,197} For example, in the past, our group has used spatially controlled doping of CdTe grain boundaries with Cl to trap holes at the grain interior and transfer the electrons to the highly conductive grain boundary.¹³⁸ The percolative network of grain boundaries allowed for detection of the photogenerated current. Impressively, these materials exhibited a specific detectivity of 5×10^{17} Jones, orders of magnitude higher than single crystal detectors. To see how this strategy could be implemented with epitaxially attached NCs, consider the results of the electronic structure calculations (Figure 3.4). In CdSe, edge dislocations lead to the trapping of holes while only minimally effecting the unbound (noninteracting) electron states. This could allow for similar minority carrier trap mediated photoconductivity, however now the un-trapped carrier resides in a single crystal domain of covalently attached NCs, and potentially will be much more mobile than percolative grain boundary conductivity.

Superlattice assembly tolerances and ideal geometries for atomic attachment

While the attachment of individual NCs provides a step towards extended solids, attachment of multiple NCs considerably complicates many of the considerations. One such complication is that a single imperfect attachment leads to orientational misalignment that can propagate disorder and lead to other imperfect attachment events. Herein, we discuss the origin of dislocations in attached NC arrays and angular alignment tolerances to avoid undesirable multiple dislocation events. The superlattice geometry, in particular whether it tiles all space, is a final consideration for preparing defect free quantum dot solids.

The traditional view of imperfect oriented attachment invokes a surface step getting trapped at the interface between two particles.³⁸ However in our samples, and in many other examples,^{34,45,48,198} the particles are pre-assembled as crystallographically aligned NCs (albeit with some mistilt) with organic ligands separating the inorganic cores, followed by ligand

removal to induce attachment. An alternative mechanism for edge dislocation formation, is that particles with pristine facets can be locked with some mistilt between them enforced by the local arrangement of NCs or size inhomogeneity. When they attach with a mistilt, initially an atomic bridge can form between the particles,¹⁹⁹ and the energy of the interface between the tilted particles is minimized by forming a dislocation through different amounts of atom migration to the opposite sides of the bridge between the misoriented particles. In this picture, pre-assembly of NCs with the smallest amount of mistilt possible will be necessary for defect free attachment. Alternatively, NCs with surface steps would likely cause angular distributions among assembled particles. Observation of the attachment process *in-situ* where the initial configuration of the NCs and their surface geometry is known will likely be needed to answer this question. If the dislocations in these attached materials result from the traditional imperfect oriented attachment view, development of step-edge free NC synthesis methods will be needed, however if the angular misalignment of otherwise pristine surfaces leads to dislocation formation, better controlled self-assembly will be needed to avoid misoriented particles.

Regardless of the origin of the mistilt between the particles, Equation 3.1 and Figure 3.8B provide a simple picture for the angular tolerance needed to avoid multiple dislocations at interfaces. An important takeaway from this plot is that the larger the particles become, the more stringent the mistilt tolerance becomes to avoid multiple dislocations which are considerably more difficult to remove. On the other hand, when assembling NCs, smaller particles would be expected to have more rotational disorder since they are less faceted and especially with the ligand shell would interact more like isotropic spheres. Studies of the rotational disorder in NC assemblies have been done using synchrotron x-ray scattering techniques and they have determined many factors that dictate the quality of the NC assembly.⁵ These studies have mostly focused on determining the fraction of NCs aligned, not on the disorder of those that are aligned. Further ensemble angular alignment may not be the best measure for NC attachment, since only the misorientation between neighboring particles is important in determining attachment success. Despite unresolved questions regarding the origin of the misorientation and the subsequent dislocations, we believe the angular alignment of the NCs can provide an indicator for success of atomic attachment of NCs.

Finally, we will consider the superlattice geometry and its importance in designing quantum dot solids. In this work, we explored the attachment of a close packed system of NCs that tiled all space. One observation was that interface defects between two particles migrated to the node where three particle edges met. Once there, the “node” defect density was not lowered even with thermal annealing at 440°C (Figure 3.7K). For an edge dislocation to be successfully removed, it must move to a free surface where it can be annihilated, or react with a dislocation with the opposite sense, the latter of which is unlikely. Thus, developing a geometry of attached NCs such that each NC interface is nearby a free surface will facilitate complete defect removal. One dimensional chains^{31,61,200} represent a scenario where the attachment interface always has a free surface for dislocations to anneal to. An example of an open 2D array of atomically attached NCs are the honeycomb lattices prepared by Vanmaekelbergh and co-workers.^{45,201} In these honeycomb lattices, the necks between

particles are surrounded on all sides by free surface where defects can anneal to. In the case of attachment of wurtzite CdSe, the hexagonal close packed layers do not afford this openness. Perhaps the co-assembly of CdSe NCs with a filler, such as a polymer micelle, would allow for the formation of honeycomb or other open lattice tilings that provide free surfaces throughout the entire assembly to serve as extended defects annihilation sites.

General insights related to atomically coherent attachment of inorganic materials

We now discuss a few general implications for oriented attachment of inorganic materials based on our careful studies on the attachment of wurtzite CdSe on the prismatic facets. First, we discuss how our work relates to GaN epitaxial growth and single crystal h-BN growth. Next, we consider the possibility of predicting dislocation character resulting from atomic attachment for arbitrary materials. Finally, we propose similar projections for planar defect engineering from NC attachment. Altogether, we hope to inspire many routes to engineering defect (free) materials.

There are many similarities between oriented attachment of wurtzite CdSe and epitaxial growth of GaN and other hexagonal materials. Due to the lattice mismatch between GaN and the typical substrates used for growth, initial films often form Stranski–Krastanov islands of GaN which subsequently grow together and merge.^{202–204} Small mistilts between the islands lead to low angle tilt boundaries when the islands fuse and, subsequently, many $\frac{a}{3}\langle 11\bar{2}0 \rangle$ edge dislocations are formed.^{204,205} This has many similarities to the preparation of CdSe NC solids where the pre-assembled NCs are misoriented by a small amount (Figure A.3.4B shows an electron diffraction pattern of attached CdSe with peak shapes characteristic of mosaicity). In this respect, it is unsurprising that we observe many of the same dislocations when attaching wurtzite CdSe NCs as are seen when growing GaN along the [0001]. In another GaN example, steps on the SiC substrate surface can cause unit displacements along the [0001] direction between neighboring islands, leading to the formation of PSFs in GaN epitaxial layers.^{93,94} In the case of NC attachment, random displacements along the [0001] direction are likely due to differences in NC ligand thickness, steps on the graphene support, or different thickness NCs.

Recently, there have been several reports of wafer scale growth of single crystal graphene and hexagonal boron nitride where island fusion is the observed growth mechanism.^{206,207} In the case of hexagonal boron nitride, researchers used a liquid gold subphase where small single layer hexagonal boron nitride grains initially formed, and subsequently self-oriented and fused into wafer scale single crystals.²⁰⁷ While the attachment facet was not explicitly determined, it will likely have a large impact on defect formation in these materials. Taken together, there are considerable similarities in growth and defect formation between the above discussed materials systems and the fields likely can learn from each other as they pursue their mutual goal of producing high quality materials by attaching nanoscale building blocks to each other.

Next, we consider if it is possible to predict the dislocation character based on the known surface steps that are present for a given facet. In Figure 3.3, we notice the step vector describing the type of surface step edge (yellow arrows Figure 3.3A,I,P) corresponds exactly with Burgers vector of the perfect edge dislocation (Figure 3.3B,M,Q). Upon reflection, this is the reverse process of an edge dislocation being expelled from a material, which leads to a step edge with the same magnitude as the Burgers vector. With this insight, it should be possible to predict the glide plane of a dislocation that may result if the common surface steps are known for a given crystal structure and attachment facet. This surface step and Burgers vector relationship is further supported by our previous work on PbTe, where a $\frac{1}{2}[110]$ surface step on a (100) facet lead to a $b = \frac{1}{2}[110]$ edge dislocation with a favorable glide plane.¹⁴⁷ Whereas a $\frac{1}{2}[110]$ surface step on a (110) leads to a $b = \frac{1}{2}[110]$ edge dislocation with an unfavorable glide plane. Details of this are shown in Figure A.3.12. The consistency of this observation in both the rock salt and wurtzite structure suggests it may be useful in predicting ideal attachment facets for many materials. Furthermore, predictions of the most probable surface step edges are possible using a variety of methods (HRTEM, geometric considerations, or theory) and can aid in attachment facet decision making.

Finally, we consider the possibility of engineering planar defects during NC attachment. We noticed that attachment on $\{11\bar{2}0\}$ facets lead to PSFs which reside in the $\{11\bar{2}0\}$ planes whereas no PSFs formed during attachment on $\{1\bar{1}00\}$ facets. In considering the generality of this observation, we can learn from the oriented attachment of CsPbBr₃ NCs on $\{100\}$ facets into extended solids.^{208–211} In this case, researchers have observed the formation of $\{100\}$ antiphase boundaries, also known as Ruddlesden–Popper planar faults, from the attachment of CsPbBr₃ NCs on $\{100\}$ facets. Based on these considerations, avoiding attachment on facets for which a planar defect in the material can reside may avoid the formation of those defects in attached NC solids. Conversely, if the planar defects have desirable properties, attachment facet choice could be used to prepare materials with engineered defects. PSFs in wurtzite CdSe attached on $\{11\bar{2}0\}$ facets and antiphase boundaries in halide perovskites attached on $\{100\}$ facets provide two supporting examples.

3.4 Conclusion

In this work, we explored many considerations for atomically attaching wurtzite CdSe NCs on $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ facets within the context of preparing defect free solids. We found that attachment on both $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ facets can lead to crystallographically coherent attachment and delocalized electron and hole states with similar electronic coupling strengths. In cases of imperfect attachment on $\{1\bar{1}00\}$ facets, we observed the formation of $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocations which lead to localized mid-gap hole traps. These dislocations can be annealed out of the interface albeit requiring dislocation climb. In the case of $\{11\bar{2}0\}$ facet attachment, we observed four distinct dislocation types resulting from imperfect attachment. Specifically, we found PSF’s across the entire interface that are very difficult to remove and are predicted to lead to shallow hole trap states. We also observed $b = \frac{a}{2}[10\bar{1}0]$

partial dislocations terminated by a PSF that likely lead to deep hole traps but were easy to remove. Finally, for $\{11\bar{2}0\}$ facet attachment, we observed two different $b = \frac{a}{3}\langle 2\bar{1}\bar{1}0 \rangle$ edge dislocation scenarios, one which had a favorable glide plane for removal and the other which had an unfavorable glide plane for removal. Regarding some aspects, the two facets have comparable (dis)advantages: in the case of CdSe, there is no obvious difference in the electronic coupling strength of the two facets, and they both lead to the formation of $b = \frac{a}{3}\langle 2\bar{1}\bar{1}0 \rangle$ edge dislocations and their associated deep hole traps. That being said, after careful consideration, we believe attaching wurtzite CdSe NCs on the $\{1\bar{1}00\}$ facet is better for several reasons including: greater synthetic maturity for preparation of $\{1\bar{1}00\}$ terminated CdSe NCs, $\{1\bar{1}00\}$ attachment avoids PSF formation, and while not ideal, $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocations can be removed with annealing though a combination of dislocation glide and climb.

While there appears to be a path forward dealing with imperfect attachment resulting in single dislocations at interfaces, we elucidated that multiple dislocations, regardless of attachment facet, were unable to be removed even with considerable annealing. Thus, an imperative design principle is to avoid the formation of multiple dislocations. Considering defective interfaces between NCs as snapshots of low angle tilt boundaries, a simple analytical model provides guidelines for angular tolerances needed to avoid multiple dislocations. Based on observations of dislocations formed in PbTe¹⁴⁷ and CdSe, we suggest that careful considerations of the step edges on surfaces can be used to predict the character of the dislocations arising from imperfect oriented attachment. A similar consideration of planar defects in CdSe and CsPbBr₃ suggests a rational design principle to control planar defects from particle attachment. Taken together, we hope this work provides guidelines for engineering (or eliminating) defects in atomically coherent arrays of attached NCs.

Despite the immense desire to realize the intriguing theorized electronic properties predicted for arrays of atomically attached semiconductor NCs,^{51,53,54} experimental realization of these materials lags considerably, having achieved delocalization lengths only on the order of tens of nanometers.³⁴ Thus, the pathways which lead to deleterious defects, identification of deleterious defects through both experimental and theoretical endeavors, and improved strategies for defect free synthesis will need to be understood and developed to realize attached NC arrays of sufficient quality to realize these delocalized electronic properties. While noble, the tolerances for realizing delocalized carriers may be too tight, and rather NC attachment can be harnessed to engineer defect states which in and of themselves provide desirable properties. In this work, many similarities were observed between defective NC attachment and dislocations in bulk materials. Considering the similarities, the NC attachment community can be inspired by strategies in traditional semiconductor processing, such as dislocation free silicon growth and high quality GaN epitaxial growth, where defects have been engineered or eliminated to provide the desired functionality.

3.5 Materials and Methods

Materials: cadmium Oxide (CdO) 99.99% Aldrich; oleic acid 90% (OA) technical grade Aldrich; oleylamine (OAm) technical grade 70% Aldrich; octadecene 90% (ODE) technical grade Aldrich; *n*-trioctylphosphine 97% (TOP) Strem; methanol 99.5% extra dry Acros; cetyltrimethylammonium chloride (CTAC) >95% TCI; dioctyl ether (OE) 99% Aldrich; selenium 99.99% Strem; sodium selenide (Na_2Se) 99.5% Alfa Aesar; CVD graphene on copper 3-5 layer ACS materials; Quantifoil R1.2/1.3 300 mesh Au holey carbon SPI supplies; Ultrathin Carbon Film on Lacey Carbon Support Film, 300 mesh, Gold (1824G Ted Pella Inc.). Nanocrystal Synthesis. Wurtzite CdSe NCs with $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ termination were synthesized based on heavily modified literature procedures.¹⁶⁵

Zinc blende CdSe Seeds: 8mmol CdO (1028 mg), 20mmol OA (6.4 ml), and 40 ml of ODE were loaded into a 100 ml round bottom flask and degassed on a Schlenk line at 110°C for 1 hour. The flask was filled with argon and heated to 210°C to form a Cd-oleate complex. Meanwhile, in a glovebox, 4 mmol Se (316 mg), 3.32 g TOP, and 5.49 g ODE were stirred until all the Se dissolved, and then loaded into a syringe. The contents of the syringe were rapidly injected into the Cd-oleate solution at 210°C and allowed to react for 20 min. The samples were cooled to room temperature and cleaned 2× in air by precipitating the NCs with ethanol and centrifuged at 8000 rpm. The resulting pellet was dissolved in hexanes. Samples were transferred to a glovebox and stored in hexanes. The concentration of the NC solution was determined photometrically using known size dependent extinction coefficients.²¹²

$\{1\bar{1}00\}$ Terminated Wurtzite CdSe: 400 μl of OA, 412 μl of OAm, 40 mg of CTAC, and 5 ml of octyl ether were loaded into a 25 ml round bottom flask and degassed at 50°C for 20 min. While still under vacuum, a hexanes solution of zb CdSe seeds were added to give a Cd:Cl ratio of 1:1 and the solution was degassed to remove the volatiles. The flask was refilled with argon and heated to 260°C. After 10 min at 260°C, a ~ 1.5 ml aliquot was removed and quenched in room temperature toluene. Samples were cleaned 2× in air by precipitating the NCs with acetone and centrifuged at 8000 rpm. The resulting pellet was dissolved in hexanes. A final centrifugation of the sample in hexanes was performed to remove any insoluble material.

$\{11\bar{2}0\}$ Terminated Wurtzite CdSe: 400 μl of OA, 412 μl of OAm, 40 mg of CTAC, and 5 ml of octyl ether were loaded into a 25ml round bottom flask and degassed at 50°C for 20 min. While still under vacuum, a hexanes solution of zb CdSe seeds were added to give a Cd:Cl ratio of 1:1 and the solution was degassed to remove the volatiles. The flask was refilled with argon and heated to 280°C for 20 min. After 20 min, the reaction was quickly cooled to room temperature using a stream of air. Samples were cleaned 2× in air by precipitating the NCs with acetone and centrifuged at 8000 rpm. The resulting pellet was dissolved in hexanes. A final centrifugation of the sample in hexanes was performed to remove any insoluble material.

Nanocrystal Attachment and TEM Sample Preparation: All samples of attached NCs were prepared using gold TEM grids. In some cases, we used homemade Graphene-

coated TEM grids which were prepared by direct transfer of 3-5 layer graphene onto holey quatifoil TEM grids.¹⁰⁷ In other cases, samples were prepared on ultrathin carbon supports (1824G Ted Pella Inc.). Dilute solutions of the desired NCs in toluene were drop cast on the TEM grid, and the large excess of solvent was wicked away, leaving a small droplet covering the TEM grid. The grid was covered with a watch glass and allowed to slowly dry. After several hours, the TEM grid was picked up using anti-capillary self-closing tweezers and carefully pumped into a nitrogen filled glovebox. The sample was then dipped in a solution of Na₂Se in anhydrous methanol (1.66 mg/ml) for 45 s followed by dipping in neat anhydrous methanol to remove excess Na₂Se. The sample was then placed in the glovebox antechamber and placed under vacuum to remove excess methanol. TEM samples were stored in air with no obvious degradation occurring over several months.

X-Ray Diffraction: To avoid orientation effects, the NCs were made into fine powders. Powders were prepared by depositing large amounts of the NCs from hexanes onto a glass slide, and allowed to dry, the film was then scraped off the glass slide with a clean razor blade onto a $\langle 510 \rangle$ oriented Si low background diffraction substrate. Diffraction patterns were collected on a Bruker Phaser D2 diffractometer with Cu $k\alpha$ source operated at 30 kV and 10 mA with a 160SSD detector. Diffraction patterns were collected from 20° to 60° 2θ with a step size of 0.02°, an integration time of 7s per step.

TEM Imaging TEM imaging was performed on a FEI Tecnai T20 S-TWIN TEM operating at 200 kV with a LaB₆ filament. Images were taken near Scherzer focus, which resulted in dark atom contrast for this crystal thickness. Time series of TEM images were collected with a Gatan Orius SC200 using a custom digital micrograph script with full 2048 $\times$ 2048 pixel readout, at a nominal magnification of 195k $\times$, resulting in a pixel resolution of 0.27 Å/pixel, an exposure time of 0.7s, and a readout time of 1.4 s, yielding a frame rate of 0.48 fps. Since the defect dynamics were beam initiated, care was taken to minimize electron dose prior to imaging. Searching was performed with a spread beam; then once a suitable defective nanoparticle was found, a custom Digital Micrograph script was used to condense the beam to reproducibly return to the same dose rate within a session for each movie acquisition.¹⁸⁴ We estimate a dose rate of $\sim 5000 \frac{e^-}{\text{\AA}^2 \cdot \text{s}}$ was used for all data collected and a conversion value of 6.7 was used to convert CCD counts to electrons. For thermal annealing experiments ~ 150 HRTEM images of attached particles were first collected, then the sample was annealed in the TEM column (8.8×10^{-8} torr pressure) at 440°C for 15min in a Gatan model 628 crucible heating holder with an inconel furnace. The sample was then cooled back to room temperature and another ~ 150 HRTEM images were collected.

TEM Image Analysis: TEM image stacks were first drift corrected with subpixel accuracy using the image alignment tools in Gatan Digital Micrograph 3.0 (GMS 3.0) and alignment success was manually inspected. In some cases, the raw images were used for drift correction and in other cases, a Sobel or Hanning filter produced better alignment. For all FTs displayed and analyzed care was taken to avoid streaking artefacts that result from image edges. Briefly in GMS 3.0, a 2^n by 2^n pixel area of interest was cropped from the image and was subsequently multiplied by a 2D Hanning window followed by computing the FT. For visualization, the log of the modulus of the FT was saved and visualized in ImageJ

using the “fire” lookup table to facilitate viewing. The position of edge dislocations were determined using the same strategy we used previously.¹⁴⁷ Prismatic stacking fault presence was determined by analyzing the streak intensity in the FT. First a Hanning filtered FT of a sub-area of each frame was computed, then a mask was used to select only the streak area, and a sum of the counts was computed. A Hanning filtered FT of the same size of a nearby sub-area from the same image series where a perfect crystal was observed was also computed. The same mask was used to determine the background intensity in the FT. To account for fluctuations in image quality with time, the FT streak intensity was normalized by the intensity of the $\{1\bar{1}00\}$ spots in the FT from the perfect crystal sub-area.

For heating experiment analysis, a custom automated Matlab routine was written to identify imperfections in the lattice which was used as an aide to manually identify dislocation density. First a Fourier transform of the image was calculated and the 6 spots corresponding to the $\{1\bar{1}00\}$ planes were automatically found to determine the rotation of the lattice in the image. Next the image was separately Fourier filtered by 3 different masks corresponding to the $(1\bar{1}00)$ $(10\bar{1}0)$ $(01\bar{1}0)$ planes. Each Fourier filtered image was then binarized and skeletonized then the endpoints and branchpoints of the skeleton image were determined (these correspond to potential edge dislocations). Only branch and endpoints from image areas with inverse FT magnitude above a certain threshold were kept by the routine. Finally, the raw image, Fourier filtered images, and image overlaid with the potential dislocation positions were displayed side by side in a Matlab Figure. In each image, the number of interfaces as well as the number of dislocations and PSFs were manually counted after careful inspection of each potential dislocation determined by the image analysis routine. The routine was written and tuned to be oversensitive to avoid missing any dislocations.

Computational Methods: Initial structures of the imperfectly attached NCs were generated by cutting from large crystal slabs which contained the desired dislocation. Slabs of wurtzite with the different dislocation structures were generated using the ATOMSK software.²¹³ Briefly, a wurtzite CdSe unit cell was generated in ATOMSK using bulk lattice constants. Next, the primitive unit cell was converted to an orthogonal unit cell with lattice vectors X, Y and Z along the $[11\bar{2}0]$, $[1\bar{1}00]$ and $[0001]$ directions in wurtzite, respectively, and a supercell of sufficient size was generated. The edge dislocations were introduced into this slab using isotropic elasticity theory using a Poisson ratio of 0.26. For the $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocations, an edge dislocation in the center of the supercell with a sense along the Z direction of the supercell and a displacement of 4.30 Å along the X direction was introduced into the supercell. The exact center of the dislocation was optimized to prevent it from occurring on an atomic position to avoid non-physical displacements. For the $b = \frac{a}{2}[10\bar{1}0]$ partial dislocations, first, an edge dislocation in the center of the supercell with a sense along the Z direction of the supercell and a displacement of 2.15 Å along the X direction was introduced into the supercell. Next, a screw dislocation with a displacement of 3.51 Å along the Z direction was introduced. For the prismatic stacking faults, a displacement of 3.73 Å in the Y direction and 3.51 Å in the Z direction was introduced into the supercell.

Imperfectly attached NCs were cut from these slabs according to the following procedure. Two spherical masks were created with their centers equidistant from the dislocation core,

and the atoms outside of these masks were removed. The intersection of the two spheres determined the particle interface and contained the relevant dislocation. The individual spheres were approximately 6.5 nm in diameter. The size and intersection of the NCs were tuned such that all the attached NC structures had approximately the same number of atoms and atoms at their interface. We used the same procedure to create the perfectly attached NCs.

We then performed molecular dynamics based geometry minimization of the NCs *via* the conjugate gradient algorithm implemented in LAMMPS²¹⁴ using previously developed Stillinger-Weber interaction potentials for CdSe.¹⁷² To obtain the final configuration for which we ran the electronic structure calculations, the outermost layer of atoms was removed and the subsequent monolayer was replaced by ligand potentials representing the passivation layer, where each Se (Cd) atom was replaced by a ligand potential for Cd (Se).²¹⁵ For the imperfectly attached NCs, care was taken to ensure that the defect site was not disrupted by this passivation procedure. Specifically, we did not passivate the interior atoms of the defects, but we did passivate the atoms on the top and bottom of the defect site. An atom was categorized as interior if all positions along the surface of a sphere centered at the atom with a radius of ~ 3.5 Å were within ~ 3 Å of at least one atom or if the atom had four bonds. All crystal structures shown in this manuscript were visualized using the VESTA software.²¹⁶

Electronic structure calculations were performed using the semi-empirical pseudopotential method.¹⁷¹ The filter-diagonalization technique^{158,173} was used to find the quasiparticle states near the band-edge. These quasiparticle states were then used to produce carrier density plots and, separately, as input to the Bethe-Salpeter equation to obtain the correlated electron-hole (*i.e.* excitonic) states.¹⁷⁴ The Bethe-Salpeter equation was solved within the static dielectric approximation ($\epsilon = 5$).

Chapter 4

Long Range Oriented Assembly and Atomic Attachment of Wurtzite CdSe/CdS Core/Shell Nanocrystals

Contents of this chapter to be published: Ondry, J. C.; Philbin, J. P.; Lostica, M.; Rabani, E.; Alivisatos, A. P. “Combining Colloidal Synthesis and Assembly with Epitaxial Growth to Fuse Nanocrystals into Tunable 0D-2D Quantum Dot-in-matrix Superlattices ”

By combining colloidal nanocrystal synthesis, self assembly and epitaxial growth techniques, we developed a general method for preparing monolayer thick atomically attached quantum dot superlattices with high quality translational and crystallographic orientational order and state-of-the-art uniformity in the attachment thickness. The procedure begins with a colloidal synthesis of hexagonally shaped core/shell quantum dots (e.g. CdSe/CdS), followed by liquid subphase assembly and immobilization of the monolayer thick quantum dot superlattice on a substrate. Lastly, epitaxial growth of additional semiconductor material fills in the voids between the particles resulting in a epitaxial quantum dot-in-matrix structure. Annealing of the resulting structures allows inhomogeneities in the quantum dot-quantum dot attachment thickness, which lead to Anderson-type localization demonstrated by our atomistic electronic structure calculations, to be removed. The step-wise nature of this procedure allows one to independently tune the size and material of the starting quantum dot core, quantum dot shell, superlattice parameter, and the interdot filling material. These three choices provide ample knobs that can be turned to control many properties (e.g. degree of quantum confinement, quantum coupling, band alignments, etc.) depending on the specific applications. Importantly, the photoluminescence emission spectra of the quantum dot-quantum well structure retains the characteristic of the 0D, quantum dot building blocks. Furthermore, cation exchange reactions can be performed on the final quantum dot-quantum well, as demonstrated herein with a CdSe/CdS to HgSe/HgS cation exchange

4.1 Introduction

Colloidal semiconductor nanocrystals have evolved into a diverse class of materials with impressive control of their size,²¹² composition,²¹⁷ shape,¹⁴⁸ and luminescence properties.²⁴ Spherical nanocrystals display atomic-like electronic structures due to the 0D confinement. These quantum confined structures have hydrogen-like wavefunctions and are often called “quantum dots” or “artificial atoms”.^{10,218} In isolation colloidal quantum dots have many unique properties making them useful for applications such as bio imaging²¹⁹ and display technologies.²²⁰

Colloidal nanocrystals are known to readily assemble into crystalline superlattices when their size distribution is sufficiently narrow.^{25,114} From a structural standpoint, the “artificial atoms” have been assembled into an “artificial solid” where the structure is described by a unit cell and lattice vectors. The electronic properties of an atomic solid is quite different than an isolated atom of the same identity due to the periodic array of atomic wavefunctions. These combine in a linear combination of atomic orbitals to give rise to the band structure of an atomic solid which in turn controls properties (e.g. band gap, electronic transport). The identity of the atoms and their arrangement both tune the properties of a material. Considering the drastic differences between an isolated atom and a crystalline solid, by analogy an isolated nanocrystal will have distinct properties compared to a crystalline superlattice of the same nanocrystals. It turns out in most cases, semiconductor nanocrystal superlattices and isolated semiconductor nanocrystals have similar properties and we don’t see the appearance of a band structure resulting from the nanocrystal super atom lattices.

The problem lies in the small magnitude of the electronic coupling between two semiconductor nanocrystals which are separated by their organic ligands used during synthesis.³⁰ Indeed this can be thought of as analogous to the nearest neighbor overlap integral (typically γ^3 or analogously β in a linear combination of atomic orbital formalism) in a tight binding model, and in the case where it is small, localized wavefunctions and trivial flat bands result. To increase the electronic overlap of the nanocrystals and thus the γ parameter, the nanocrystals must be brought much closer together and the potential barrier significantly lowered to realize meaningful communication between neighboring nanocrystals. Short organic linkers and inorganic molecules have been used to replace the long insulating ligands.⁸⁹ The transport in these materials is still dominated by a hopping mechanism^{221–223} rather than band-like transport, indicating the barriers to transport are still too large.

One way around this is to completely eliminate all foreign material at the interface between two nanocrystals and form a homoepitaxial bridge between two crystallographically aligned nanocrystals. In essence a thin neck between the two nanocrystals maintains the individual quantum confinement, but allows sufficient communication between the nanocrystals. This is achieved by self assembling PbX nanocrystals at a liquid interface and selectively displace lead oleate ligands from the surface, leading to bare facets. Next the facets fuse leading to all inorganic bridges between the nanocrystals.³¹ This strategy has resulted in well-ordered superlattices of PbSe with square and silicene morphologies. Despite the improved coupling between the nanocrystals, these materials are still defined by hopping based

transport despite theoretical predictions of mini-band states. It appears that disorder in the energy landscape and coupling strength between neighboring nanocrystals is too large and leads to Anderson-like localization.^{34,133,224}

Whitham *et al.*³⁴ showed that the variation in the nearest neighbour coupling strength was a limiting factor leading to localized states. There are two structural parameters which cause coupling strength variations, the dot-to-dot spacing and the thickness of the neck. Considerable strides have been made to understand and mitigate the positional ordering in PbSe superlattices,³³ and long range positional ordering has been achieved. Less attention has been paid to neck thickness variations which likely contribute more to carrier localization.³⁴ In the direct attachment of PbSe nanocrystals, the inorganic bridges have considerable variation in their diameters likely due to the stochastic nature of the attachment process and inherent size inhomogeneity in nanocrystals.³³ These variations lead to large variations in the coupling strength between nearest neighbors.⁵⁵ There doesn't seem to be a clear path towards improving uniformity of the neck thicknesses, for example subsequently growing additional material via layer by layer growth increases the average neck thickness, but the variation remains.¹⁰² An inherent problem with this design is the coupling is controlled by a thin bridge of material between the dots, which is difficult to control. Ultimately this structure is thermodynamically unstable since it has a high surface area compared to competing structures, thus annealing the samples with the hopes of achieving uniform necks may not be possible and ultimately the local thermodynamic equilibrium is uniform thick 2D sheet of PbSe, destroying the 2D quantum dot superlattice.

Instead we propose creating a quantum dot superlattice based on composition variations. In such a design, the properties of the quantum dot and matrix material (band offsets, effective masses, dielectric constants) tune the distance dependent coupling. Importantly, in this design the neck (matrix) material can be made arbitrarily thick while still maintaining quantum confinement of the quantum dot levels. In this work we develop a strategy to prepare 2D composition superlattices of CdSe/CdS quantum dot-in-matrix structures which display long range positional order, single crystal like diffraction, and well-defined CdSe dots in a CdS matrix. We start with colloidal hexagonal prism shaped CdSe/CdS core shell nanocrystals terminated with $\{1\bar{1}00\}$ facets. These self assemble into 2D hexagonal superlattices where the hexagonal prisms lie face down, resulting in face-to-face alignment of the $\{1\bar{1}00\}$ facets which encodes atomic lattice alignment of the nanocrystals in the superlattices. Finally the inorganic matrix of CdS is epitaxially infilled into the voids from the organic ligands *via* SILAR growth. We show that we can achieve well-ordered superlattices with single crystal atomic domains. Further STEM-EDS characterization shows we can deterministically place the CdSe dots at well-defined lattice positions in the CdS matrix. Importantly we show that we can achieve uniform neck thicknesses upon thermal annealing, resulting in a more uniform quantum dot coupling landscape. Finally we demonstrate the CdSe/CdS arrays can be transformed into HgSe/HgS arrays *via* cation exchange. Our results pave the way for preparing 2D composition superlattices of II-VI semiconductors.

4.2 Results

Synthetic Design

One overarching goal of this work is to develop a highly tuneable and modular semiconductor nanocrystal (quantum dot) self assembly and epitaxial attachment scheme to result in a quantum-dot-in-matrix structure. Ultimately to possibly realise emergent physical properties, many sources of disorder must be eliminated.^{33,34,133,225} In 2D quantum dot superlattices prepared from colloidal nanocrystals, position, crystallographic orientation, and quantum dot-quantum dot coupling strength order must be achieved. Positional order is typically achieved with nanocrystals that have narrow size distributions so they crystallize into superlattices. Crystallographic orientation order in nanocrystal assemblies is typically achieved by using faceted polyhedral shapes which encodes a preferential crystallographic alignment through the asymmetric interaction potential of the particles. Coupling between quantum dots in colloidally derived systems is typically achieved by homoepitaxial bridges where the thinner neck tunes the electronic coupling strength of the quantum dots. Experimentally there is considerable variation in neck thickness for the PbSe system,³³ and there is no obvious path to improvement. To this end, we developed a clean sheet redesign of nanocrystal assembly and subsequent attachment which aims to address all three sources of disorder (Figure 4.1). We start with well-faceted wurtzite CdSe/CdS nanocrystals (Figure 4.1A) which have an approximate shape of a regular hexagonal prism. The base shape of the particles are defined by the 6 $\{1\bar{1}00\}_{AL}$ facets of the wurtzite structure (Figure 4.1A i) and iii), and the caps are defined by the $[0001]$ and $[000\bar{1}]$ facets (Figure 4.1A ii) and iv). The nanocrystals have a average size of 11 ± 0.8 nm and a powder x-ray diffraction pattern consistent with the wurtzite structure (Figure A.4.1A-C). Our samples are similar to those reported by others for CdSe@CdS dot@platelet structures, however our synthesis is distinct and results in particles with more uniform size and shape.^{161,226,227} The majority of the nanocrystals have hexagon shaped cross sections (Figure A.4.2) however they had non-negligible populations of misshapen nanocrystals (Figure A.4.3). Ultimately the hexagonal prisms can self assemble at a liquid-liquid interface²²⁸ such that a single crystal alignment is achieved across the sample (Figure 4.1B) when the thin prisms lie flat at the interface and the hexagons interlock. Importantly, choice of the initial core/shell structure (see Figure A.4.1D-G) encodes an electronic potential variation in the composition that can later be used in lieu of neck thickness variations at nanocrystal interfaces to create coupled quantum dot superlattices.

In these initial assemblies, the inorganic nanocrystals are separated by their organic ligands and thus won't be strongly coupled. The goal is to remove these ligands and replace them with an inorganic bridge that is isostructural to the nanocrystals themselves. Typically this is achieved by chemically removing the ligands exposing bare nanocrystal facets, and allowing nanocrystal fusion.⁴⁶ A complication of this strategy is the subsequent large volume change that results upon ligand removal which must be managed before the nanocrystals attach otherwise disordered and highly cracked arrays result. In the optimized system of

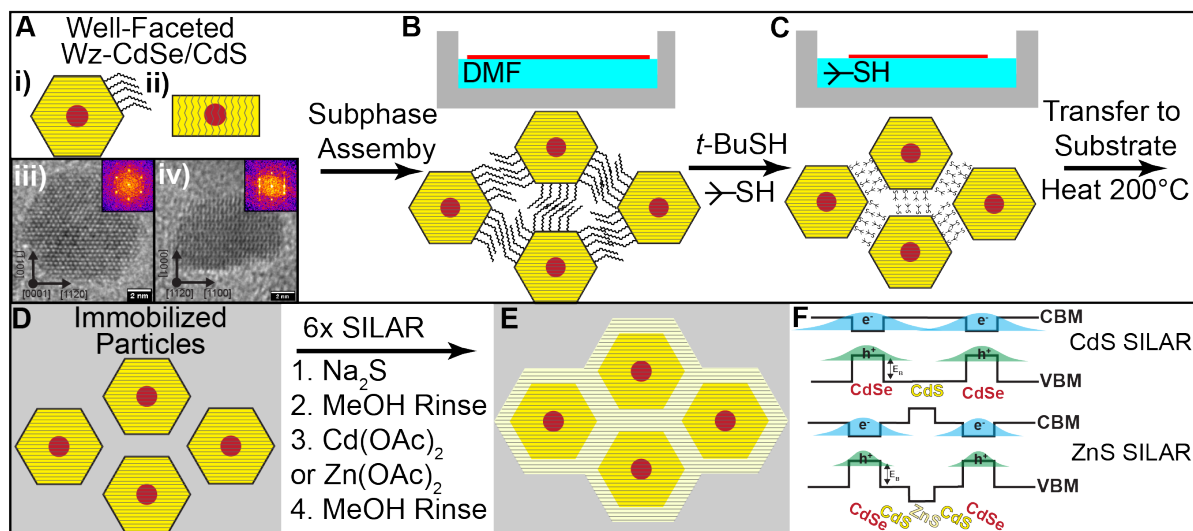


Figure 4.1: Scheme for assembling and attaching wurtzite CdSe/CdS core/shell nanocrystals into crystallographically fused arrays (A) Schematic representation of the prepared CdSe/CdS core shell nanoplatelets viewed down the (i) $\langle 0001 \rangle$ zone axis and (ii) the $\langle 11\bar{2}0 \rangle$ zone axis with representative HRTEM images (iii) and (iv) respectively. (B) DMF liquid subphase assembly of CdSe/CdS nanocrystals into hexagonal ligand separated superlattices followed by (C) *in-situ* ligand exchange to t -BuSH. (D) Transfer of t -BuSH terminated superlattices to substrate followed by a 5 min 200°C anneal to thermally decompose the ligands. (E) SILAR treatment to epitaxially grow bridges between the particles. (F) Schematic energy band alignment for CdSe/CdS/CdS (top) and CdSe/CdS/ZnS (bottom) prepared by assembly and subsequent SILAR.

PbSe, the rates of ligand removal and attachment are appropriately balanced where the nanocrystal superlattice can contract in a concerted manner and thus mitigate the ligand loss induced volume change.³² Such favorable kinetics are not universal to other classes of inorganic materials and thus the concerted nature of this transformation is not generally applicable. For example it is much more difficult to remove oleate from the surface of CdX nanocrystals compared to PbX,²²⁹ and our attempts to remove the ligands while still at the liquid liquid interface resulted in either disordered attachment or no attachment. To circumvent this we completely decoupled nanocrystal assembly from attachment. First the native oleate ligands are replaced by a t -BuSH ligand *via* a subphase ligand exchange^{127,128} (Figure 4.1C) and then transferred (scooped) onto a substrate. Gentle annealing of the superlattice leads to the thermal decomposition of the t -BuSH²³⁰ leading to an immobilised nanocrystal superlattice without surface ligands (Figure 4.1D) and thus locking in the initial assembly configuration. Finally epitaxial layer-by-layer deposition of CdS and ZnS *via* successive ion layer adsorption and reaction (SILAR)^{231–233} of additional semiconductor material at the interfaces results in a crystallographically fused array of core/shell/shell heterostructures. The modularity of this step allows many possibilities including homoepitaxial growth lead-

ing to bi-material heterstructures (Figure 4.1F top), and heteroepitaxial growth leading to tri-material heterostructures (Figure 4.1F bottom).

Atomic and Mesoscale Structural Characterization

Structural characterization of the nanocrystal assemblies via TEM, HAADF STEM, electron diffraction, and HRTEM throughout the process are presented in Figure 4.2. Initial assemblies of oleate capped nanocrystals are prepared by evaporating dilute octane solutions of nano-hexagonal prisms on a DMF liquid subphase in a teflon well. Figure 4.2A part i) shows a Bright field TEM image showing the well-ordered superlattice on short ranges, ii) shows a high angle annular dark field scanning transmission electron microscopy image (HAADF-STEM) of the superlattice, showing linear thickness contrast, highlighting the lack of inorganic material between the nanocrystals. In iii), we show a small angle electron diffraction pattern which probes the superlattice ordering, collected over an $11 \mu\text{m}^2$ area. The pattern shows distinct spots with a hexagonal pattern, consistent with a single crystal hexagonal superlattice domain, indicating the samples have large single crystal domains. Further, large field of view TEM images and Fourier analysis in Figure A.4.4 show we can obtain single superlattice domains of at least $7 \mu\text{m}$ by $7 \mu\text{m}$ ($49 \mu\text{m}^2$). We probe the atomic lattice in (iv) by collecting a wide angle electron diffraction pattern over the same area. In this case, we observe a non-uniform distribution of diffracted intensity. Importantly we only see intensity corresponding to $\{1\bar{1}00\}_{AL}$, $\{11\bar{2}0\}_{AL}$ and $\{2\bar{2}00\}_{AL}$ planes of the wurtzite lattice. This is indicative of the particles oriented with their c-axis perpendicular to the substrate. Additionally, the $\{1\bar{1}00\}_{AL}$, $\{11\bar{2}0\}_{AL}$ and $\{2\bar{2}00\}_{AL}$ peaks appear as 6 distinct arcs, indicating there is also preferential orientation of the nanocrystal atomic lattice in plane (quantitative analysis of this will be presented later). The arcs rather than spots indicate there is some variation in the atomic lattice orientation in-plane within the sample. (we note the diffraction patterns are displayed on a log scale, so the widths of the peaks are exaggerated). HRTEM of the native lattice shown in Figure 4.2A v), paints a clearer picture where the $\{1\bar{1}00\}$ facets of the hexagons are matched face to face separated by the space occupied the oleate ligands. These structures are similar to the atomically aligned bi-pyramid and bi-frustum ZnS nanocrystals.^{234,235} Taken together, the TEM and diffraction data suggests we have prepared monolayer hexagonal superlattices of wurtzite CdSe/CdS nano hexagonal prisms where the nanocrystal share a common crystal alignment.

Next we wanted to quantify the translational order in the superlattices so we can understand how the ordering changes as the samples are subsequently processed. One way to do this is though calculating the 2D autocorrelation of the image.^{236,237} This provides a measure of the self similarity of an image across different length scales. To this end we calculated the 2D autocorrelation of the a large field of view TEM image (Figure 4.2A vi)) which was carefully normalized to account the effects of diffraction contrast²³⁶ and random noise²³⁸ (See Figure A.4.5 for details of the normalization). We observe peaks in the autocorrelation function for each lattice translation vector and the amplitude of the peaks decays for larger shifts indicating decreasing self-similarity at larger translations. Linecuts along the Γ -M directions

are shown in vii) which show a smooth decay of the autocorrelation envelope. We quantify the correlation length, $\xi_{0.5}$ of the assembly where the autocorrelation envelope decays to 0.5 of the initial value²³⁷ along the Γ -M direction. In the case of the initial assembly, $\xi_{0.5}$ extends to 300 nm or ~ 23 superlattice periods. The correlation length measured here is among the best achieved for spherical nanocrystal self assembly.²³⁷

Upon treatment with *t*-BuSH via a subphase ligand exchange and thermal annealing at 200°C for 5 min (Figure 4.2B), TEM and electron diffraction show qualitatively similar superlattices as before. This indicates the superlattice structure and atomic alignment of the superlattices have been well maintained. The only difference is the particles have been brought slightly (~ 1 nm) closer due to the smaller size of the *t*-BuSH molecule. Although at this point, the nanocrystals are still completely unattached, as clearly seen by the HAADF STEM image in ii). The 2D autocorrelation in Figure 4.2B vi) for the ligand exchanged samples show similar isotropic amplitude and a $\xi_{0.5}$ which extends to ~ 225 nm or 18 superlattice periods indicating some loss of order during the ligand exchange. Importantly, the nanocrystals no longer have long-stabilizing ligands on their surfaces and thus the monolayer nanocrystal films can be exposed to a variety of polar or non-polar solvents without dissolution or notable loss of order. This opens up considerable possibilities for post assembly growth of additional semiconductor material.

While there are many possibilities for post assembly growth of inorganic material, in this work we focus on successive ion layer adsorption and reaction (SILAR) techniques because of implementation ease and exquisite layer thickness control. For the growth of CdS in between the nanocrystals we subsequently treat our samples with methanolic solutions of Na₂S and Cd(OAc)₂ with neat methanol rinses in between. The amount of material deposited can be simply controlled by differing the number of SILAR cycles. In Figure 4.2C i), a bright field TEM image of a CdSe/CdS nano-hexagon with 6 monolayers of SILAR grown CdS show quite uniform contrast across the image, though in some parts, faint outlines of hexagons can be observed. This is consistent with a uniform inorganic film without ligands between the nanocrystals. HAADF STEM images in Figure 4.2C ii) confirm inorganic material has grown in between the individual nanocrystals into a uniform thin film. We note the necks between the particles are still slightly thinner, and a few areas without material at the interfaces. Small angle electron diffraction in Figure 4.2C iii) confirms large area superlattice domains remain. Figure 4.2C iv) shows that the atomic lattice orientation of the nanocrystal superlattice is also maintained.

HRTEM in Figure 4.2C v) of the SILAR grown CdS at the interface between nanocrystals shows an epitaxial relationship between the nanocrystals and the material infilling the gaps. Indeed the nanocrystals appear considerably larger and have crystalline material with an epitaxial relationship to the center of the nanocrystal across the entire interfaces. Further, a Fourier transform of the HTREM image reveal only peaks consistent with $\{1\bar{1}00\}$ lattice planes, which appear as 6 distinct arcs, further supporting the epitaxial relationship of the material grown between the interfaces. We note that the small misfits between the particles result in edge dislocations in the interfaces between the particles, consistent with what we have observed.^{147,239} The 2D autocorrelation of the CdS SILAR sample in Figure 4.2C vi)

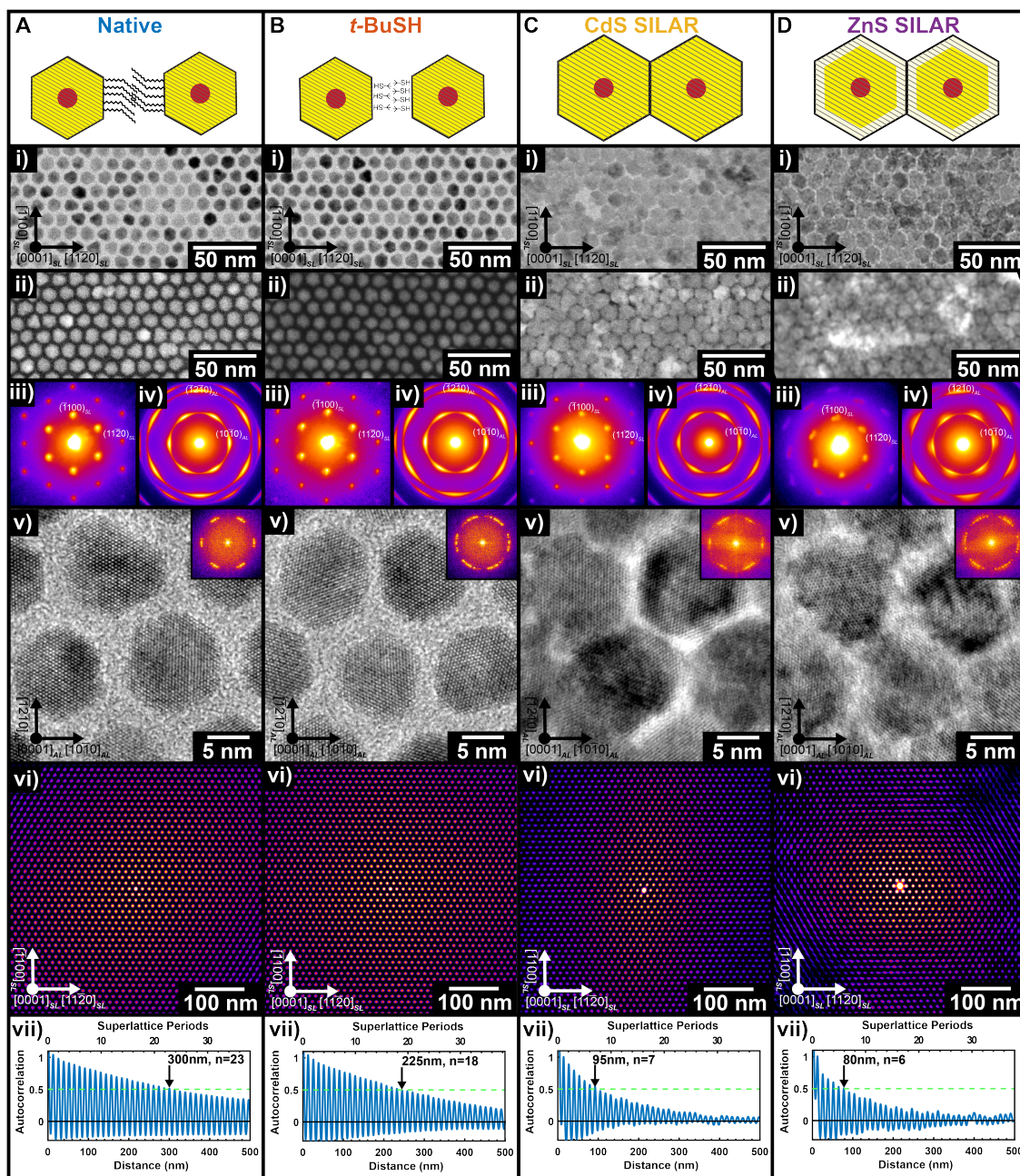


Figure 4.2: Structural characterization of (A) the native assembly of CdSe/CdS dots, (B) after ligand exchange to *t*-BuSH and 200°C anneal, (C) after growing 6ML of CdS via SILAR, and (D) after growing 6ML of ZnS. (i) Bright field TEM and (ii) HAADF STEM images of the superlattices. (iii) Small angle electron diffraction and (iv) wide angle electron diffraction collected of an $11 \mu\text{m}^2$ area. (v) HRTEM image of the nanocrystal superlattice. (vi) Normalized 2D autocorrelation function from a large area TEM image of a nanocrystal superlattice and (vii) a linecut along the $\Gamma - M$ direction.

shows a considerably smaller area with a large autocorrelation envelope. Indeed a line-cut along the Γ -M direction (Figure 4.2C vii) reveals a $\xi_{0.5}$ of ~ 95 nm and 7 superlattice periods. Indeed it appears the in-growth of material between the nanocrystals has disturbed the quality of the superlattice order.

The modularity of the our synthesis strategy allows for heteroepitaxial growth of material in the interface. As an example we use SILAR to grow 6 monolayers of ZnS using methanolic solutions of Na_2S and $\text{Zn}(\text{OAc})_2$ (Figure 4.2D). Similar to the case of CdS SILAR, we observe TEM and STEM images with quasi uniform contrast (Figure 4.2D i) and ii) across the images suggesting inorganic material has successfully been deposited at the interfaces. Small and wide angle electron diffraction show in Figure 4.2D iii) and iv) respectively similar large area superlattice domains which display atomic lattice alignment. HTREM images in 4.2D v) confirm epitaxial growth of the ZnS inorganic material between the nanocrystals. Finally 2D autocorrelation analysis and the Γ -M linecut shown in Figure 4.2D vi) and vii) respectively shows a degradation of the superlattice ordering to $\xi_{0.5}$ of 80 nm upon ZnS growth at the interface comparable to the CdS SILAR case.

Together the data presented here demonstrates the tuneable method we have developed to convert colloidal semiconductor nanocrystals into thin films with epitaxial bridges between the nanocrystals. These materials display long range superlattice positional order and long range atomic lattice alignment. Indeed this method does not rely on carefully balanced kinetics for the nanocrystal assembly and attachment at any step suggesting it may be generally applicable as long as suitably shaped nanocrystals of the desired material can be synthesized. Unfortunately there are pitfalls, while we were able to successfully synthesize and assemble much smaller ~ 6 nm CdSe/CdS core shell nanocrystals (see Figure A.4.6) with atomic alignment. However upon ligand exchange, loss of well-defined arcs in the $\{1\bar{1}00\}$ peaks in the wide angle diffraction suggest the in-plane crystallographic order was lost during the ligand exchange. The small size of these nanocrystals causes them to have less well-defined polygonal shapes which may contribute to the loss of orientational order. However size distribution or shape distribution may also affect this transition. More work will be needed to understand the limits of preparing and maintaining orientational order in smaller nanocrystal assemblies.

Next we seek to better understand the structural evolution of the CdSe/CdS superlattices through careful analysis of the small and wide angle electron diffraction patterns. The diffraction geometry of the sample in a transmission electron microscope is shown in Figure 4.3A. In this case we can collect the small angle signal, corresponding to nanocrystal spacings, and wide angle diffraction corresponding to inter-atomic planes. Radially integrating 2D diffraction patterns (black line Figure 4.3B) give us 1D line profiles of the diffracted intensity as a function of scattering vector $Q = 2\pi/d$. For small angle diffraction in Figure 4.3D, we observe 3 peaks corresponding to the $\{1\bar{1}00\}_{SL}$, $\{11\bar{2}00\}_{SL}$ and $\{2\bar{2}00\}_{SL}$ for all 4 samples. Comparing the sample with native oleate ligands (blue) to that after treatment with *t*-BuSH we observe a shift to larger Q , consistent with the small contraction of the lattice due to shorter ligands. The position of the peaks for the SILAR infilled samples and the *t*-BuSH sample remain constant, suggesting no further lattice contraction due to

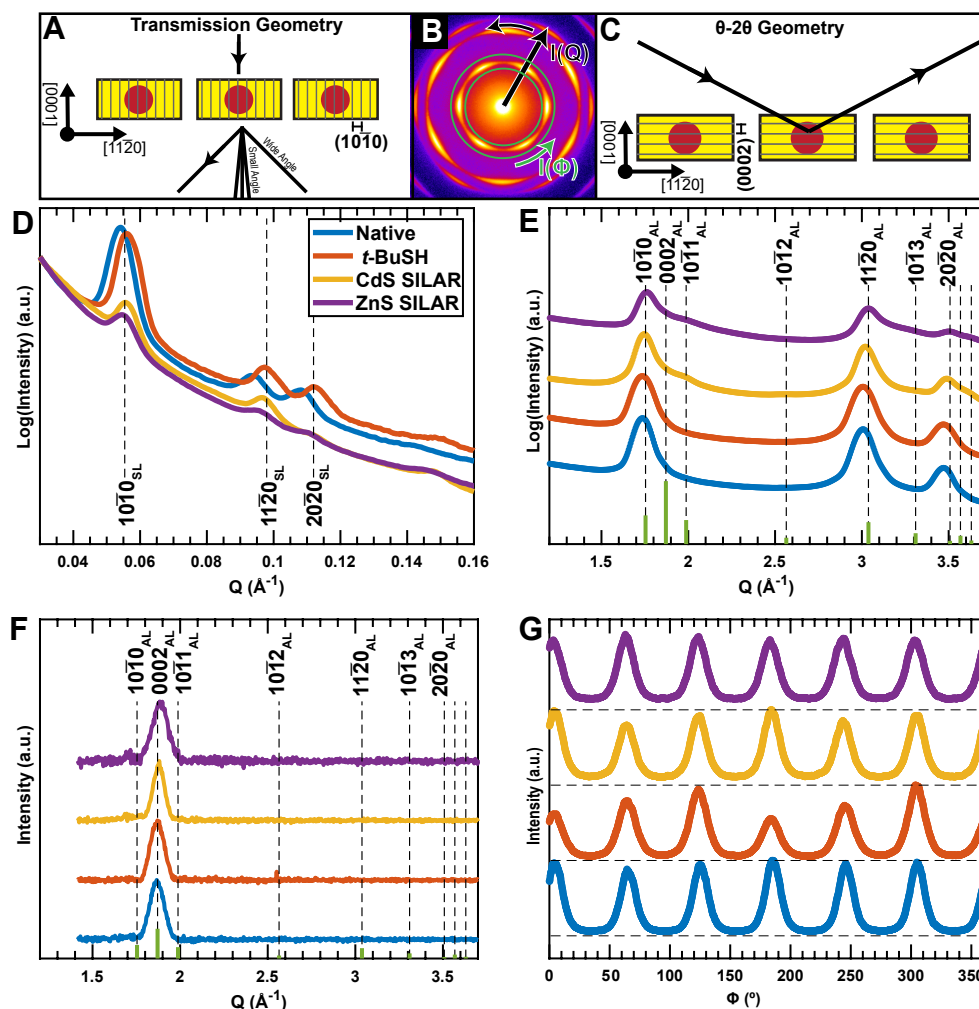


Figure 4.3: (A) Schematic of transmission diffraction geometry (TEM electron diffraction) in the context of $\langle 0001 \rangle$ out of plane oriented wurtzite CdSe/CdS. (B) Schematic showing radial integration, $I(Q)$ and azimuthal integration, $I(\Phi)$. (C) Schematic of reflection diffraction geometry (powder x-ray diffraction) in the context of $\langle 0001 \rangle$ out of plane oriented wurtzite CdSe/CdS. (D) Radially integrated small angle-SAED, (E) radially integrated wide angle-SAED, (F) azimuthal integrated wide angle-SAED, and (G) wide angle powder x-ray diffraction (reflection geometry) for Native (blue), t -BuSH treated (red), 6ML of CdS SILAR (yellow) and 6ML ZnS SILAR (violet).

infilling. We should note that we carefully controlled for effects of beam convergence and focus of the small angle electron diffraction patterns (see methods). This is consistent with our hypothesis that the t -BuSH and subsequent annealing treatment sufficiently locks the particles into a given superlattice geometry and periodicity on a long, multiple μm range. We observe the amplitude of the small angle diffraction peaks decrease upon infilling with either CdS or ZnS (yellow and violet curves respectively). Small angle diffraction amplitude

is determined by modulations in electron density in a periodic sample. Upon infilling the necks with inorganic material, there is considerably less modulation in electron density in the material, and thus the diffracted intensity is diminished. Indeed we observe as additional monolayers of inorganic material is subsequently grown, the SA-SAED peaks decrease in intensity (Figure A.4.11A). Increased disorder in a crystal can also damp the amplitude of small angle scattering signal, and thus may also play a role here. While small angle scattering alone cannot decouple these two effects, the scattering intensity changes observed are consistent with both the formation of inorganic bridges in our materials and the slight decreases in order measured via HAADF-STEM and autocorrelation analysis respectively.

Next we turn our attention to radially integrated wide angle diffraction patterns in 4.3E. In transmission geometry (4.3A), the $[0001]$ direction is parallel to the incident beam and thus only the $\{xxx0\}_{AL}$ planes are oriented such that they meet the diffraction condition. Consistent with that we see strong diffracted intensity from $\{1\bar{1}00\}_{AL}$, $\{11\bar{2}00\}_{AL}$ and $\{2\bar{2}00\}_{AL}$ planes for all samples. In the case of the CdS and ZnS SILAR infilled samples, we see a shoulder on the $\{1\bar{1}00\}_{AL}$ peak, which could correspond to non-epitaxially grown necks which is inconsistent with the epitaxial infilled growth observed by HRTEM. More likely, homo nucleated CdS or ZnS also deposits on the TEM grid during infilling (possibly on the opposite side of the carbon support film) and this is what is giving rise to the powder diffraction-like signal. Electron diffraction from areas without a superlattice show small particles with isotropic powder diffraction patterns giving peaks consistent with wurtzite $\{0002\}_{AL}$ and $\{10\bar{1}0\}_{AL}$ or zinc blend $\{111\}_{AL}$ and $\{220\}_{AL}$ which appear at nearly identical angles. The diffraction data presented here confirms the preferential alignment of the $\langle 0001 \rangle$ ("c-axis") of the wurtzite lattice perpendicular to the DMF surface and thus substrate the samples are transferred to. It is important to note that the polarization of the wurtzite lattice (i.e. $[0001]$ or $[000\bar{1}]$) pointing normal to the substrate has not been determined and is difficult to access experimentally. Nonetheless the $\langle 0001 \rangle$ alignment is maintained through SILAR growth processes to grow inorganic bridges between the nanocrystals in the assemblies.

Further evidence for the out of plane orientation of the wurtzite c-axis come from collecting x-ray diffraction in a $\theta - 2\theta$ geometry schematically depicted in Figure 4.3C. In this geometry, only the $\{0002\}_{AL}$ family of planes are oriented such that the diffraction condition is met. Indeed for all 4 samples, we only observe the $\{0002\}_{AL}$ diffraction peak, consistent with the determination made by transmission electron diffraction. Further the x-ray diffraction measurements were collected from $\sim 1 \text{ cm}^2$ areas highlighting the large area orientational purity in our samples.

To understand the orientational order of the crystal lattice in the substrate plane, we azimuthally integrate the $\{1\bar{1}00\}_{AL}$ diffraction depicted as a green annulus in Figure 4.3B. A perfect single crystal of wurtzite CdSe viewed down the $\langle 0001 \rangle$ would give rise to 6 distinct spots with 60° angles between the spots. In this case, we observe 6 distinct maximum in Figure 4.3G however the peaks have a characteristic broadening in Φ which is greater than the instrument broadening. As such, we conclude that the nanocrystals have a preferential orientation in plane leading to single crystal like diffraction patterns where all the nanocrystals have the same average in-plane orientation. We measured the full width at half max for

the peaks for each sample and the initial sample had a FWHM of 13.9° . Upon treatment with *t*-BuSH, a 15.2° FWHM and after growing CdS and ZnS, 15.2° and 14.3° FWHM respectively. Based on this data, our attachment strategy does not seem to cause additional in-plane orientational order to be introduced. Taken together the data presented above shows there is minimal disruption to superlattice structure and ordering, and atomic alignment during processing and attachment of our nanocrystal superlattices.

Material	Reference	Lattice Type	AL Peak	FWHM ($^\circ$)
SA CdSe/CdS	This Work	1 Layer Hexagonal	$\{1\bar{1}00\}$	13.9
AA CdSe/CdS SILAR	This Work	1 Layer Hexagonal	$\{1\bar{1}00\}$	15.2
SK (Pb,Eu)Te on PbTe	[240]	Hexagonal	$\{\bar{2}11\}$	$<<1$
AA PbSe NCs	[225]	1 Layer Square	$\{200\}$	5.0
AA PbSe NCs	[201]	1 Layer Silicene	$\{111\}$	3.1
AA PbSe NCs	[241]	3D Distorted Simple Cubic	$\{200\}$	13.5

Table 4.1: Analysis of atomic lattice in-plane orientational ordering different quantum dot superlattice growth strategies. We present the FWHM of azimuthally integrated electron diffraction patterns to probe the degree of in-plane orientational order of the atomic lattice. For reference [225], we determined the FWHM ($\text{FWHM}=2.355\sigma$ for a Gaussian distribution) from the standard deviation of a histogram of the angular orientations of individual nanocrystals. We note that these values should be taken approximately since Scherrer broadening or to a lesser extent, instrumental broadening may be different in each case.

To put our results in context we compare our wide angle electron diffraction peak widths (FWHM) to those reported for other self assembly strategies. The comparison is tabulated in Table 4.1. In our samples, we have achieved a FWHM of the $\{1\bar{1}00\}$ peak of $\sim 15^\circ$ for assembled and attached cases. In the case of monolayer square and silicene superlattices, there are reports of in-plane rotation FWHM of $3\text{--}5^\circ$ which is considerably narrower than what we have achieved. However if we compare our results to state-of-the-art 3D superlattices,²⁴¹ our angular coherence is comparable. It is important to consider that the PbSe cases shown here are a result of ~ 8 years of optimization of that materials system, and the size and shape distribution of our starting CdSe/CdS hexagonal prisms is far less uniform than the state-of-the-art PbSe systems. Comparable coherence likely can be achieved if optimized starting materials (size and shape distribution) are prepared.

Chemically Resolved Structural Characterization

Next we focus on the elemental distribution within our samples. Since we have focused on preparing assembling, and infilling isostructural materials, standard TEM and HRTEM are not sensitive to the composition changes. We turn to energy disperse x-ray spectroscopy

in a scanning transmission electron microscope (STEM-EDS) to map the elemental distributions. Figure 4.4A shows a HAADF image of a CdSe/CdS superlattice with 6 monolayers of SILAR grown CdS at the interface. In Figure 4.4B,C,D we show a cadmium, sulfur, and selenium map respectively. In the case of cadmium and sulfur, we observe relatively uniform distributions, with perhaps less x-ray signal coming from thinner necks seen by HAADF. Fourier transforms of the Cd and S signal mostly consist of a diffuse signal corresponding to a uniform background and faint peaks with hexagonal symmetry, consistent with the lattice. In the case of the selenium signal (the only signal unique to the position of the CdSe core), we observe distinct Se positions in a hexagonal lattice which is quite well ordered by eye. Quantification of the EDS signal in a higher resolution map for the core area and the shell confirms this Selenium signal modulation is real and not a result of thickness variations (Figure A.4.7). Further in the high resolution map in Figure A.4.7 a decrease in sulfur signal correlating with the selenium signal can be resolved. Finally, a Fourier transform of the Se signal shows a distinct hexagonal pattern, indicating the well defined lattice. Indeed the elemental maps presented here shows we have successfully translated core/shell nanocrystals assembled into a hexagonal superlattice into a hexagonal CdSe superlattice in a CdS matrix while qualitatively maintaining the structure.

The positional order of the CdSe cores is a critical metric when considering electronic coupling in a super-atom array. While the order measured for the nanocrystal positions in Figure 4.2 is instructive for understanding superlattice evolution, it does not account for possibly non-centered locations of the cores in individual nanocrystals. To this end, we measured large field of view STEM-EDS maps in Figure A.4.8 with sufficient resolution to still observe the individual selenium cores. The 2D autocorrelation of the selenium signal is displayed in Figure 4.4E which shows strong relatively uniform amplitude with slightly better ordering in the y direction. Figure 4.4F shows a profile along the Γ -M direction. $\xi_{0.5}$ extends to ~ 68 nm or 5 superlattice periods. We note that for the STEM-EDS autocorrelation images, we normalize to the amplitude of the 0-order peak (neglecting the exact zero shift artifact) since the STEM-EDS signal is linear and thus diffraction contrast effects are not present. $\xi_{0.5}$ measured for the selenium positions is slightly less than measured for the positional order of the nanocrystals via bright field TEM. The STEM EDS images used for autocorrelation analysis have a considerably lower pixel resolution, signal to noise ratio, and the particles (the Se core) is considerably smaller than the TEM images. The autocorrelation function (and it's normalization) is quite robust to these aspects and for an image which we artificially binned, or decreased the particle size relative to the lattice spacing, the autocorrelation results in an identical $\xi_{0.5}$ in all cases (Figure A.4.9). Thus we can confidently conclude that the disorder in the Se core positions is ultimately a convolution of the positional disorder of the nanocrystals and the disorder of the CdSe core position within individual nanocrystals.

To put our results in context, we compare our correlation length measurement, $\xi_{0.5}$, to other state of the art examples of 2D semiconductor superlattices *via* Stranski-Krastanov growth using molecular beam epitaxy methods, ligand separated nanocrystal superlattices, and nanocrystal assembly/ attachment approaches. The results are summarized in Table

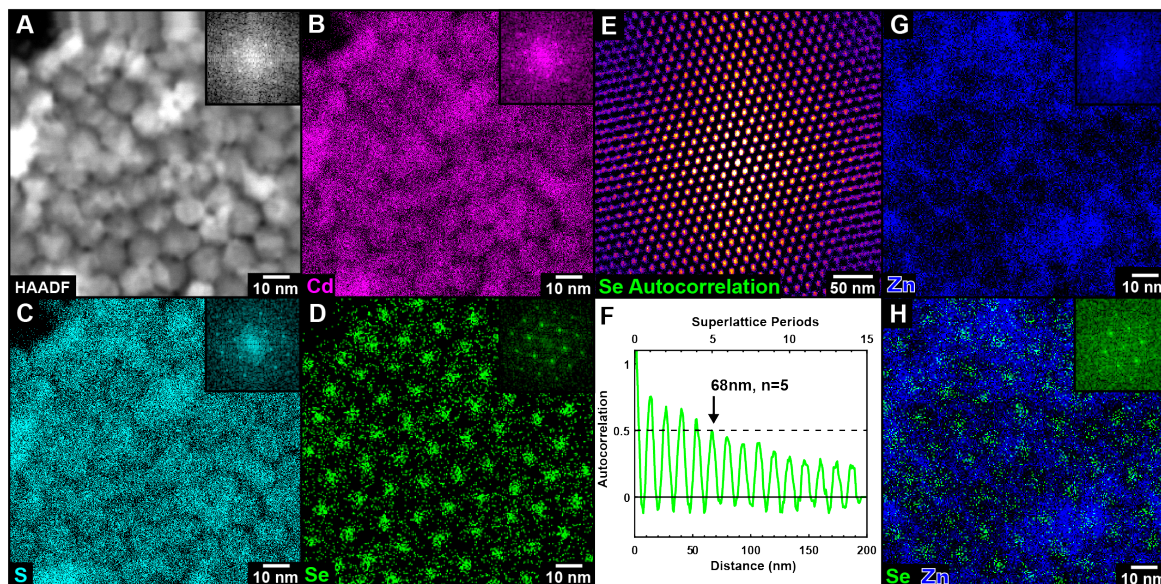


Figure 4.4: (A) High angle annular dark field STEM signal, (B) cadmium L, (C) sulfur K, and (D) selenium K signal for a CdSe/CdS array with 6 monolayers of SILAR grown CdS at the interface. (E) 2D autocorrelation function of the selenium signal for a large area selenium map (see Figure A.4.8) and (F) a linecut along the $\Gamma - M$ direction. We note that the $\xi_{0.5}$ here is normalized relative to the zero shift peak since the EDS signal is linear, if we normalize relative to the first peak in the $\Gamma - M$ direction (consistent with Figure 4.2 vii)) the $\xi_{0.5}$ is now 8 repeat units for the Se signal. (G) zinc K signal and (H) selenium K signal from a CdSe/CdS sample with 6 monolayers of SILAR grown ZnS at the interface.

4.2. Strain ordered Stranski- Krastanov quantum dots have been explored extensively and a few systems have been explored which resulted in highly ordered quantum dot arrays. To the authors knowledge the best ordered examples of the SK quantum dot superlattices (without resorting to lithography which limits the superlattice spacing to large ~ 100 nm periodicities) at most achieved $\xi_{0.5}$ of 3 superlattice repeats. We note that x-ray measurements of the best ordered PbEuTe samples indicate they may be more ordered than images suggest.²⁴⁴ In stark comparison, self assembled colloidal nanocrystals routinely achieve $\xi_{0.5} > 20$ superlattice spacings and in exceptional cases 30 repeat units is achieved clearly far exceeding the achievements of SK growth. However these materials do not have atomic bridges between the nanocrystals and thus don't have the coupling necessary to observe collective phenomena. The atomic attachment cases for PbSe nanocrystals falls intermediate to the SK grown superlattices and the assembled but not attached nanocrystal superlattices. Our assembled hexagons are comparable in positional ordering compared to the PbSe case but the strategy is considerably more tuneable in other aspects

To demonstrate the hierarchical chemical tunability of our synthesis strategy, we examine the CdSe/CdS/ZnS system via STEM-EDS. The Zn signal shown in Figure 4.4G shows a

Material	Reference	Lattice Type	$\xi_{0.5}$
SK (In,Ga)As on GaAs	[242]	Square	2
SK (Pb,Eu)Te on PbTe	[240]	Hexagonal	3
SK SiGe on Si	[243]	Square	<1
SA In NCs	[237]	Few Layer FCC	31
SA CdSe/CdS	This Work	1 Layer Hexagonal	23
AA PbSe NCs	[34]	3-5 Layer Square	18
AA PbSe NCs	[225]	1 Layer Square	3
AA PbSe NCs	[201]	1 Layer Silicene	7
AA PbSe NCs	[46]	1 Layer Square	15
AA PbSe NCs	[241]	3D Distorted Simple Cubic	13
AA CdSe/CdS SILAR	This Work	1 Layer Hexagonal	8

Table 4.2: Analysis of ordering using the autocorrelation to measure $\xi_{0.5}$ for different quantum dot superlattice growth strategies. SK refers to Stranski Krastanov strain grown quantum dots. AA refers to superlattices prepared by atomic attachment of colloidal nanocrystals. SA refers to nanocrystals which have been assembled but not atomically fused. $\xi_{0.5}$ is listed in number of repeat units. $\xi_{0.5}$ for the literature references were measured by extracting the image of interest from the published paper, and calculating the 2D autocorrelation. All examples regardless of imaging modality used were normalised the the first lattice translation peak in the autocorrelation function. $\xi_{0.5}$ for hexagonal and honeycomb systems were evaluated along the $\Gamma - M$ direction and for square lattices along the $\Gamma - X$ direction.

faint honeycomb pattern indicating that the ZnS has primarily deposited in the gaps between the particles. A hexagonal spot pattern is also observed in the inset Fourier transform indicating some degree of ordering. In Figure 4.4H we show the selenium signal overlaid on the zinc signal, and we clearly see the Se cores are located inside the honeycomb of Zn. Full STEM-EDS maps and quantification are in Figure A.4.10. The structure is consistent with the initial structure of the nanocrystal (CdSe/CdS core shell) dictating the Se core positioning, and only the final deposition of ZnS via SILAR giving rise to the infilled honeycomb structure. The impressive synthetic tunability of colloidal II-VI (and to a lesser extent III-V/II-VI) core/shell nanocrystals and the versatility of SILAR chemistry suggests a considerable diversity of heterostructures could be engineered.

Theoretical Analysis of Quantum Dot Coupling Strength

At this point we have shown that we can achieve CdSe quantum dots in a CdS matrix where the CdSe quantum dots are part of a well ordered superlattice. Next we wanted to understand the electronic coupling in these materials. In particular, we focus on the effects of different types of disorder on the electronic coupling of the CdSe quantum dots. To do

this, we performed electronic structure calculations using the semiempirical pseudopotential model (see methods) on dimers of epitaxially connected CdSe/CdS nanocrystals. In these calculations, we observe the hole states strongly localized on the CdSe cores due to the large valance band offset in our system (Figure 4.5A). The conduction band offset in CdSe/CdS systems is considerably smaller and thus the electron states can be shared between the two nanocrystals as seen by electron density in the neck region in Figure 4.5A on the top. The coupling between the electron states is quantified by calculating the energy splitting of the “bonding” orbital which is the symmetric addition of the $1S_e$ state in individual CdSe/CdS nanocrystals giving rise to a σ -like orbital. Anti-symmetric addition of the $1S_e$ states give rise to a σ^* -like state. The energetic splitting of the σ , σ^* states is a measure of the electronic coupling in our CdSe/CdS systems. In this system both the distance between the cores (i.e. bond length) and the neck thickness between the nanocrystals can vary. The coupling strength between two nanocrystals is the starting point for understanding the band structure in these materials via a tight binding model.

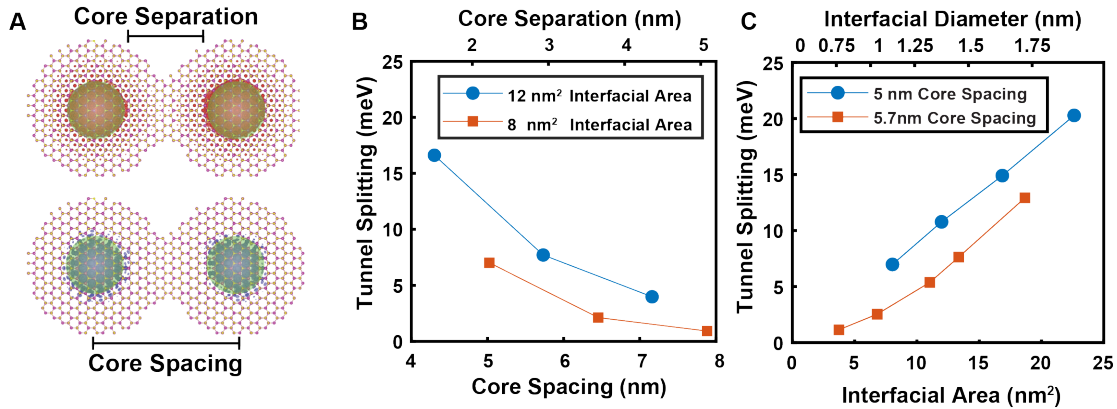


Figure 4.5: Electronic coupling strength in CdSe/CdS dimers as a function of distance and neck thickness. (A) Example CdSe/CdS dimer with the CdSe core region highlighted in green, highest energy hole state (blue, bottom), lowest energy electron state (red, top), and definition of the core spacing and separation. (B) Tunnel splitting of the coupled $1S_e$ state resulting in a σ and σ^* like orbital as a function of core-to-core separation for a fixed neck thickness. (C) Tunnel splitting as a function of neck thickness for a fixed core spacing thickness. (computations performed by Michael Lostica and John Philbin)

Disorder in the electronic coupling of atoms in a lattice will lead to localised states rather than the delocalized bands desired here.^{34,224} To understand the sensitivity of the CdSe/CdS system to different forms of disorder, we performed calculations varying the CdSe core-to-core distance and the amount of CdS material at the neck for a fixed core-to-core spacing. To quantify the coupling, we measured the $1S_e$ tunnel splitting. In Figure 4.5B we show how the tunnel splitting varies as a function of core-to-core spacing. Regardless of neck thickness, as the core spacing increases, the coupling strength decreases with what appears

to be an exponential decay. The variation in tunnel splitting with distance represents the effects of positional order on energetic disorder our samples. While the autocorrelation decay is a powerful tool to understand the coherence length of a superlattice, it is difficult to extract actual variations in distance from the sample. To this end, we measured the core-to-core distance variation by determining the centroids of the Se STEM EDS signal and using the Delaunay triangulation to measure the nearest neighbor bond lengths. We find for the CdS SILAR sample, the average particle-to-particle distance is 12.9nm, with a standard deviation of ~ 1 nm consistent with a variation of ± 1 unit cell variation. While we can't directly access this size in calculations, we consider a similar bond length deviation in the size range we have considered theoretically. Fitting the distance dependent tunnel splitting to a exponential decay, we consider the coupling for a given spacing ± 0.5 nm to understand the maximum variation in the tunnel splitting (see Figure A.4.12) for a given average spacing. For an example 6 nm core-to-core spacing, we calculate a coupling of 7.5 meV at the average distance of 6nm based on the fit, 5 meV and 9 meV at a distance of 5.5 nm and 6.5 nm respectively. Thus the positional disorder contributes to a variation in coupling energy $\Delta E/E$ of ~ 0.6 indicating the coupling strength is still greater than the variation due to disorder. If we consider a ± 1 unit cell variation in spacing (i.e. fixed absolute disorder) for all possible spacings (Figure A.4.12A,C)) we observe a constant tunnel splitting variation relative to the tunnel splitting. If however the core-to-core distance has a distribution relative to the magnitude of spacing, we observe that the coupling variation, $\Delta E/E$, increases for larger spacings. Better understanding the experimental size dependent bond length variation in these materials will indicate optimal spacings which minimize energetic disorder. Taken together the tunnel splitting variation with distance is a contributor to the disorder, but there are other sources of disorder which must be considered.

Next we consider the tunnel splitting variation with neck thickness. In this case, we observe a linear relationship between the interfacial area and the tunnel splitting. The strong dependence of the coupling strength on interfacial area indicates this may be the dominate factor contributing to the energetic disorder. We did not directly measure variations in bridge width, but Savitzky *et al.* found bridge width variations of 2.3 ± 0.8 nm which indicates (assuming a circular cross section) interfacial areas of 5.3 ± 3.7 nm.³³ While the contact area of their PbSe particles is much smaller than the ones we are considering here, it indicates variations in interfacial area are comparable to the absolute contact area. If the whole range of interfacial areas were encountered in a sample, the tunnel splitting variation (for a 5nm core spacing, Figure 4.5C) would range from 7.5 meV to 20 meV, considerably larger than the effect of positional disorder. This indicates a more important metric to improve the homogeneity of the energy landscape is to improve the uniformity of the neck thicknesses.

Annealing to Minimize Neck Thickness Variation

As shown in the previous subsection, neck thickness variations lead to considerable variation in the coupling strength. Indeed in the longest reported delocalization lengths in attached PbSe arrays, the neck thickness variation is a considerable component to the ener-

getic disorder in these materials.³⁴ While strides have been made to quantify and strategies are in place to improve structural disorder in PbX based materials, neck thickness disorder persists and is propagated upon post synthesis growth of additional neck material.¹⁰² In the PbX systems typically explored, thin necks are necessary to preserve quantum confinement in quantum dots and in order to achieve uniform coupling, the size of the inorganic bridges must be uniform. Unfortunately a system of nanocrystals connected with thin inorganic bridges has a much higher surface area than a few atomic layer 2D sheet, and as such thermal annealing leads to the systems transforming to uniform 2D sheets. In our system, the quantum confinement is enforced by the composition, and thus the entire neck can be filled with the shell material while still maintaining quantum confined coupling between the quantum dots. The thermodynamic penalty of surfaces can be harnessed to engineer uniform thickness quantum dot in matrix samples via thermal annealing. In the left side of Figure 4.6A, we show 3 attached CdSe/CdS nanocrystals viewed side on ($\langle 11\bar{2}0 \rangle$ zone axis). In the case of a thinner neck, it has a more concave surface and thus a higher surface energy. Upon thermal annealing at a temperature sufficient to allow surface diffusion and there will be a net flux of atoms migrating to the higher curvature interface. This will lead to an overall reduction in interface thickness variations and as such a lower surface area, and thus energy. Importantly a uniformly thick quasi 2D sheet represents a local thermodynamic sink for the system.

In Figure 4.6B we show a HAADF STEM image of a small area of a superlattice of CdSe/CdS nanocrystals with 6 monolayers of CdS grown at the interface via SILAR. The linear thickness contrast of the HAADF signal allows us to clearly observe the thickness heterogeneity in the sample. Indeed a line cut across 3 particles in Figure 4.6D highlights a case of neck thickness variation. Upon annealing the sample at 300°C for 20 min, we qualitatively observe considerably less contrast variation in the HAADF image in Figure 4.6E. These images were collected with identical imaging conditions (beam current, probe size, TEM grid, HAADF detector gain and brightness) and displayed using identical brightness and contrast limits. A linecut across 3 particles shows nearly identical contrast from the necks to centers of the particles. To confirm the increased uniformity across the entire image, a histogram of pixel intensities in Figure 4.6F shows a distinct tail at low intensities which corresponds to the non-uniform necks. Whereas the annealed sample displays a symmetric intensity distribution. Further evidence for the increased uniformity of the neck thicknesses is the decrease in intensity of the small angle electron diffraction peaks upon annealing (Figure A.4.11B). While annealing successfully healed the interface thicknesses on local scales, some inorganic bridges were likely too thin initially and dewetted upon annealing, leading to small networks of voids in the sample (Figure A.4.13).

A critical design element of our system is encoding the composition variation (and thus quantum dot electronic structure) on the anion sub-lattice since inter-diffusion of the anions in the II-VI systems is typically much slower than cation diffusion. This allows us to activate surface diffusion pathways to heal the thickness variations without interdiffusion on the underlying CdSe/CdS quantum dot superlattice at the temperatures employed to heal neck thickness variations. Indeed after the annealing to improve neck thickness uniformity, STEM-

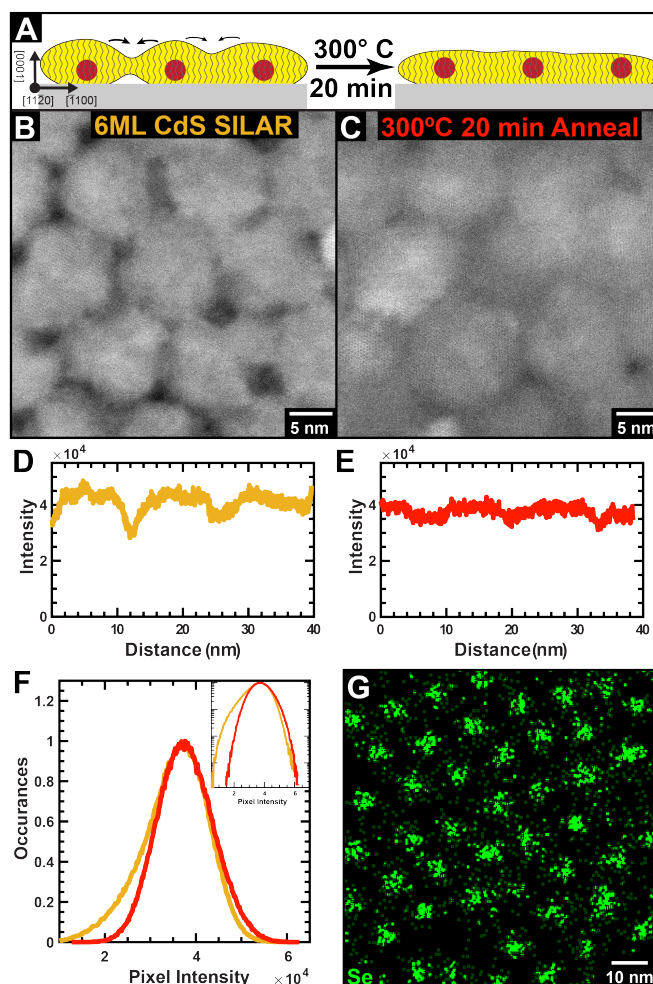


Figure 4.6: (A) Schematic showing thermal annealing driving this same to a more uniform neck thickness. (B) HAADF STEM image of an initial CdSe/CdS superlattice with 6 monolayers of SILAR CdS grown at the interface and (C) after annealing at 300°C for 20 min in a argon environment. (D) and (E) show HAADF line profiles across 3 dots before and after annealing respectively. (F) Plot of the image pixel intensities for 6ML sample before and after annealing at 300°C. (G) STEM EDS map of the selenium core positions after annealing at 300°C for 20 min.

EDS in Figure 4.6G reveals well-defined Se dots within the lattice.

Annealing to Improve In-plane Atomic Lattice Orientational Order

Next we turn our attention to the in-plane orientational order. Wide angle diffraction studies showed that the angular orientation was $\pm 7.5^\circ$ relative to the average angle. To

understand the length scale of the angular disorder, we performed selected area wide angle electron diffraction experiments with diffraction apertures ranging from 200 nm to 16 μm diameter (Figure A.4.14). We focus on the $\{1\bar{1}00\}_{AL}$ peaks since they are the most intense, and we qualitatively observe that regardless of the diffraction area selected, the peaks appear to have the same width in ϕ . Next we azimuthally integrated the peak $\{1\bar{1}00\}_{AL}$ peak and collapsed the 6 peaks onto one in Figure A.4.14F. Indeed in all cases, the diffraction peaks appear to have a large $\sim 15^\circ$ FWHM indicating the length scale of angular coherence is much smaller. Performing the same analysis of windowed Fourier transforms of different areas ranging from 200 nm to 50 nm, we find that the envelope of the $\{1\bar{1}00\}_{AL}$ peak is quite wide (although much spottier) but it is difficult to accurately determine a FWHM. We thus conclude that the in-plane angular variation is on a length scale smaller than probed by diffraction experiments.

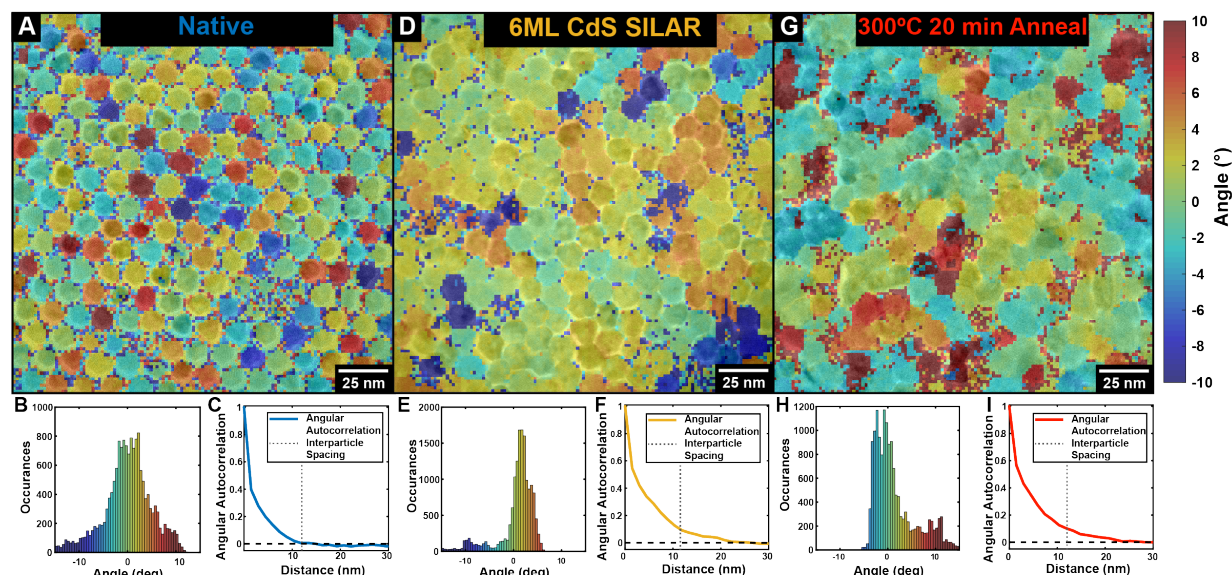


Figure 4.7: Large area HRTEM images with overlaid atomic lattice angle deviation relative to the average angle in (A) native assembled dots, (B) samples after 6 monolayers of CdS grown at the interfaces via SILAR, and (C) after annealing the sample at 300°C for 20 min. (B), (E), and (H) Histogram of the angles present in the 3 samples respectively. (C), (F), and (I) Autocorrelation of the angle map for the 3 samples respectively

To understand the angular variation on a single nanocrystal level, we implemented a sliding window Fourier transform (see methods) to measure the local in plane orientation of the $\{1\bar{1}00\}_{AL}$ planes in HRTEM images. In Figure 4.7A we show large field of view HRTEM image with an overlaid color map corresponding to the angle of the $\{1\bar{1}00\}_{AL}$ peak relative to the average orientation. In this case we observe a broad distribution of angles and it appears that there is no correlation of the angles even in adjacent nanocrystals. In Figure 4.7B a histogram of the angles measured by the SWFFT reveals a FWHM of 8.7° which is narrower

than the diffraction measurements. Understanding the discrepancies in the FWHM values determined via diffraction, radial integration of FFT patterns and the SWFFT method is beyond the scope of this work. However we will use the SWFFT method to compare local orientational order within sample after various treatments. Quantification of the angular alignment between nanocrystals is done by computing the autocorrelation of the angle map in Figure 4.7C. We observe the autocorrelation envelope is damped to zero at distances beyond a single interparticle spacing indicating lack on nearest neighbor alignment. Based on this data, we conclude that in the initially assembled samples, even nearest neighbor nanocrystals have angular misalignments.

Upon attaching the nanocrystals with 6 monolayers of SILAR grown CdS, the angle map in Figure 4.7D appears to have larger domains which contain the same color indicating angular coherence between multiple particles. Indeed in figure 4.7E we observe that the histogram of the angles is much narrower indicating a greater degree of orientational uniformity. Further it appears the distribution is multi-modal, consistent with the domain like structure. Finally the autocorrelation of the angles in Figure 4.7F shows amplitude extending beyond the interparticle spacing indicating some nearest neighbors share identical angles. Based on the angle maps presented here, we observe that the local angular coherence is improved upon attachment which is consistent with the results in annealed PbSe lattices reported by Walravens *et al.*²⁴⁵

Next we wanted to understand the effect of annealing on the angular coherence in the attached nanocrystals. To this end, we annealed the same sample used in Figure 4.7D at 300°C in argon for 20 min. Wide angle electron diffraction patterns did not show a considerable change in the FWHM of the $\{1\bar{1}00\}_{AL}$ (Figure A.4.11C). The same sliding window Fourier transform analysis for the annealed sample is shown in Figure 4.7G. In this case, we again observe small domains which contain multiple particles that share the same alignment. There are a greater number of domains with distinct angles in this case. This is seen in the histogram of the angles in Figure 4.7G where the main peak is split into at least 2 distinct populations. It appears that within a *single* domain there is a smaller distribution of angles however this is difficult to discern based on the histograms since there are multiple grains. To this end, we manually analyzed the standard deviation of the angles measured across 2 distinct particles within the same domain for 9 cases. Comparing the case of the 6 monolayer SILAR case (Figure A.4.15A) and the annealed sample (Figure A.4.15A) we observe that the angles measured across the two particles is tighter after annealing. To further quantify this, we analyzed the standard deviation of the angles in a 13.5 by 13.5 nm area (which samples ~ 2 particles at any time) (Figure A.4.16). In the annealed sample, we observe more cases with a narrow ($>0.5^\circ$ standard deviation) indicating the annealing has improved the angular coherence *within* a domain. Taken together, our data shows there is angular disorder in the atomic lattice within our initial samples, but attachment and subsequent annealing yields domains with high angular coherence.

Optical Properties of Attached Nanocrystal Arrays

The CdSe cores embedded in the CdS matrix maintain a 0D quantum confinement with a large valence band offset for the hole and a smaller conduction band offset for the electron. As such we should be able to observe 0D quantum confined photoluminescence from the CdSe quantum dots embedded in the CdS matrix. In Figure 4.8A we measured the steady state photoluminescence using a 405 nm excitation (which excites both the CdSe core and the CdS matrix) from the initially assembled samples and with increasing layers of SILAR grown CdS between the CdSe/CdS nanocrystals. We observe band edge photoluminescence from all the samples indicating the 0D confinement is maintained once the nanocrystals are attached. Qualitatively we observe the photoluminescence intensity decreases (as evidenced by the increased noise in the normalized spectra) as we increase the number of SILAR layers of CdS grown at the interface. We didn't attempt to quantify the luminescence intensity since for thin films the excited area, collection efficiency, and film density varies between subsequent measurements, nonetheless we confidently conclude the intensity decreases significantly upon full attachment with 6 monolayers of CdS. To better understand the luminescence decrease, we measured time resolved photoluminescence using a 405 nm excitation (Figure 4.8B). We observe for assembled and *t*-BuSH treated samples (dark blue) a monoexponential decay indicative of low trap state density core shell quantum dots. Upon treatment with increasing monolayers of CdS via SILAR, we observe multi-exponential decays which appear to have increasing amounts of a fast decay component with increasing monolayers added. Typically fast decay components are associated with deep trap states in semiconductor nanocrystals, thus the time resolved data is consistent with decreased luminescence intensity observed in Figure 4.8A.

Next we consider the case of ZnS grown at the interfaces between the CdSe/CdS nanocrystals where we observe band edge photoluminescence from samples with 2-6 monolayers of SILAR grown ZnS Figure 4.8C. In this case we observe a less dramatic decrease in photoluminescence intensity as we increase the numbers on monolayers of infilling material. In the time resolved photoluminescence of the ZnS infilled samples (Figure 4.8D), we observe a non-monoexponential decay for the SILAR samples, but there isn't an obvious increase in the fast non-radiative component as the number of monolayers is increased. This is consistent with the more intense band edge photoluminescence for all the samples in Figure 4.8C. Based on the results presented here, it appears that upon fusion of the CdSe/CdS nanocrystals with a CdS shell, there is a greater increase of non-radiative pathways in our samples compared to identical samples with ZnS at the interface.

Next we attempt to understand the origins of the decreased photoluminescence upon attachment and the variation of the intensity depending on the infilling material. We know from the wide angle electron diffraction data that a average mistilt of $\sim \pm 7.5^\circ$ exists in our samples and that the angular coherence exists in small domains. As such, the mistilts in attached samples are accommodated by low angle tilt boundaries between the particles. In a crystalline material, a low angle tilt boundary can be understood as an array of dislocations

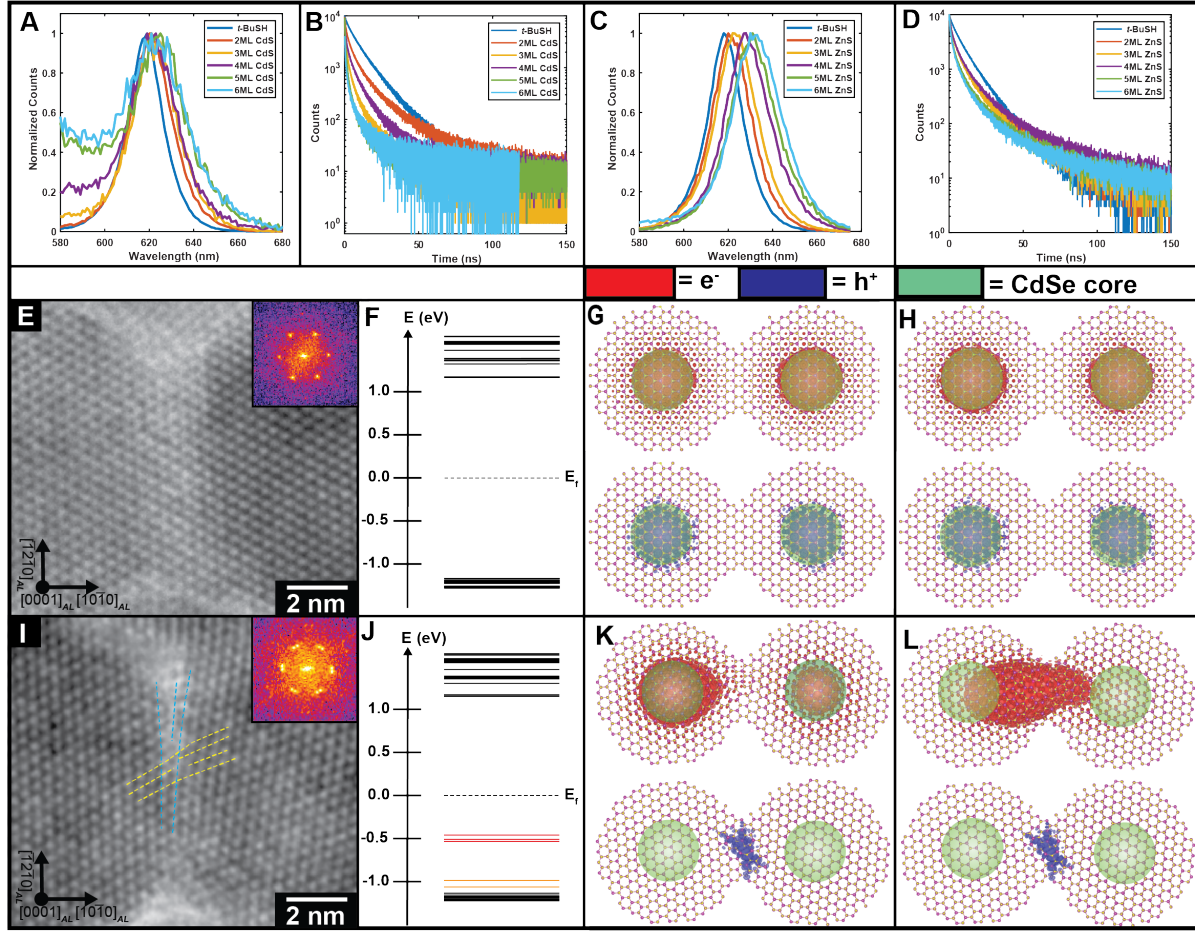


Figure 4.8: Optical characterization of attached CdSe/CdS and CdSe/CdS/ZnS attached quantum dots. (A) Room temperature photoluminescence from a assembled CdSe/CdS nanocrystals with different amounts of SILAR grown CdS at the interface and (B) time resolved photoluminescence of the same sample. (C) Room temperature photoluminescence from a assembled CdSe/CdS nanocrystals with different amounts of SILAR grown ZnS at the interface and (D) time resolved photoluminescence of the same sample. (E) Example HRTEM image of an un-tilted boundary between 2 nanocrystals and (I) a tilted interface between 2 nanocrystals with overlaid extra $(10\bar{1}00)$ (blue) and $(\bar{1}100)$ half planes of atoms trapped at the interface resulting in a $b = \frac{a}{3}\langle\bar{2}110\rangle$ edge dislocation. Calculated electronic states for (F) perfect interface between two CdSe/CdS nanocrystals and with a $b = \frac{a}{3}\langle\bar{2}110\rangle$ edge dislocation in the CdS interface. (G,H,K,L)) Electron (red) and hole (blue) probability densities for (G, K) the single-particle (i.e. non-interacting electron and hole) states and (H, L) the excitonic (i.e. correlated electron-hole) states. All probability densities are shown at the same isosurface value and are room temperature Boltzmann weighted averages over the low energy (G, K) single-particle and (H, L) excitonic states. The CdSe core position is highlighted in green. (computations performed by Michael Lostica and John Philbin)

with a characteristic spacing (D) in Equation 4.1.

$$D \cong \frac{b}{\theta} \quad (4.1)$$

Thus we would expect edge dislocations to be present in our materials due to the angular misalignment. We show one example in Figure 4.8E where two perfectly aligned (as evidence by the single spots in the inset Fourier transform) particles are attached with a perfect atomic lattice (i.e. no dislocations). In a case where there is a misalignment of the nanocrystal lattices in Figure 4.8I, we observe extra $\{1\bar{1}00\}_{AL}$ planes at the interface, resulting in a $b = \frac{a}{3}\langle\bar{2}110\rangle$ edge dislocation. The mistilt in the atomic lattices is evident by the two distinct spots present in the inset Fourier transform. Edge dislocations result in dangling bonds which often result in mid-gap electronic states which trap carriers and decrease luminescence yield.

We performed electronic structure calculations of perfectly and imperfectly attached dimers of CdSe/CdS core shell nanocrystals using a semi-empirical pseudopotential model to understand the effect of structural defects on electronic properties. Figure 4.8F shows the valence and conduction band states for a perfectly attached dimer where we see a clean bandgap free of mid-gap states. In the case of the imperfectly attached nanocrystal with a $b = \frac{a}{3}\langle\bar{2}110\rangle$ edge dislocation, we observe a series of states that are ~ 0.5 eV from the valence band edge indicating that the edge dislocations which we observe can lead to deep trap states. In Figure 4.8G and K respectively, we display the non-interacting electron (red) and hole (blue) states for the perfect and imperfectly attached nanocrystal respectively. In the perfect case, we observe the hole preferentially localized on the CdSe cores, as expected by the large valence band offset between CdSe and CdS and for the electron, we observe two more delocalized nodes on the nanocrystal lobes and importantly we see a non-zero electron density shared between the two nanocrystals. In the case of the imperfect attachment we observe that the hole density is localized on the defect at the interface of the two nanocrystals, and the electron density while still delocalized across the two nanocrystals is non uniform. In the case of interacting electron and hole states (i.e. excitonic) for the perfect attachment in Figure 4.8H, we observe a case similar to the non-interacting case, but the electron states are more localized on the nanocrystals due to the Coulomb interaction. In the case of the imperfect attachment in Figure 4.8L, we observe the hole localized on the dislocation core, and the electron appears to be pulled into the interface between the particles *via* the Coulomb interaction. Based on the electronic structure calculations presented here, $b = \frac{a}{3}\langle\bar{2}110\rangle$ edge dislocations lead to deep hole trap states which is consistent with the degraded optical performance of the attached nanocrystals. Further these results indicate that the electron states in a single particle case are relatively unaffected by the most prevalent dislocation type, and thus electron (and not hole) transport may be defect tolerant.

Chemical Conversion *via* Cation Exchange

An underlying requirement for the process we have developed here are nanocrystals which are have narrow size and shape distributions. While this has been achieved for the CdX

materials, few other semiconductor nanocrystal systems have realized the level of control needed and thus would not be directly accessible via our method. It is well known that cation exchange in semiconductor II-VI materials is a versatile tool to expand the chemical diversity of semiconductor nanostructures with exquisite control. To this end, we demonstrate one possible conversion of many and convert, *via* a 2 step cation exchange, wurtzite CdSe/CdS to wurtzite HgSe/HgS. All aspects of the structure which we have engineered in the CdSe/CdS superlattice have been maintained including the single crystal-like atomic structure, nanocrystal superlattice ordering and the Se/S superlattice on the anion sublattice.

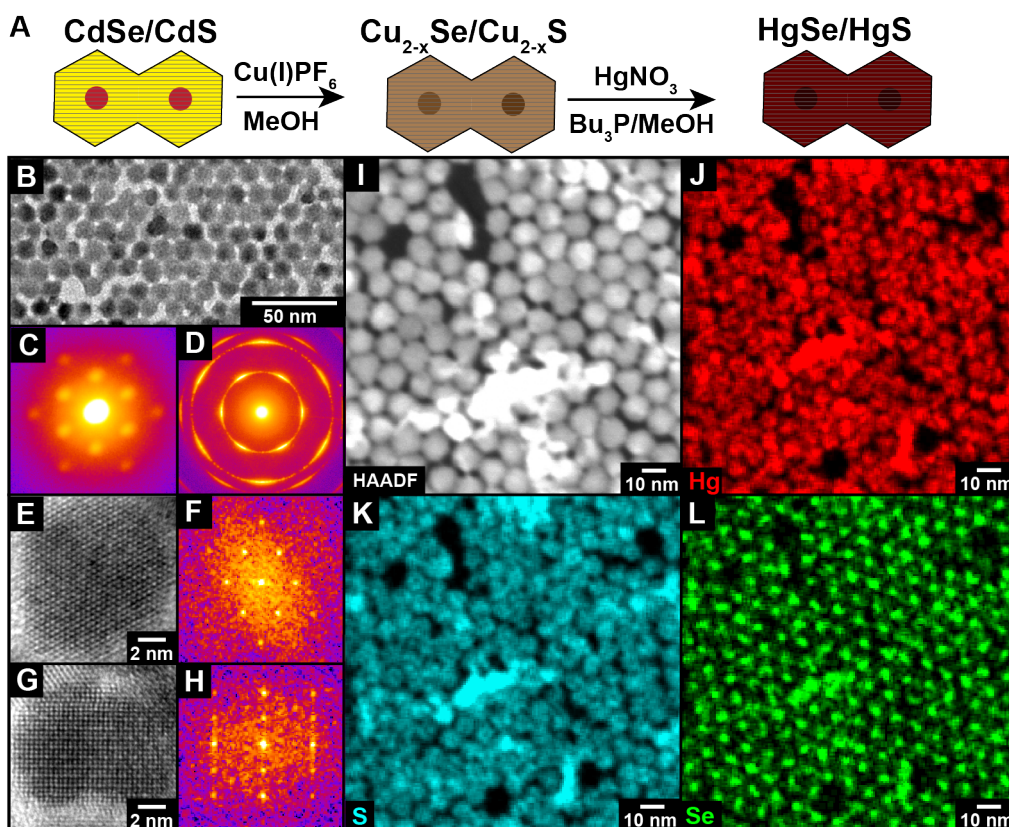


Figure 4.9: (A) schematic for converting CdSe/CdS superlattices to HgSe/HgS via a $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ intermediate. (B) TEM image, (C) small angle and (D) wide angle electron diffraction of a HgSe/HgS superlattice. (E) HRTEM image and (F) corresponding Fourier transform of a single HgSe/HgS particle within a superlattice viewed down the $\langle 0001 \rangle$ zone axis. (G) HRTEM image and (H) corresponding FT viewed down the $\langle 11\bar{2}0 \rangle$ zone axis. (I) HAADF, (J) mercury L, (K) sulfur K, (L) and selenium K maps for a HgSe/HgS superlattice

To begin, we start with the wurtzite CdSe/CdS core shell nanocrystals infilled with 6 monolayers of SILAR grown CdS (Figure 4.9A) and upon exposure to tetrakis(acetonitrile) copper(I) hexafluorophosphate in methanol, the film is converted to a $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ film.

This transformation is driven by the preferential solvation of Cd^{2+} (a hard acid) by methanol (a hard base). In a second step, the sample is exposed to $\text{Hg}(\text{NO}_3)_2$ in methanol and tributylphosphine, where the copper (soft acid) is extracted by tributylphosphine and a large excess of Hg^{2+} drives the conversion. We found the $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ samples to be quite beam sensitive, so we focus on characterization of the final HgSe/HgS lattice however we note that STEM EDS (Figure A.4.17) quantification shows removal of the majority of the cadmium from the system and it appears the Se cores remain intact. Upon treatment with $\text{Hg}(\text{NO}_3)_2$ in methanol and tributylphosphine, EDS spectra of the sample after conversion indicates almost complete conversion to HgSe/HgS with some small amounts of copper ($\sim$ at 6%) remains (Figure A.4.18).

In Figure 4.9B we show a bright field TEM image of a HgSe/HgS sample showing a well ordered nanocrystal superlattice albeit with some vacancies and incomplete necks. The samples used to develop cation exchange chemistry were not fully optimized for nanocrystal order or domain size. Small angle electron diffraction in Figure 4.9C Shows that single crystal superlattices have been achieved on a large scale. In Figure 4.9D we observe a sixfold symmetric wide angle electron diffraction pattern consistent with viewing a wurtzite crystal down the $\langle 0001 \rangle$ zone axis. To better understand the atomic lattice of the resulting HgSe/HgS materials, we collected HRTEM images of the particles viewed such that they displayed a hexagonal shape cross section (all the particles assembled in the superlattice) (Figure 4.9E. In this orientation, the samples show a hexagonal atomic lattice similar to the wurtzite structure and a Fourier transform in Figure 4.9F is consistent with the wide angle electron diffraction, indicating this is the orientation of the majority of the particles. The lattice spacing of the $\{1\bar{1}00\}_{AL}$ plane for the HgSe/HgS sample was 3.58 Å which is nearly identical to the lattice spacing of the initial CdSe/CdS samples (3.56 Å). This is consistent with the observation by Manna and co-workers that CdTe and (yet unreported) HgTe had nearly identical lattice parameters.²⁴⁶ Next to understand what has happened to the atomic stacking sequence of the HgSe/HgS exchanged samples, we found particles which were oriented on their side allowing us to probe the stacking sequence (Figure 4.9G. The outline of the shape is similar to the initial CdSe/CdS viewed down the $\langle 11\bar{2}0 \rangle$ zone axis (Figure 4.1A iv)) and a Fourier transform of the HRTEM image (Figure 4.9 appears identical to a $\langle 11\bar{2}0 \rangle$ zone axis of a wurtzite lattice. We observe the lattice spacing of the $\{0002\}_{AL}$ plane to be 3.39 Å for the HgSe/HgS sample (compared to 3.4 Å for the CdSe/CdS case) *via* HRTEM.

We performed elemental mapping *via* STEM-EDS to determine if the Se/S superlattice anion sublattice has remained intact. The HAADF, mercury and sulfur signal (Figure 4.9I, J, K respectively all over lay on each other indicating the Hg signal is resulting from the nanocrystal superlattices. In Figure 4.9L we see that the selenium signal reveals a distinct hexagonal pattern indicative of the Se (in this case HgSe) containing cores remain in the sample. The HgSe cores appear to have a high degree of order comparable to those of the original CdSe cores in the CdSe/CdS superlattices. The cation exchange presented here represents only one of countless materials accessible from the original CdSe/CdS superlattices. Importantly this allows access to highly ordered 2D quantum-dot-in-matrix semiconductor

superlattices using materials where size and shape controlled colloidal synthesis has not yet been developed.

4.3 Discussion

Comparison of Strategies for Preparing 2D Quantum Dot Superlattices

In this section, we will discuss the pros and cons of the different routes to atomically coherent semiconductor superlattices; Stranski- Krastanov (SK) growth,²⁴⁷ direct atomic attachment of colloidal nanocrystals,⁴⁵ and the new method we presented here. We consider three important aspects; positional order, atomic lattice orientational order, and synthetic tunability. In this, we will only consider self assembled superlattices since lithography is limited to larger structures and lattice parameters, too large for the most exciting emergent phenomena.

Positional Order: The SK quantum dot superlattice community has developed several strategies for preparing ordered superlattices. One strategy includes self ordering *via* the 3D strain fields that result from multi-layer quantum dot structures grown *via* MBE.^{248,249} Another is using high miller index facets for growth to control nucleation positions.²⁴² While these strategies have resulted in ordered superlattices, they are considerably less ordered compared to self assembled nanocrystal superlattices (see Table 4.2). While strain fields control nucleation in these systems, once a particle is nucleated, it can't move on the surface to the optimal superlattice site. This is in comparison to pre-formed nanocrystals with their organic ligands which can reversibly interact, and thus the nanocrystals can find their optimal super-lattice position. As such self assembled semiconductor nanocrystal superlattices are considerably more ordered than SK semiconductor superlattices (Table 4.2). The challenge in the atomic attachment community has been to translate the ligand separated nanocrystals into a material with atomic attachment and orientational alignment. Early attempts resulted in small ~ 50 nm domains of attached nanocrystal superlattices,⁴⁷ and gradually as techniques improved, μm scale domains have been achieved.²⁰¹ Still troubling for this community is irreproducibility, and phase purity due to the need for a coherent phase transition from hexagonal to square³⁴ or silicene^{45,201} lattice. Recent advances in the atomic attachment community has resulted in a topo-epitaxial scheme where a phase transition between ligand separated superlattices and the attachment phase is not needed.²⁴¹ This has allowed for 3D atomic attached superlattices which display impressive positional order (Table 4.2) to be prepared.

With regards to positional ordering, there are two considerations, the quality of the superlattice within a domain, and the size of the domains. With regards to ordering within a domain, our work has achieved positional order which is comparable to the best direct atomic attachment routes, and is much better than SK superlattices. Indeed our strategy shares many similarities with the work of Abelson *et.al.*²⁴¹ in that the transition from the initial

superlattice to the final attached superlattice is a topotactic transition (i.e. hexagonal initial assembly and hexagonal attached assembly). As discussed above, ligand capped nanocrystal self assembly is reversible and as such it is possible to achieve large grain sizes ($7\ \mu\text{m}$ by $7\ \mu\text{m}$ Figure A.4.4). This is much larger than of the reported grain sizes in the direct atomic attachment field. Importantly ligand separated superlattices can be reliably transformed into superlattices of attached nanocrystals *via* SILAR infilling while maintaining the large grain sizes. Taken together, colloidal routes to preparing quantum dot superlattice provide superior positional ordering, and the SILAR infilling we have developed provides positional ordering comparable to direct atomic attachment, but likely allows for larger single crystal domains to be prepared.

Another aspect of our method is reproducibility, in the case of all the PbSe direct attachment cases a careful balance of the ligand density and oleate removal rate is needed to achieve the attached nanocrystal lattice. Slight changes in these parameters will change the structure of a ligand separated superlattice, attachment geometry, or prevent attachment entirely. In addition oxidation of the materials will also prevent attachment. Parameters such as ligand density are difficult to control and as such lead to issues reliably preparing a given structure. In our work, the only self assembly that occurs is for the ligand separated superlattices, which can be achieved over wafer scale areas. As such we have reliably achieved identical hexagonal superlattices across many synthetic attempts.

Atomic Lattice Orientational Order: A second important consideration for 2D quantum dot superlattices is the degree of disorder in the atomic lattice orientation. Misorientations can lead to dislocations and other defects in the case where they are large ($>5^\circ$). Smaller misorientations ($<5^\circ$) will lead to strain at the interfaces. Both dislocations and strain can lead to carrier localization or scattering. SK self assembled quantum dot superlattices have a clear advantage in this case since they are mated to a single crystal substrate and thus the atomic orientation of all the dots are in nearly perfect registry. In the case of attached colloidal quantum dots, we see angular variations from $3\text{--}15^\circ$ (Table 4.1) meaning these materials will have a much higher atomic defect density than SK grown samples. Within the colloidal based methods, the direct atomic attachment community has thus far achieved narrower angular deviations. This may be because the dots are allowed to reorient at a liquid-liquid interface as the attachment proceeds whereas our method they are locked on substrates.

With that said, there are two interesting features of our atomic attachment which suggest paths forward for increasing the angular coherence in the materials. First, the initial nanohexagons have significant size and shape distributions which likely lead to angular disorder in the initial assembled sample. Importantly our method maintains the orientational ordering during processing, thus if the order in the initial assemblies can be improved, the order of the final product can likely be improved. Another aspect which points to the possibility of improving orientational order is the increase of local angular coherence upon attachment via SILAR (Figure 4.7). This means even if the initial assemblies aren't perfect with regards to angular alignment, collective alignment can be achieved. This effect will be further enhanced with improved initial alignment of the assemblies.

Synthetic Tunability: One goal of the nanocrystal superlattice community is to be

able to engineer a desired property into a material by designing a given architecture. Thus it is necessary to be able to access a broad range of structures with a given synthetic method to be able to understand the structure-function relationship and ultimately engineer materials properties. In general the SK quantum dots have a limited synthetic landscape because certain elastic conditions must be met to form islands, and for those islands to self-organize. Further, parameters such as dot size, superlattice periodicity, and dot composition are linked, thus preventing independent variation of these parameters. In the direct atomic attachment case, there are fewer synthetic constraints. Namely optimal strain imbalances are no longer required to achieve island growth. Thus far this has allowed for attachment of PbS, PbSe, and PbTe nanocrystals into ordered superlattices. However in this case, there are still two distinct limitations. First, the delicate balance of ligand removal rates is needed which has, thus far, limited the direct atomic attachment to the PbX class of materials. The second limitation is the quantum dot size and superlattice vector are directly tied, thus preventing the independent control of the "super-atom" properties (i.e. energy gap) and the superlattice periodicity. In our approach, the size of the quantum dot and the superlattice periodicity can be independently tuned by controlling the core size and shell thickness respectively. Further the ligand length is an additional knob to tune the spacing between the core shell nanocrystals, thus controlling the thickness of the third material grown via SILAR. All three of these knobs can be independently controlled within limits.

Further, since the infilling of the voids is done *via* substrate supported growth, many traditional gas-phase crystal growth methods (e.g. metal organic chemical vapor deposition, molecular beam epitaxy, atomic layer deposition) may be used to infill the voids between the nanocrystals. Thus making materials traditionally inaccessible to colloidal synthesis compatible with the colloidal nanocrystal superlattices. For example, III-V materials are difficult to prepare colloidally, but it is possible to grow some III-V materials on II-VI substrates. Naturally this could be extended to grow a honeycomb III-V material patterned by the voids between the II-VI nanocrystals. Ultimately substrate supported growth is incredibly mature, and the potential compatibility of our state-of-the-art nanocrystal assembly and overgrowth techniques teems with possibilities.

Finally we discuss the ability to post-synthetically modify the samples *via* cation exchange. Both the direct atomic attachment samples and our samples have successfully been transformed to additional daughter materials. For example rock salt PbSe honeycomb lattices have been successfully transformed to mixed wurtzite and zinc blende CdSe *via* a one step cation exchange. The inability to control the phase of the daughter material is because the relationship of the anion sublattice is not topotactic between the rock salt and either wurtzite or zinc blende. Instead there are competing sites for the anion sublattice resulting in a mixed phase. In two step cation exchanges in using the $\text{CdX} \rightarrow \text{Cu}_{2-x}\text{X} \rightarrow \text{AX}$ ($\text{A}=\text{Zn}, \text{Cd}, \text{Hg}$) maintains the phase (i.e. cubic or hexagonal for zinc blend and wurtzite starting CdX materials respectively).⁵⁹ As demonstrated here, with the wurzite CdX to wurtzite HgX exchange, there are advantages for starting from phase pure tetrahedral semiconductors.

Optimal Parameters for Electronic Coupling

Now that we have discussed the synthetic tunability of our system, we now consider the optimal parameters for realizing delocalized electronic states. As we have seen, there is a considerable variation of the coupling strength with core-to-core distance and the neck thickness variation. Ultimately to realize delocalized states, the strength of the electronic coupling must be stronger than any energetic variations due to sample inhomogeneity to beat our Anderson-like localization. Unfortunately colloidal nanocrystal synthesis has not yet achieved atomic precision. In the best case, precision within 1 atomic layer has been achieved in the case of small nanocrystals. as they grow larger though, typically the size distribution is relative to the diameter, not an absolute 1 atomic layer variation. If we consider the analysis of the sensitivity of the coupling strength on distance (Figure A.4.12), we see that if there is an absolute variation in the distance regardless of size or neck thickness, the difference in coupling strength relative to absolute coupling strength is not lattice parameter dependent. However in the case where the distance variation is relative to the magnitude (more likely case), at larger distances the coupling strength variation increases at larger separation. Thus smaller superlattice parameters should be targeted since they likely will have the least coupling strength variation relative to absolute coupling.

Next we consider what the variation of the neck thickness teaches us about the ideal sample for realizing delocalized states. We observe that for a thicker neck, the system is less sensitive to variations in distance (i.e. the exponential decay constant is smaller), highlight the importance of uniform, thick, necks. The annealing strategy presented here allows this to be achieved. In essence, the larger neck makes it easier for the electron to occupy a larger volume (smaller decay constant κ), and feel the presence of the nearest neighbor more. Other factors such as the carrier effective mass and the valence band offset will have an effect here too and ultimately both of those parameters will also modulate the coupling strength and sensitivity to positional disorder. In general, our intuition suggests materials with smaller effective masses and smaller band offsets will create strongly coupled states between quantum dots which are less sensitive to positional disorder. Importantly the cation exchange shown here allows one to modify parameters like the effective mass and band offsets directly from the same starting CdSe/CdS material.

Comparison with Oriented Attachment and Traditional Growth Mechanisms

We now consider the how our new nanocrystal synthesis and assembly strategy fits in context with other known materials growth mechanisms. Oriented attachment is a well known solution phase growth mechanism where individual nanocrystals in solution collide, their crystal lattices align, and the nanocrystals fuse leading to single crystal, often anisotropic, structures.^{38,250} One characteristic of this mechanism is rapid favorable alignment of the nanocrystals to a common crystal alignment when the collide. The direct atomic attachment of nanocrystals at a liquid interface, is just restricting the translations of the nanocrystals

on the 2D plane allowing for the fused superlattice sheets to be formed. In this work, the fusion of the nanocrystals by growing additional material at the interfaces also shows similarities to the way wurtzite GaN grows as we discussed previously.²³⁹ In the GaN case, small islands initially nucleate and subsequently grow together with small mistilts. In our case, the small islands are similar to the initially mistilted CdSe/CdS nanocrystals which grow then subsequently grow together during the SILAR growth. Interestingly, upon fusion of the nanocrystals, we observe increased coherence of the atomic lattice across several nanocrystals (Figure 4.7). This indicates rotation of the nanocrystals during the substrate supported growth is possible. While not specifically investigated, it is unlikely that in the GaN case, the large grains would undergo rotations when they merge.

Our new methods have similarities with both oriented attachment crystal growth (e.g. crystal alignment) and grain merging (e.g. growth leading to the fusion). Perhaps one way to organize these growth mechanisms is on a continuum with decreasing degrees of freedom for the nanocrystals where solution OA has 3D translational and rotational freedom. Liquid subphase direct atomic attachment has 2D translational freedom and 3D rotational freedom. The case of nanocrystal fusion *via* SILAR, there is little to no translational freedom, but there is rotational freedom in-plane and possibly out of plane. Finally fusion of large grains have no translational or rotational freedom. There are a tradeoffs as the freedom the individual nanocrystals is restricted. More freedom allows the nanocrystals more chances to achieve perfect alignment with other crystals in the solution. However the additional freedom limits the control the researcher has to deterministically prepare a desired structure.

4.4 Conclusion

We have thus demonstrated a clean sheet redesign of colloidal nanocrystal assembly and subsequent fusion to create atomically coherent quantum dot superlattices. Starting from well faceted hexagonal prism shaped, CdSe/CdS nanocrystals, we successfully assembled the nanocrystals into superlattices with well defined positional and orientational order. SILAR was used to grow semiconductor material in the voids between the nanocrystals resulting in a well-defined quantum dot-in-matrix array with 2D ordering. STEM EDS confirmed the composition variation of the system. Importantly annealing shows that the neck thickness between the individual nanocrystals can be driven to uniform thickness which electronic structure calculations show is a dominate source of energetic disorder in these materials. Further we observe that upon attachment of nanocrystals via SILAR, multi-nanocrystal domains of atomic coherence are achieved, highlight the similarities of our method with traditional oriented attachment. Finally we demonstrate our material can be transformed to additional semiconductor superlattices *via* cation exchange. The highly tuneable aspects of the developed method considerably expands the potential materials space available for 2D semiconductor superlattices.

4.5 Materials and Methods

Materials: Cadmium oxide (CdO) 99.99% Aldrich; oleic acid 90% (OA) technical grade Aldrich; oleylamine (OAm) technical grade 70% Aldrich; octadecene 90% (ODE) technical grade Aldrich; trioctylphosphine oxide (TOPO) 99% Aldrich; Sulfur Aldrich; Octadecylphosphonic Acid (ODPA) XXX; *n*-trioctylphosphine 97% (TOP) Strem; *t*-BuSH Aldrich *n*-tributylphosphine Strem; Hg(NO₃)₂ Aldrich; tetrakis(acetonitrile) copper(I) hexafluorophosphate Aldrich; anhydrous Na₂S Strem; methanol 99.5% extra dry Acros; selenium 99.99% Strem; 0.2M Cd(oleate)₂ in ODE was prepared by degassing appropriate amounts of CdO, OA, and ODE under vacuum at 110°C until all gasses and water had evolved. The flask was switched to argon and heated to 240°C until a clear (slightly yellow) solution was obtained. The flask was then cooled to 110°C and degassed a second time to remove additional water.

Wurtzite CdSe Seeds: CdSe cores were synthesized using a modified version of a previously published procedure.²¹ Typically, 120 mg of CdO, 560 mg of ODPA, and 6 g of TOPO were combined and degassed at 150°C under vacuum for one hour. The reaction was then heated to 320°C under argon, and held at that temperature until the solution turned clear, indicative of Cd-ODPA complexation. At 320°C, 3 g of TOP was injected, and then the solution was heated to between 360°C, at which point a solution of Se (120 mg) dissolved in TOP (0.72 g) was quickly injected. The reaction was stopped after approximately 4 min, and quickly cooled. Changing reaction temperature and reaction time allows for synthesis of different-sized cores. In this work we used large CdSe cores to facilitate STEM EDS identification, typical 1st exciton absorption was ~570 nm. The QDs were purified from free ligand and excess precursors via precipitation with acetone and redispersion in hexanes several times. Sizing and concentrations were determined using previously established calibration curves.²⁵¹

{11̄00} Terminated Hexagon Shaped CdSe/CdS Core Shell Nanoplatelets: Samples with a nominal shell thickness of 6 monolayers were synthesized based on heavily modified previous procedures¹⁴⁹ as follows. 100 nmol of wurtzite CdSe seeds (570 nm 1st exciton), 3 ml ODE and 3 ml OAm were loaded into a 50 ml 3 neck round bottom flask and degassed at 110°C for ~30 min. Under Ar, the reaction was heated to 310°C. At 240°C, slow injection of a 3.14 ml of 0.2 M Cd(oleate)₂ in ODE solution and 3.14 ml of 0.2M TOP-S solution in TOP in separate syringes commenced at a rate of 1ml/hr. TOP-S in TOP was prepared by stirring 20 mg of S in 2.6 g TOP in a glovebox for ~30 min. After the injection completed, the reaction was kept at 310°C for 10 min and then rapidly cooled to room temperature. Nanocrystals were isolated from the reaction by precipitating the nanocrystals with acetone and redissolving in hexanes 2×. Finally the nanocrystals were centrifuged at 8000 rpm in hexanes to remove any remaining insoluble impurities. Samples were stored in a N₂ glovebox and small aliquots were removed for subsequent self assembly experiments

Nanocrystal Assembly: Monolayer nanocrystal superlattices were prepared at the liquid-air interface.²²⁸ Briefly, 1 ml of anhydrous DMF was placed in a 1cm² square teflon well. Next CdSe/CdS hexagonal platelets were diluted in octane to an appropriate concentration

to achieve monolayer coverage and 100 μl of the diluted nanocrystal solution was floated on top of the DMF layer. The well was covered with a glass slide to slow solvent evaporation, and was allowed to sit for at least 8 hours. Subphase ligand exchange¹²⁷ with *t*-BuSH was performed by slowly and carefully injecting 100 μl of a 0.17 mM solution of *t*-BuSH in DMF into the DMF subphase. The sample was allowed to sit for ~ 2 hours with the *t*-BuSH/DMF subphase. The samples were transferred *via* scooping from below to the desired substrate (amorphous carbon coated TEM grid for microscopy or a glass coverslip for X-ray diffraction and spectroscopy) for further processing. Samples were placed in a vacuum oven under house vacuum at $\sim 50^\circ\text{C}$ to remove any remaining subphase solvent. Next the samples were placed on a glass slide and placed on a 200°C hotplate in air for 5 min to thermally decompose the *t*-BuSH. We found that this step could be performed in air without noticeable deleterious effect on the structure or properties of the samples.

SILAR Attachment Successive ion layer ab and reaction (SILAR) was performed in a N_2 glovebox with anhydrous solvents. 20 mM stock solutions of anhydrous Na_2S in MeOH and 20 mM CdOAc_2 in MeOH were prepared. A sample after the above described *t*-BuSH treatment was loaded into self closing anti capillary tweezers and sequentially dipped in the Na_2S solution for 30 s, then a neat MeOH rinse for 30 s, then the CdOAc_2 solution for 30 s, and finally a second MeOH rinse which was separate from the first rinse solution. This process constitutes 1 mono-layer of SILAR and was repeated until the desired number of layers was grown between the materials. Zinc sulfide was grown using a similar procedure as above using 0.2 mM ZnOAc_2 in MeOH. Samples were annealed in a tube furnace under flowing N_2 at 300°C for 20 min

Cation Exchange Reactions Cation exchange reactions were performed on attached CdSe/CdS samples with 6 monolayers of CdS grown at the interfaces. For conversion to $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ we used methods similar to those previously reported however we did not precisely control for concentration of metal ions exchanged.²⁵² Briefly, we dipped our CdSe/CdS assemblies (on a Au TEM grid) in a 2 mg/ml solution of tetrakis(acetonitrile) copper(I) hexafluorophosphate in methanol for 5 min followed by rinsing the film in methanol. For subsequent conversion to HgSe/HgS the previously prepared $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ films were immersed in a solution containing 6 mg $\text{Hg}(\text{NO}_3)_2$ in 3 ml of MeOH with 2 μl of tributylphosphine added for 5min and subsequently rinsed with MeOH.

TEM and Electron Diffraction Characterization: TEM, selected area electron diffraction (SAED), and HRTEM was performed on an FEI Tecnai T20 S-TWIN TEM operating at 200 kV with a LaB_6 filament. TEM images and diffraction patterns were collected using a Gatan Rio 16IS camera with full 4k by 4k resolution and images were collected using the drift correction feature, which collects images at 20 fps, calculates the drift between subsequent images, removes the drift, and sums the images. Diffraction patterns are collected in a summing mode (without drift correction) to simultaneously achieve high dynamic range and high signal to noise. Low magnification images were collected with a 30 μm objective aperture and HRTEM images were collected without an objective aperture. HRTEM images were taken near Scherzer focus, which resulted in dark atom contrast for this crystal thickness. Wide angle and small angle SAED patterns were collected using

an $\sim 11\mu\text{m}^2$ area diffraction aperture with a nominal camera length of 300mm and 4.6m respectively. For small angle-SAED the convergence angle of the illumination was kept constant by using a fixed “spot size” and C2 lens excitation for all samples. For small angle-SAED, the diffraction stigmatism was carefully adjusted to ensure a round transmitted beam. The diffraction camera length for small angle-SAED was calibrated using the inter-planar spacing of the native assembled sample determined *via* TEM images. Diffraction rotation for wide angle SAED was measured using a MoO_3 standard and for small angle-SAED was determined by comparing real-space superlattice images with diffraction patterns.

TEM Image Analysis: All images and diffraction patterns were rotated using bilinear interpolation in ImageJ so that the crystal alignment was consistent throughout the figures. For all FTs displayed and analyzed, care was taken to avoid streaking artifacts that result from image edges. Briefly in Gatan Digital Micrograph 3.0 (GMS 3.0), a $2^n \times 2^n$ pixel area of interest was cropped from the image and was subsequently multiplied by a 2D Hanning window followed by computing the FT. For visualization, the log of the modulus of the FT was saved and visualized in ImageJ using the “fire” lookup table to facilitate viewing. Diffraction patterns were radially and azimuthally integrated using the Difftools package²⁵³ for (GMS 3.0). 2D Autocorrelation functions were calculated from raw TEM images or STEM EDS maps using GMS 3.0. for TEM images, the autocorrelation was normalized to the intensity of the first peak in the $\Gamma - M$ direction to eliminate diffraction contrast modulations damping the autocorrelation envelope.²³⁶ Since STEM-EDS maps provide linear contrast, the autocorrelation was normalized to the height of the central peak avoiding the exact origin (zero pixel shift).²³⁸ 2D autocorrelation images were displayed using the “fire” lookup table ensuring the same minimum and maximum values were used to define the lookup table bounds. Autocorrelation profiles were extracted along the $\Gamma - M$ direction using ImageJ.

Sliding window Fourier transform angle mapping was performed using a custom written Matlab routine. 4k by 4k HRTEM images with a pixel resolution of 2.15 pixels/ Å and collected with a 2 s drift corrected exposure time were used. Next a subarea of 256×256 pixel subarea was extracted, a 2D Hanning window was applied. The modulus of the FFT was calculated and the $\{1\bar{1}00\}$ peaks were identified using a Fast 2D Peak Finder²⁵⁴ routine. Subpixel accurate peak positions for the 2 most intense $\{1\bar{1}00\}$ were determined by fitting each peak to a quadratic function and finding the maximum and the angle relative to the Cartesian plane was determined. This analysis was slid across the image with a 50% overlap between each window and used to populate a new angle image. Images and histograms were plotted relative to the average angle in the image. Angle images were visualized using the “Jet” lookup table in Matlab since it distinctly displays positive and negative values. The original HRTEM images were overlaid with the angle images using Adobe Illustrator and applying a 50% transparency to the angle image.

HRSTEM and STEM-EDS Characterization: High angle annular dark field- HAADF STEM and STEM EDS maps was collected on the FEI TitanX 60-300 microscope at the National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory (LBNL). An FEI low background double tilt holder was used for all experiments.

HAADF STEM was performed at 300kV with a beam convergence semi-angle of 10 mrad using a Fischione high-angle annular dark-field (HAADF) detector with an inner semiangle, β , of 63 mrad. STEM-EDS mapping was performed at 200kV with a typical probe current of ~ 850 pA using an FEI Super-X Quad windowless detector with a solid angle of 0.7 steradians. Data was collected using the Bruker Esprit software utilizing drift correction. High resolution maps were collected with a 2 Å pixel size with a typical collection time of ~ 15 min, after which the sample was damaged too much. Data displayed in Figure 4.4 and Figure A.4.8 are unmodified raw counts while Figure 4.9 used a 3 pixel average filter. Fourier transforms and autocorrelations used the unmodified maps for all cases. Quantification was performed using the Bruker Esprit software using the Cliff-Lormer method. The following spectral lines were used for each element: Cd L-series, Se K-series, S K-series, Cu K-series series Hg L-series series. Samples for cation exchange experiments were prepared on Au TEM grids.

X-ray Diffraction: For ensemble characterization of NC starting materials, solids were made into fine powders to avoid orientation effects. Powders were prepared by depositing a large amount of NCs from hexanes onto a glass slide, and allowed to dry, the film was then scraped off the glass slide with a clean razor blade onto a $\langle 510 \rangle$ oriented Si low background diffraction substrate. For XRD characterization of nanocrystal assemblies, NCs were assembled as described above and scooped onto thin glass coverslips where subsequent attachment reactions were performed. The thin glass coverslip was placed on top of the $\langle 510 \rangle$ oriented Si substrate. Diffraction patterns were collected on a Bruker Phaser D2 diffractometer with Cu $k\alpha$ source operated at 30 kV and 10 mA with a 160 SSD detector. Diffraction patterns were collected from 20° to $60^\circ 2\theta$ with a step size of 0.02° , an integration time of 7s per step. For samples on glass coverslips, the amorphous scattering background was removed using the diffracEVA software. X-ray diffraction and electron diffraction data were plotted in Q ($Q = \frac{2\pi}{d}$) space for easier comparison.

Optical Characterization: Samples for optical characterization were prepared by scooping initial samples onto glass coverslips and performing the desired SILAR or heat treatments. Steady state PL spectra and lifetimes were collected using a Picoquant Fluotime 300 spectrometer, a PMA 175 detector, and a LDH-P-C-405 diode laser with a 407 nm excitation wavelength (50 ps pulse width) and typically using a laser repetition rate of 4MHz.

Computational Methods: Methods used in this work were identical to those we previously used.²³⁹

Chapter 5

Conclusions and Outlook

5.1 Conclusions

As we saw in Chapter 2 and 3, the careful understanding of nanocrystal attachment geometries and the resulting defect chemistry pointed to ideal facets for nanocrystal attachment. The design principle for rock salt PbTe attachment in Chapter 2, suggests that the $\{100\}$ facets are ideal for attachment since defect removal was easiest. Indeed most of the PbX attachment community already attaches their materials on $\{100\}$ facets thus the work reinforces the synthetic design of those materials. The case of wurtzite CdSe attachment had not been extensively explored when investigations into the attachment began, and as such this presented a unique opportunity to let *in-situ* TEM guide materials synthesis. Indeed the prevalence of prismatic stacking faults were not considered until they were observed *via* TEM imaging. Their observation indicated that the $\{1\bar{1}00\}$ was a better facet for attachment. The results from Chapter 3 fed directly into the design of the attachment strategy presented in Chapter 4. We showed the attachment strategy in Chapter 4 also had favorable features including improved uniformity in neck thicknesses which may ultimately lead to delocalized states in attached nanocrystals. Unfortunately there are still serious issues with material quality including high dislocation density which will need to be addressed in the future. Currently the materials display luminescence dominated by trap states which also may be a result of the low temperature growth of additional material at the interfaces. Converging colloidal assembly with high temperature solution phase²⁵⁵ or gas phase growth²⁵⁶ may yet allow high quality materials to be prepared. Careful study of treatments to improve attachment, improve angular coherence, decrease nanocrystal size distribution or improve the shape distribution will likely point to new synthetic parameters to improve material quality. An additional factor to consider is identifying materials systems which have stronger coupling between neighboring dots, this will make the bandwidth broader, and likely less sensitive to positional disorder .

5.2 Outlook for Nanocrystal Attachment

The attached nanocrystal superlattices presented in this thesis and those recently reported by others²⁴¹ indeed are visually striking. They, to the naked eye, have impressive atomic order and superlattice order. However, electrons are picky, a few dangling bonds can trap a charge carrier as we observed in Chapter 3. Misorientation of nanocrystals in the assembled lattices eventually lead to dislocations in fused semiconductors as we saw in Chapter 4. The degree of crystal misalignment in nanocrystal derived quantum dot superlattices are much higher compared to epitaxial growth mechanisms. It is unclear if sufficient angular coherence (i.e. $\ll 1^\circ$) across a superlattice domain can be achieved and this will be needed to realize low defect density materials.

Other issues which electrons are sensitive to include strain, which is observed in many necks, can scatter carriers again perturbing electronic properties. Finally, There are issues with phase matching the wavefunctions between neighboring NCs, even a single atomic plane variation can disrupt coupling and lead to disorder.¹⁹⁰ We presented in Chapter 1, the atomic like wavefunctions of excitons in spatially confined semiconductors can interact and form bands with reasonable bandwidths. However these simple models don't account the atomic structure of the materials. As we have seen, it is difficult to achieve perfection in the atomic lattice despite the apparent perfection on the mesoscale. A better path forward may be to use the insights of nanocrystal assembly and attachment to prepare well defined artificial molecules made of a few attached quantum dots.^{257,258} There it may be easier to achieve defect free materials since the volumes and length scales are much smaller. Further, there are many applications where crystal quality requirements are lower, and specific defects in materials are critical for device operation. If those can be controlled in attached nanocrystals, 2D films of these materials may prove useful in applications such as photo-detectors.¹³⁸

Ultimately an electron (or hole) feels the atomic lattice first, the the superlattice potential is secondary, and thus the emergent mini-bands depend on a perfect atomic lattice in the heterostructure. Any defect on the atomic scale will ultimately affect electrons more than the perturbation on the mesoscale. It is unclear if the levels of perfection in attached nanocrystals will be achieved, however the limit likely has not been reached. Future endeavours to understand improvements to nanocrystal assembly and attachment should also consider fundamental limits for perfection and whether those limits will be sufficient to realize the exciting goal of engineered band structures in self assembled quantum dot based semiconductors.

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Appendix A

Supplementary Figures

A.1 Chapter 1 Supplementary Figures

A.2 Chapter 2 Supplementary Figures

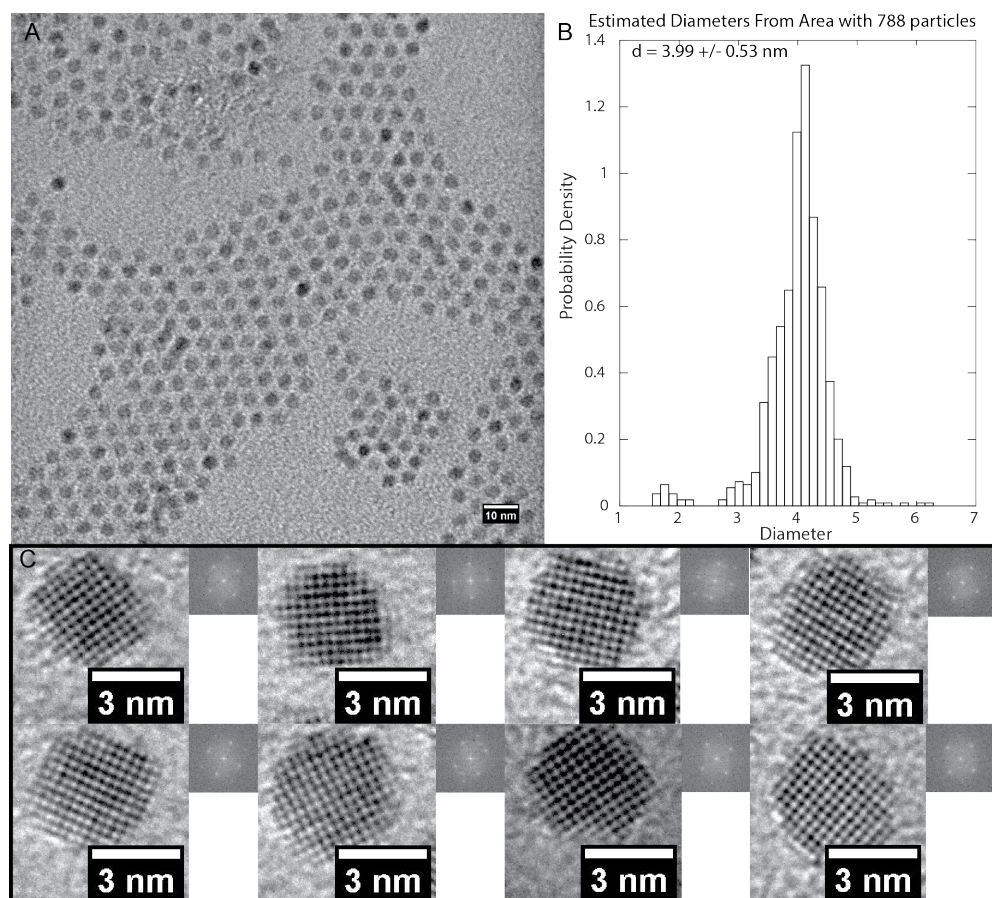


Figure A.2.1: Overview of the characterization of the initial PbTe nanocrystals. A) low resolution TEM image of the nanocrystals. B) size and size distribution of the PbTe nanocrystals used in this work. C) several HRTEM images of individual PbTe nanocrystals down the $\langle 100 \rangle$ zone axis showing the quasi cubic shape mostly terminated with $\{100\}$ facets. Several of the nanocrystals have step edges which are necessary for imperfect oriented attachment. In addition, some of the particles have significant $\{110\}$ termination.

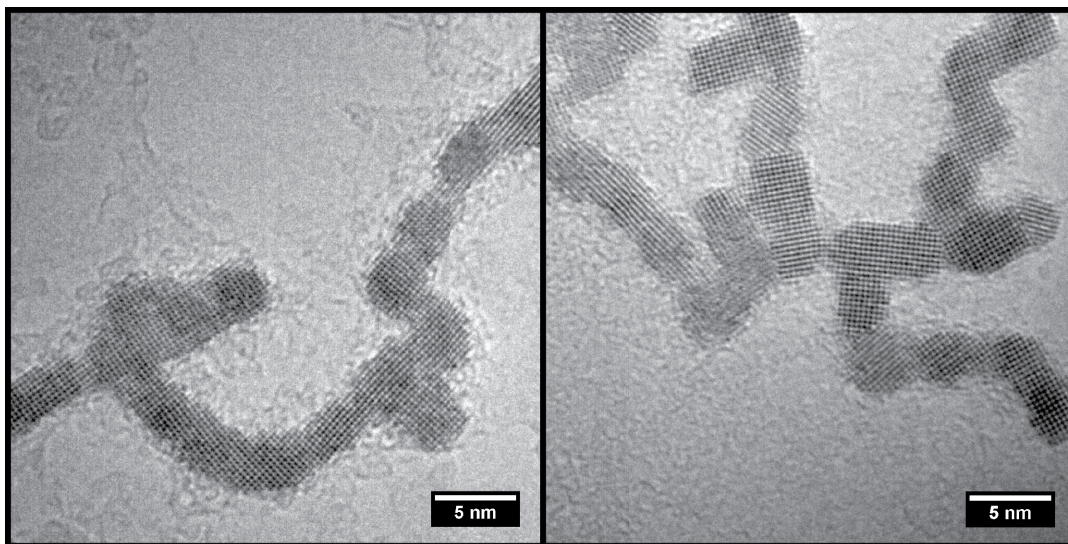


Figure A.2.2: HRTEM of the PbTe nanocrystals after solvent mediated sandwiching between multilayer graphene sheets. Particles show significant attachment on the $\{100\}$ facets, and to a lesser extent attachment on $\{110\}$ facets.

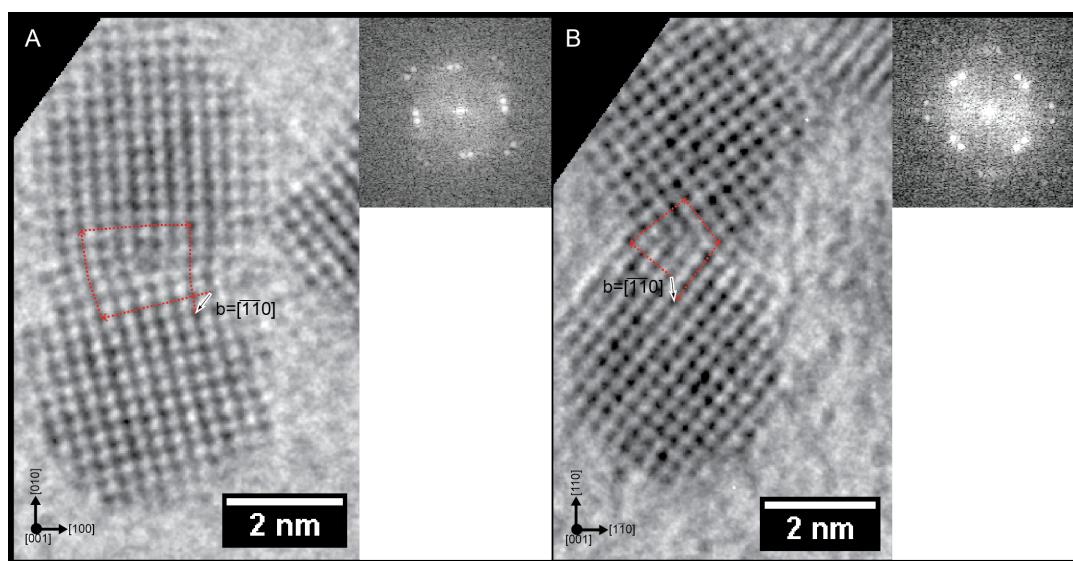


Figure A.2.3: Additional examples of imperfect oriented attachment. A) HRTEM image of 2 PbTe particles which have imperfectly attached on $\{100\}$ facets giving rise to a $b = \frac{a}{2}[\bar{1}\bar{1}0]$ edge dislocation. B) HRTEM image of 2 PbTe particles which have imperfectly attached on $\{110\}$ facets giving rise to a $b = \frac{a}{2}[\bar{1}\bar{1}0]$ edge dislocation.

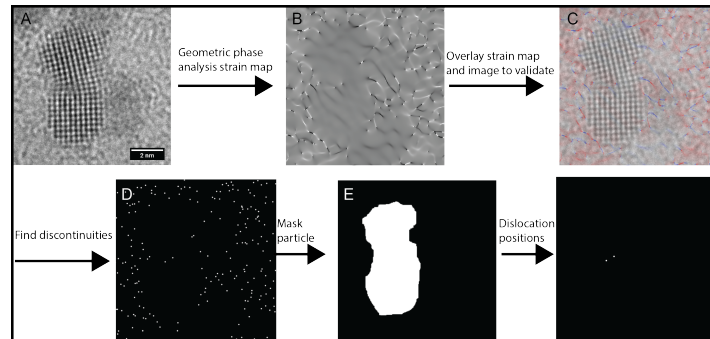


Figure A.2.4: Method for objectively determining dislocation position. Automated scripts in Gatan Digital Micrograph and ImageJ were used to perform this analysis on each frame automatically. We show an example progression of the analysis for one frame of the imperfect attachment on the $\{100\}$ facets shown in in Figure 2.3. The raw data and each step of the analysis for both Figure 2.3 and 2.4 are available on the DASH repository at <https://doi.org/10.6078/D17675>. First, the movies were drift corrected using a cross correlation method using the raw images as inputs and manually checked and corrected where necessary (Stack Alignment, Dave Mitchell’s DigitalMicrographTM Scripting Website, http://www.dmscripting.com/stack_alignment.html). The geometric phase analysis (GPA) and all other analysis was performed with the raw but drift corrected unrotated images from our CCD camera to avoid introducing artifacts. Geometric phase analysis was performed using the GPA tool contained in the FRWRtools plugin (https://www.physics.hu-berlin.de/en/sem/software/software_frwrtools) for Gatan Digital Micrograph. The (200) and (020) peaks were used for analysis with a reference lattice with a and b parameters of $3.09\text{\AA}$ with a 90° angle between the two, a resolution of 0.7 nm and a smoothing of 0.6 with a symmetric strain matrix. After this analysis, all images were rotated to the same orientation, using a bilinear interpolation in ImageJ, as shown in Figure 2.3 to facilitate comparison. A) Raw HRTEM image of the imperfectly attached particles. B) ϵ_{xx} map determined by GPA analysis for the imperfectly attached PbTe particles. We note that the ϵ_{yy} and ϵ_{xy} strain output from the GPA will produce the same result for dislocation position (within a pixel) however the ϵ_{xx} map was used for all the samples shown here for consistency. C) The ϵ_{xx} strain map was overlaid with the HRTEM image of the particles and each frame was manually inspected to ensure erroneous results were avoided. For some frames, an instability in the microscope (sample vibration, CCD readout error, etc.) produced suboptimal images which gave several discontinuities in the strain map within the particle. These frames were carefully inspected and only points where the dislocation resided were retained. D) Discontinuities in the strain map were determined with single pixel accuracy by finding the maximum in the strain map using ImageJ. Finding the minima also produced the same result, only shifted one pixel adjacent. For consistency, we use the maxima for all analysis. E) A mask was applied to remove the discontinuities which result from the amorphous background. F) Final position of the dislocation which was imported into matlab for plotting. We note that this analysis picks out the two components of the dislocation resulting from the extra (100) and (010) plane respectively although no effort was made to plot those separately in the graphs shown in Figures 2.3 and 2.4.

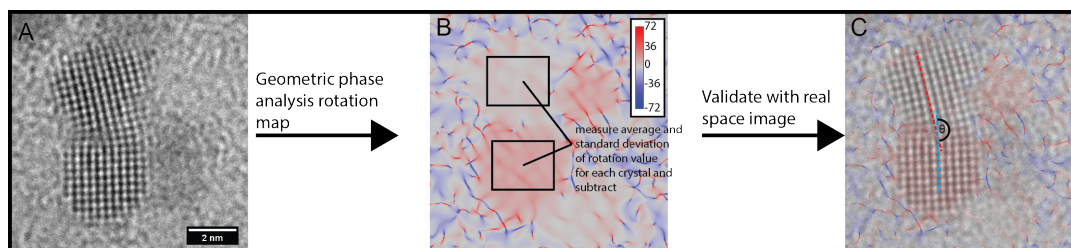


Figure A.2.5: Strategy for analyzing the average misorientation angle. The same initial analysis protocols were used as discussed in Figure A.2.4. A) Raw HRTEM image of the two particles. B) rotation map from the GPA of a single frame. The colors correspond to rotation of the lattice relative to a reference lattice. Two boxes were drawn that contained the top and bottom particle. The average and standard deviation of the rotation value were calculated for each box and the difference was taken as the misorientation angle between the two crystallites. The standard deviation of the misorientation angle was determined by adding the standard deviation of the rotation value for each domain in quadrature. This error is both a metric for the intrinsic error in the measurement and to variations in the orientation across individual crystallites due to strains imposed by the dislocation. C) the misorientation angle was measured in real space for some frames to validate the GPA determined misorientation angle.

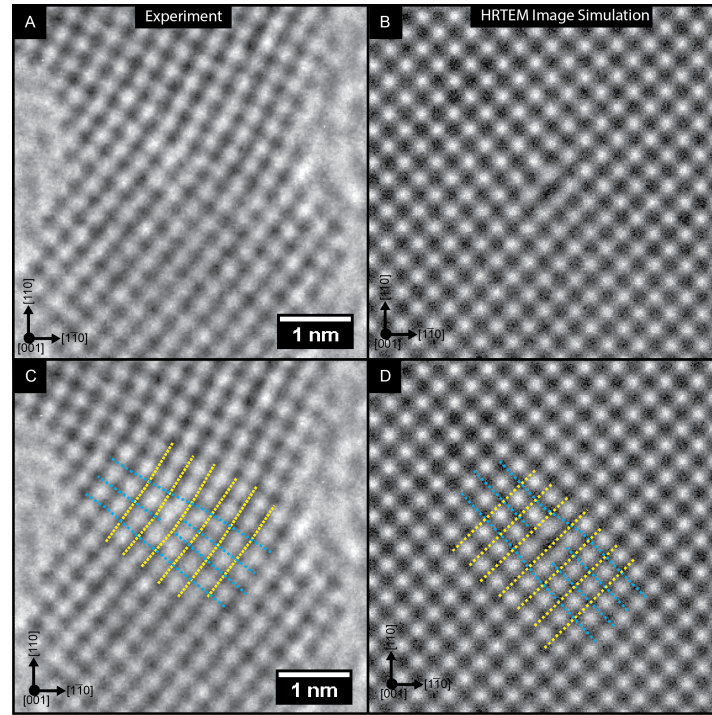


Figure A.2.6: Comparison of experimental and simulated HRTEM images for the $b = \frac{a}{2}[101]$ mixed dislocation. A) Experimental HRTEM image of a $b = \frac{a}{2}[101]$ mixed dislocation. B) Simulated HRTEM image of the mixed dislocation structure presented in Figure 3.3E. The mixed dislocation structure was generated using the Atomsk software using anisotropic elasticity. Briefly a $54\text{\AA}$ by $60\text{\AA}$ by $35\text{\AA}$ thick supercell of PbTe was generated, then a $b = \frac{a}{2}[101]$ mixed dislocation was cut from the crystal using anisotropic elasticity theory and elastic constants for bulk PbTe. The Atomsk software displaces the atoms based on strain fields around a dislocation in an infinite crystal. No efforts were made to further relax the structure beyond continuous elastic theory for an infinite crystal. For these reasons, the simulated dislocation structure does not capture the misorientation observed in the experimental imperfectly attached particles. HRTEM images from the mixed dislocation structure were simulated using the multislice method implemented in the computem software.²⁵⁹ The dislocation structure was placed in the center of a $180\text{\AA}$ by $180\text{\AA}$ by $35\text{\AA}$ supercell surrounded by vacuum. Imaging parameters for the simulated images were set for near Scherzer conditions based on estimated parameters for our Tecnai T20 S-Twin TEM. Simulation parameters are as follows: Accelerating voltage 200keV, C_3 Spherical aberration coefficient: 1.2mm, Defocus: -45nm, δ Defocus: 15nm, Beam convergence angle: 0.3mrad, Objective aperture: 20mrad, transmission function size: 1024 by 1024-pixels and slice thickness: $2\text{\AA}$. All higher order aberrations were set to be zero since our instrument is C_3 limited and all higher order aberrations are insignificant compared to C_3 . Images were simulated at 0K (no atom vibrations). Gaussian noise was added to the simulated image to account for camera noise. The simulated images have improved contrast compared to the experimental images. This increase in contrast is a result of not including atom vibrations in the simulated image and is a well-known artifact in HRTEM image simulation.⁹² Further in the simulated images we did not account for the modulation transfer function of our TEM camera which would lead to further blurring of the image. C) and D) Blue and yellow lines are overlaid on the (100) and (010) planes respectively as guides to the eye showing the apparent screw dislocation.

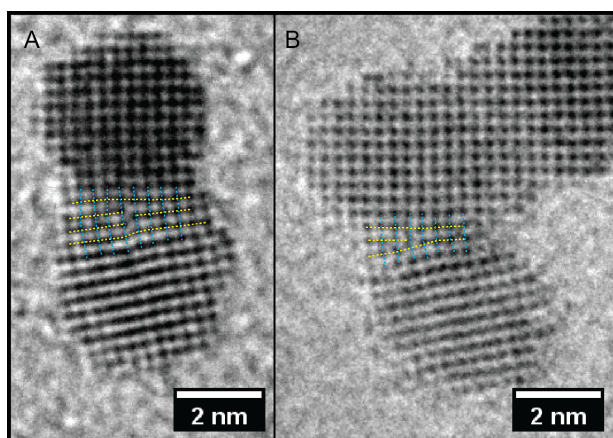


Figure A.2.7: A) and B) HRTEM images of imperfectly attached PbTe nanocrystals which show dislocations which have partial screw character initially. It is unclear if these dislocations were pure edge dislocations initially and converted to partial screw character during electron beam irradiation while focusing. Further the loss in contrast of the bottom crystal in both cases is indicative of a rotation around the attachment axis.

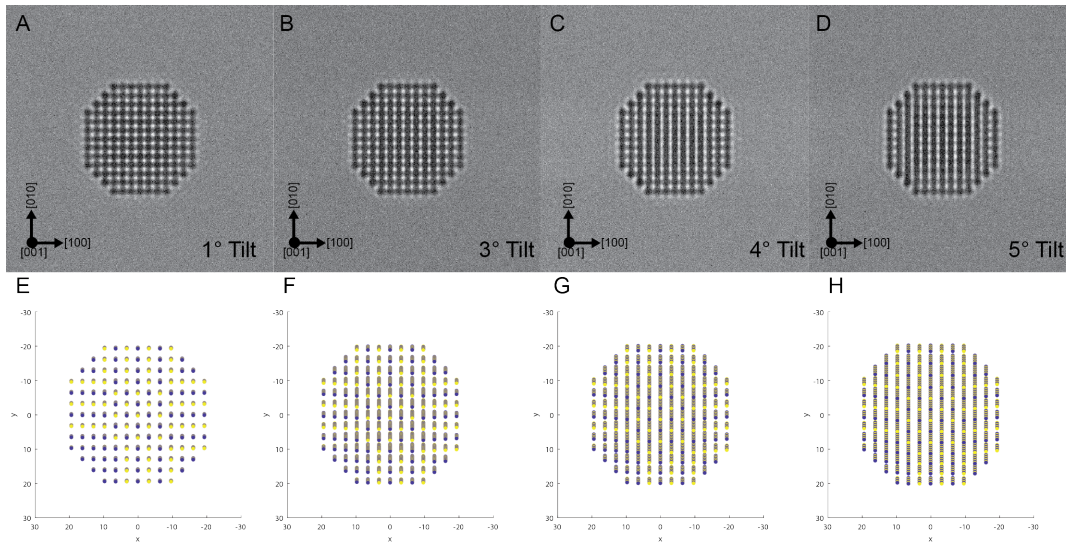


Figure A.2.8: (A-D) HRTEM image simulations of a 3.8nm PbTe cuboctahedra with different degrees of rotation around the $[100]$ axis. This shows that a slight tilt of the crystal coming from the screw dislocation can reduce the contrast of the corresponding (010) planes which are perpendicular to the rotation axis. This is consistent with the reduced contrast of the planes perpendicular to the rotation imparted by the screw dislocation seen in Figure A.2.7 A and B. (E-H) crystal models used to generate the simulated images. Yellow corresponds to Te and blue corresponds the Pb. Crystal models were cut from a bulk crystal of PbTe using VESTA with $\{110\}$ cutoff planes $22.59\text{\AA}$ from the origin and $\{111\}$ cutoff planes $21.59\text{\AA}$ from the origin. The structures were exported as .XYZ files from VESTA and imported into matlab where a custom script was used to rotate the particle the specified amount around the given axes. The rotated nanocrystals were placed in a $100\text{\AA}$ by $100\text{\AA}$ by $100\text{\AA}$ supercell. Simulations were performed using the same parameters as used for Figure A.2.6.

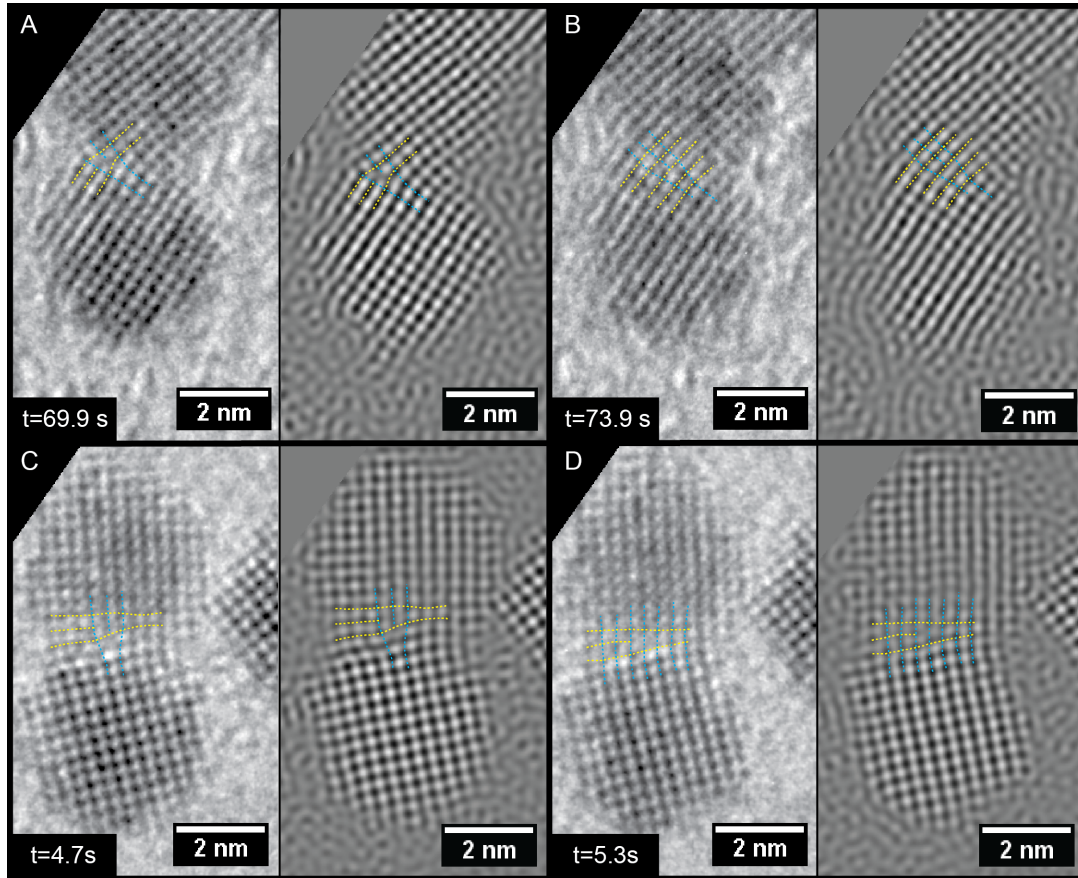


Figure A.2.9: Additional examples of edge to partial screw conversion during electron beam exposure of imperfectly attached PbTe particles. A) HRTEM (left) and $\{100\}$ bandpass Fourier filtered (right) image of two particles attached on $\{110\}$ facets with a pure edge dislocation exemplified by the extra (100) and (010) planes outlined by blue and yellow lines respectively. B) HRTEM image and $\{100\}$ bandpass Fourier filtered (right) image of the same particles 6 frames later with only an extra (100) plane indicative of conversion to a screw dislocation. C) HRTEM (left) and $\{100\}$ bandpass Fourier filtered (right) image of two particles attached on $\{100\}$ facets with a pure edge dislocation exemplified by the extra (100) and (010) planes outlined by blue and yellow lines respectively. B) HRTEM image (left) and $\{100\}$ bandpass Fourier filtered (right) image of the same particles a single frame later with only an extra (010) plane indicative of conversion to a screw dislocation. We note that in panel D, the top crystallite is rotated off the $[001]_c$ zone axis as seen by the change of contrast which is consistent with the expected out of plane rotation for a screw dislocation.

A.3 Chapter 3 Supplementary Figures

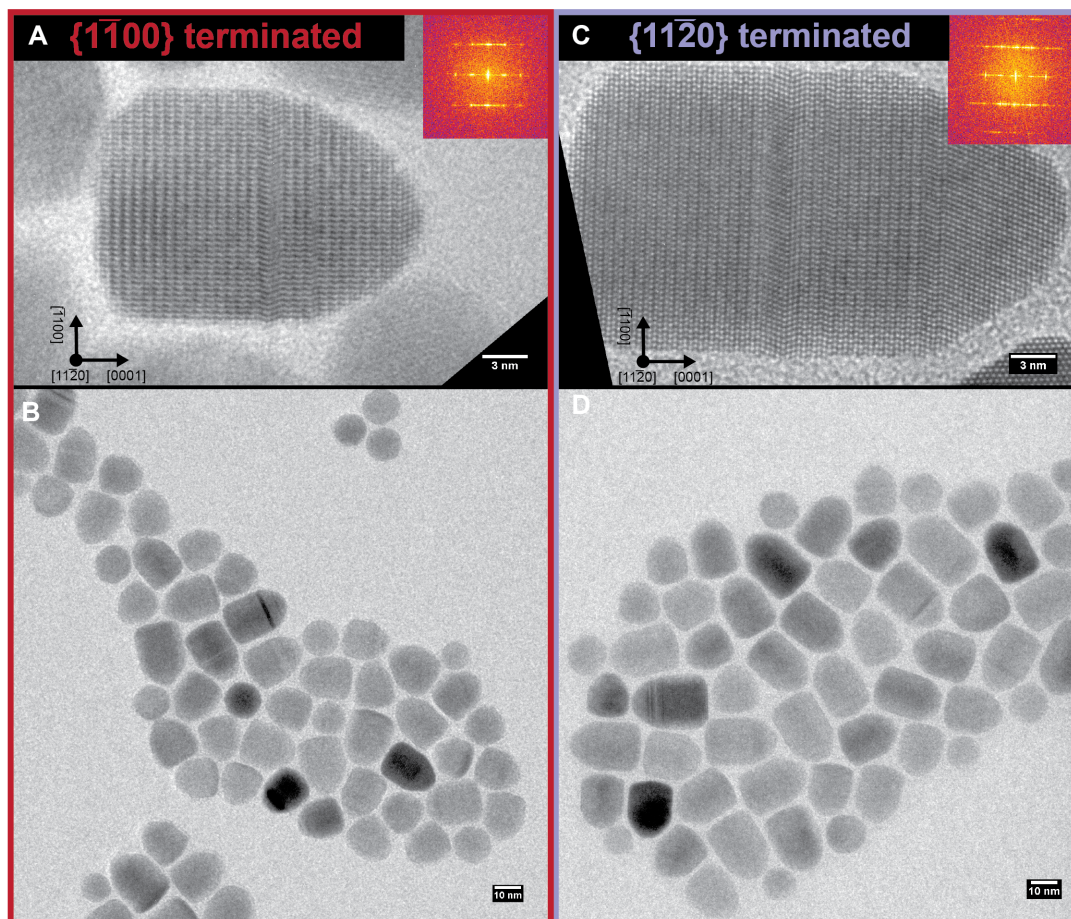


Figure A.3.1: (A) HRTEM image of a $\{1\bar{1}00\}$ terminated CdSe NC viewed down the $[11\bar{2}0]$ zone axis showing the basal plane stacking disorder. (B) Low magnification TEM image of the $\{1\bar{1}00\}$ terminated sample where the quasi-rod shape is apparent. High and low contrast bands observed in the images come from diffraction contrast due to stacking disorder in the samples. (C) HRTEM image of a $\{11\bar{2}0\}$ terminated CdSe NC viewed down the $[11\bar{2}0]$ zone axis showing the basal plane stacking disorder. (D) Low magnification TEM image of the $\{11\bar{2}0\}$ terminated sample where the quasi-rod shape is apparent. High and low contrast bands observed in the images come from diffraction contrast due to stacking disorder in the samples.

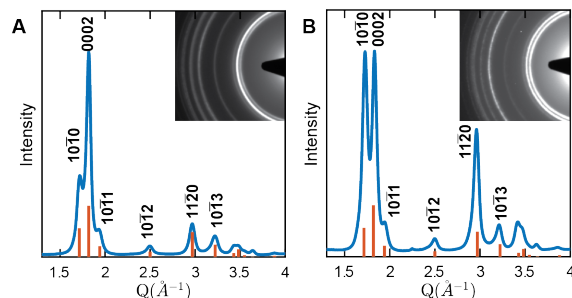


Figure A.3.2: (A) and (B) Wide angle electron diffraction and inset 2D pattern collected for $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$ terminated samples respectively. Relative peak intensities for the $\{1\bar{1}00\}$, $\{0002\}$, and $\{10\bar{1}0\}$ peaks give an idea of the ensemble level ordering in the sample. For the $\{1\bar{1}00\}$ we observe preferential orientation of the rods lying on their sides ($[0001]$ parallel to the substrate), as evidenced by the strong $\{0002\}$ peak and some rods standing up ($[0001]$ perpendicular to the substrate), as evidenced by increased intensity of the $\{1\bar{1}00\}$ peak relative to the $\{10\bar{1}0\}$ peak. For the $\{11\bar{2}0\}$ terminated sample, we observe preferential orientation of the rods standing up as evidenced by the strong $\{1\bar{1}00\}$ diffraction peak

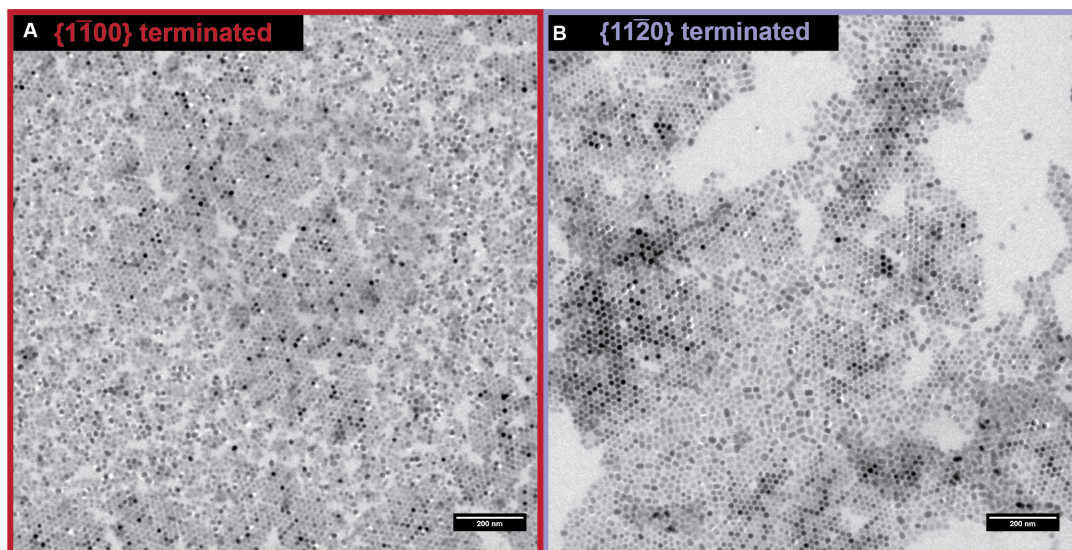


Figure A.3.3: Low magnification TEM images of (A) $\{1\bar{1}00\}$ and (B) $\{11\bar{2}0\}$ terminated CdSe NCs where the electron diffraction in Figure A.3.2A and B were collected

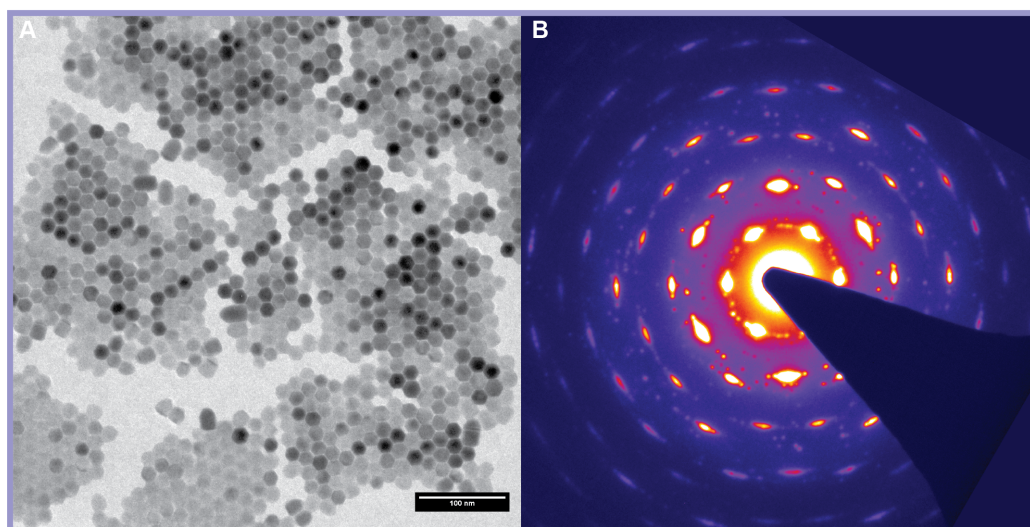


Figure A.3.4: A) low magnification TEM image and (B) selected area electron diffraction pattern showing large area atomically coherent attachment of $\{11\bar{2}0\}$ terminated wurtzite CdSe NCs using the Na_2Se treatment.

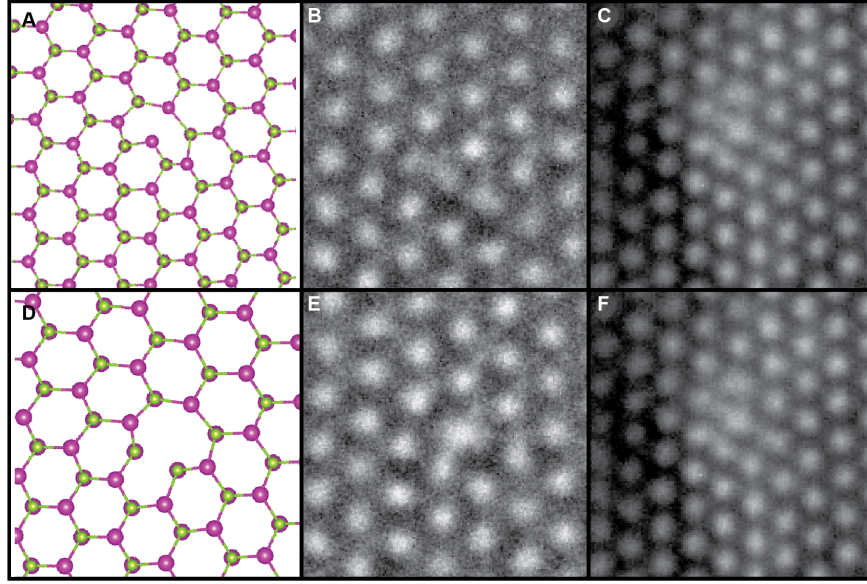


Figure A.3.5: (A) full-core model of a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation in wurtzite CdSe with the characteristic 8-member ring. (B) Multislice TEM image simulation of the structure in panel A using conditions similar to those used for all experimental HRTEM imaging. For this dislocation, we see a characteristic merging of two white spots at the position of the 8-member ring. TEM image simulation methods are as follows: A slab $70\text{\AA}$ thick along the $[0001]$ direction with a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation was generated using atomsk. The center position of the strain field was moved to different locations within the lattice to generate the 8- and 5/7- structure respectively.²⁶⁰ HRTEM images from the edge dislocation structure were simulated using the multislice method implemented in the computem software.²⁵⁹ Imaging parameters for the simulated images were set for near Scherzer conditions based on estimated parameters for our Tecnai T20 S-Twin TEM. Simulation parameters are as follows: Accelerating voltage 200keV, C_3 Spherical aberration coefficient: 1.2mm, Defocus: -45nm, δ Defocus: 15nm, Beam convergence angle: 0.3mrad, Objective aperture: 20mrad, transmission function size: 1024 by 1024-pixels and slice thickness: $2\text{\AA}$. All higher order aberrations were set to be zero since our instrument is C_3 limited and all higher order aberrations are insignificant compared to C_3 . Images were simulated at 0K (no atom vibrations). Gaussian noise was added to the simulated image to account for camera noise. The simulated images have improved contrast compared to the experimental images. This increase in contrast is a result of not including atom vibrations in the simulated image and is a well-known artifact in HRTEM image simulation.⁹² (C) Experimental HRTEM image of a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation which also shows contrast consistent with the full core structure. (D) An open-core model of a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation in wurtzite CdSe with the characteristic 5 and 7-member rings. (E) Multislice TEM image simulation of the structure in panel D using conditions similar to those used for all experimental HRTEM imaging. For this dislocation core structure, we see a characteristic slightly merged small and large dot, characteristic of the 5- and 7-member ring respectively. (F) HRTEM image of a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation which does not show contrast consistent with this dislocation core model.

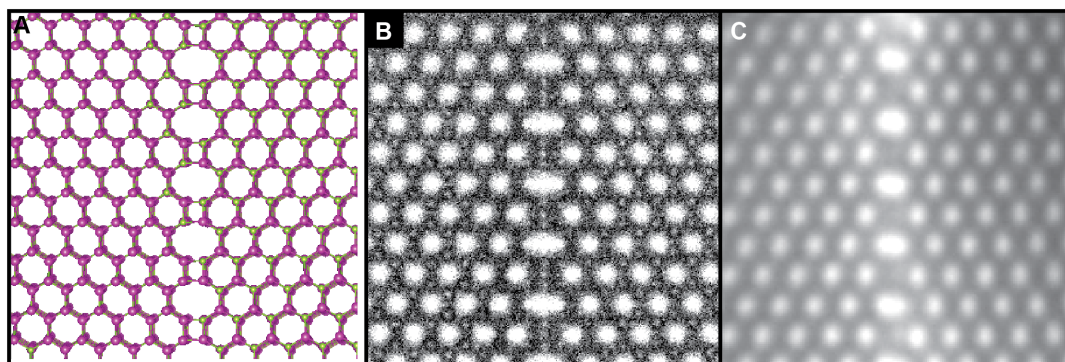


Figure A.3.6: (A) Model of a prismatic stacking fault with the Drum model $\frac{1}{2}\langle 10\bar{1}1 \rangle$ displacement. (B) Multislice TEM image simulation of the model shown in panel A showing the characteristic elongated bright spots from the 8-member rings. (C) HRTEM image of a PSF between two $\{1\bar{2}10\}$ terminated particles with contrast consistent with the Drum model.

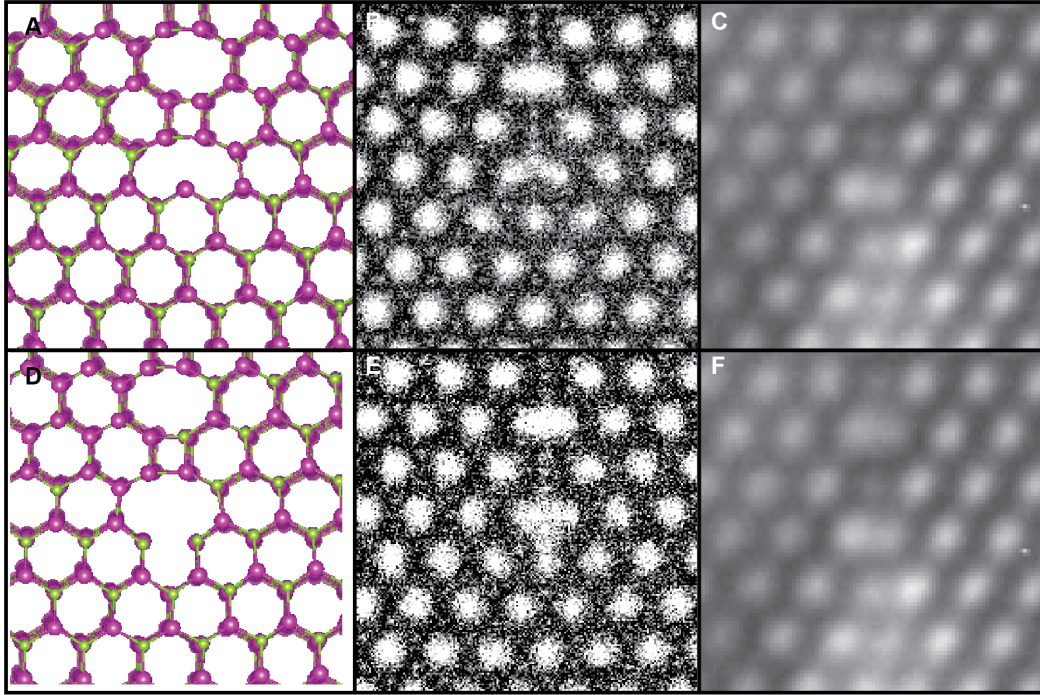


Figure A.3.7: (A) The full core model for $ab = \frac{a}{2}[\bar{1}011]$ partial dislocation bound by a PSF. (B) Multislice HRTEM image simulation of the structure in panel A showing a distorted blob associated with the 9-member ring. (C) HRTEM image of the core area of the partial dislocation. (D) The open core model for $ab = \frac{a}{2}[\bar{1}011]$ partial dislocation bound by a PSF. (E) Multislice HRTEM image simulation of the open core model showing a large merged blob associated with the dislocation core. (F) HRTEM image of the core area of a partial dislocation. Using conventional HRTEM imaging, it is difficult to confidently confirm the core structure of this dislocation however it appears the full core structure image simulations are more consistent with the experimental images. Unfortunately, at this time, we cannot find any other reports in the literature of the core structure of this dislocation determined by more reliable techniques such as aberration corrected high angle annular dark field STEM imaging.

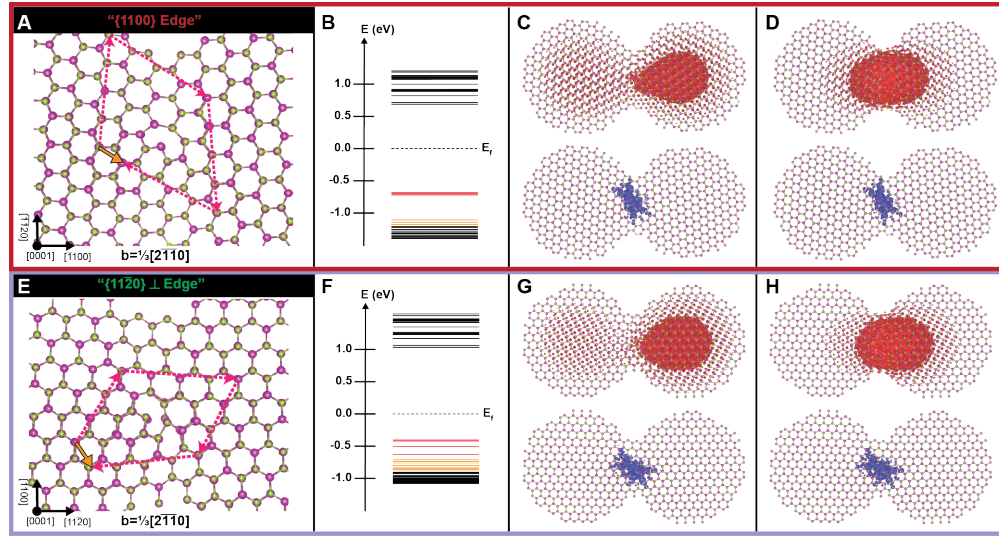


Figure A.3.8: Electronic structure calculations of attached quantum dots with a (A-D) “ $\{1\bar{1}00\}$ Edge” interfacial defect and (E-H) “ $\{11\bar{2}0\} \perp$ Edge” interfacial defect. (A, E) Interface of the attached particles used in electronic structure calculations, with a Burgers circuit included in (E). (B, F) Energy level diagrams (in eV) for the single-particle states. Defect related shallow and deep hole trap states are shown in orange and red, respectively. The Fermi energy, E_f , was chosen to be the midpoint of the calculated fundamental gap, E_g , for the attached quantum dots that underwent perfect oriented attachment on the $\{11\bar{2}0\}$ facet. (C, D, G, H) Electron (red) and hole (blue) probability densities for (C, G) the single-particle (*i.e.* noninteracting electron and hole) states and (D, H) the excitonic (*i.e.* correlated electron-hole) states. All probability densities are shown at the same isosurface value and are Boltzmann weighted averages over the low energy (C, G) single-particle and (D, H) excitonic states.

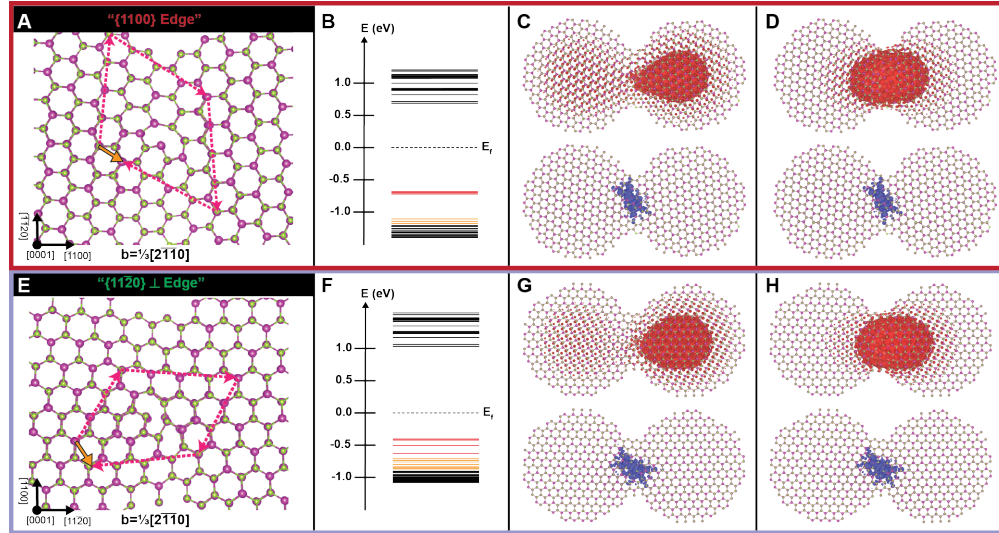


Figure A.3.9: HRTEM image of a PSF at the interface of $\{11\bar{2}0\}$ terminated CdSe NCs after annealing at 440°C for 15 min.

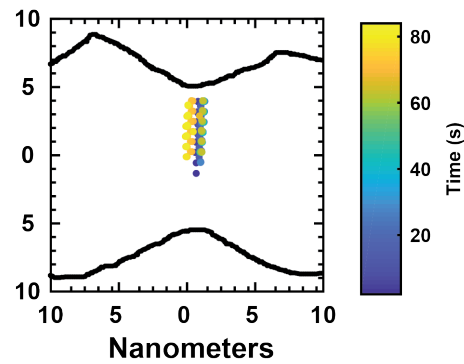


Figure A.3.10: Prismatic stacking fault position as a function of time for the “partial PSF” shown in Figure 3.5E-F. This shows the PSF does not change length during annealing and thus the $b = \frac{a}{2} [\bar{1}011]$ partial dislocation do not move up until the PSF removal at 84 seconds.

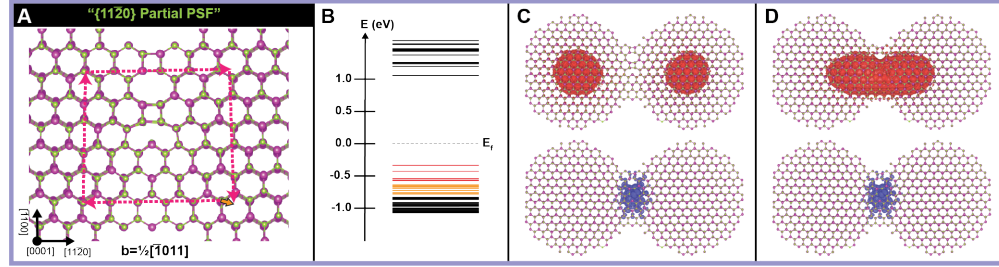


Figure A.3.11: Electronic structure calculations of attached quantum dots with a “ $\{11\bar{2}0\}$ Partial PSF” defect at the interface. (A) Interface of the attached particle used in electronic structure calculations, with a Burgers circuit included. (B) Energy level diagrams (in eV) for the single-particle states. Defect related shallow and deep hole trap states are shown in orange and red, respectively. The Fermi energy, E_f , was chosen to be the midpoint of the calculated fundamental gap, E_g , for the attached quantum dots that underwent perfect oriented attachment on the $\{11\bar{2}0\}$ facet. Electron (red) and hole (blue) probability densities for (C) the single-particle (*i.e.* noninteracting electron and hole) states and (D) the excitonic (*i.e.* correlated electron-hole) states. All probability densities are shown at the same isosurface value and are Boltzmann weighted averages over the low energy (C) single-particle and (D) excitonic states.

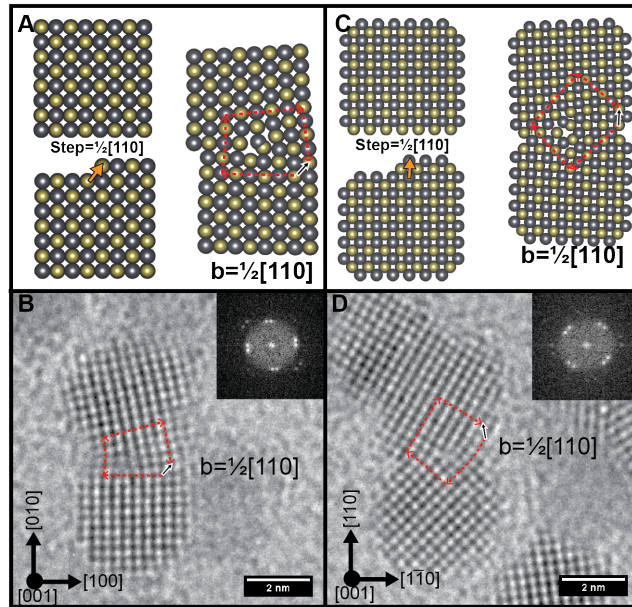


Figure A.3.12: Relationship of surface step vectors and Burgers vectors for rock salt PbTe attached on $\{100\}$ facets (A, B) and $\{110\}$ facets (C, D).

A.4 Chapter 4 Supplementary Figures

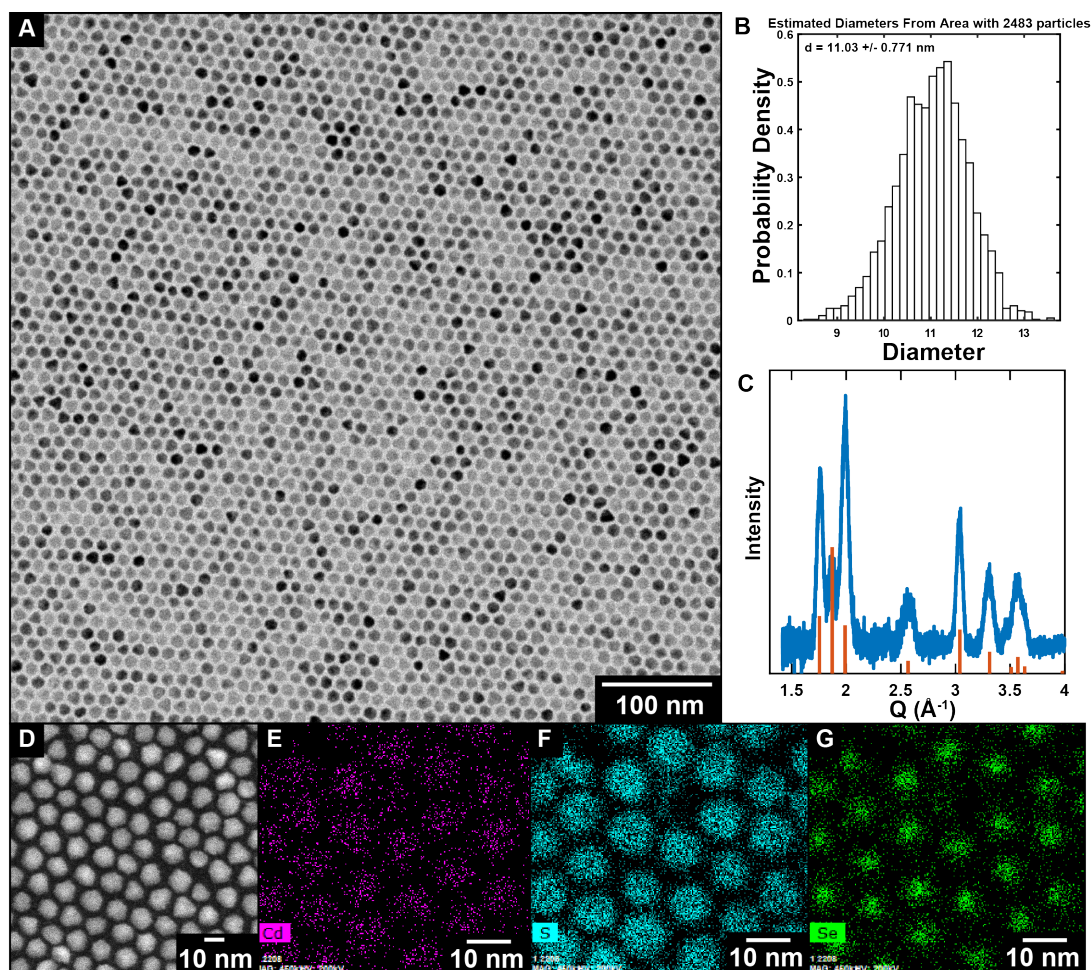


Figure A.4.1: (A) wide field of view TEM image, (B) size histogram via automated particle analysis and (C) wide angle powder XRD pattern of hexagonal shaped CdSe/CdS core shell nanocrystals with 6 monolayers of a CdS shell grown on an ~ 5 nm diameter core. Stick pattern represents wurtzite CdS (ICSD code 154186). XRD was collected with a carefully prepared powder to avoid preferential orientation effects. (D) HAADF STEM image, and elemental maps *via* STEM-EDS of the (E) cadmium, (F) sulfur, and (G) selenium positions

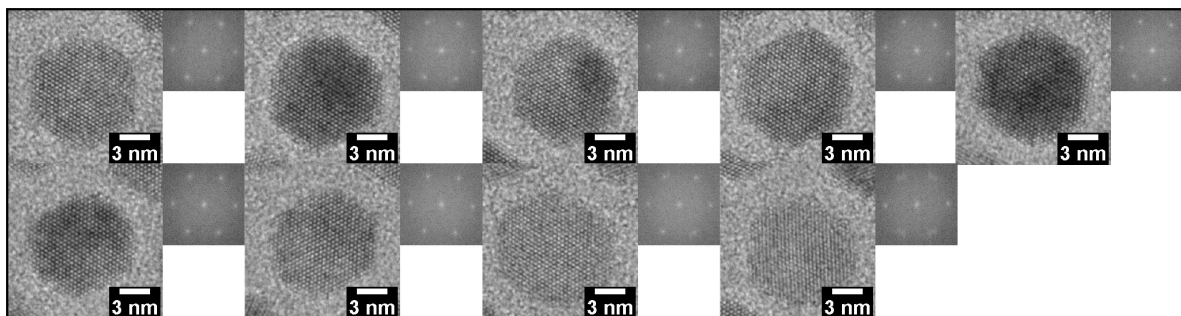


Figure A.4.2: HRTEM images of 6 monolayer CdSe/CdS nanocrystals with an ideal hexagonal cross section.

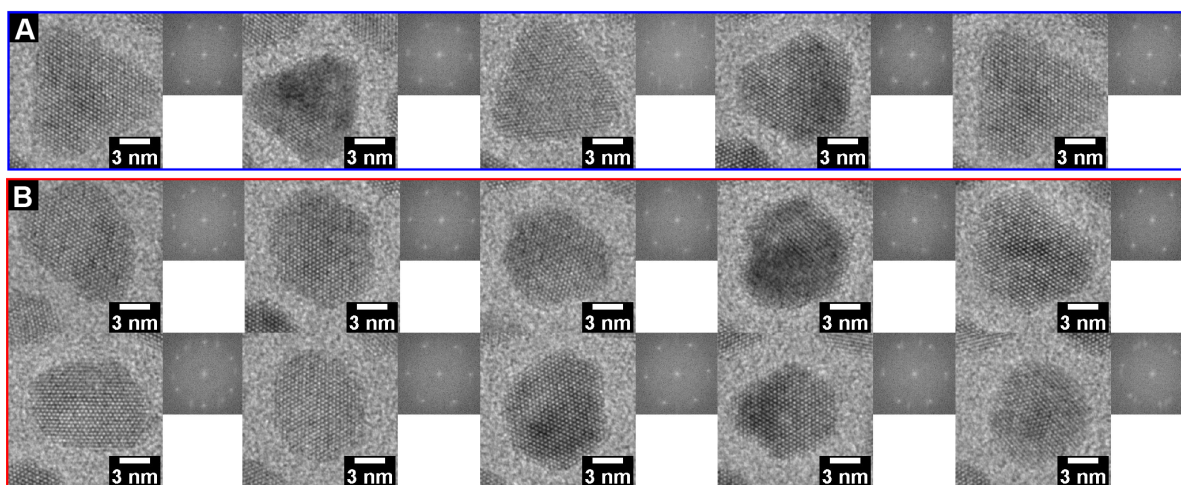


Figure A.4.3: HRTEM images of 6 monolayer CdSe/CdS nanocrystals with (A) truncated triangular and (B) quasi-irregular cross sections.

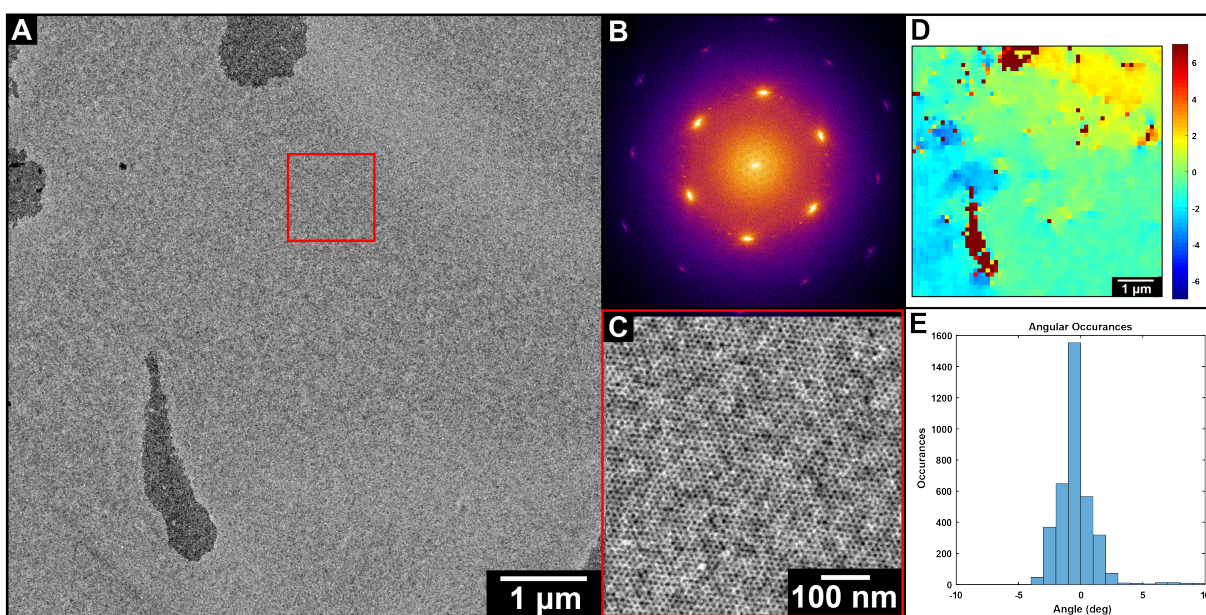


Figure A.4.4: (A) Large field of view TEM image ($7\ \mu\text{m}$ by $7\ \mu\text{m}$ area) (B) full field of view Fourier transform from (A). (C) Zoomed in TEM image from the red square. (D) local superlattice angle measured by the sliding window Fourier transform and (E) histogram of the angles in (D)

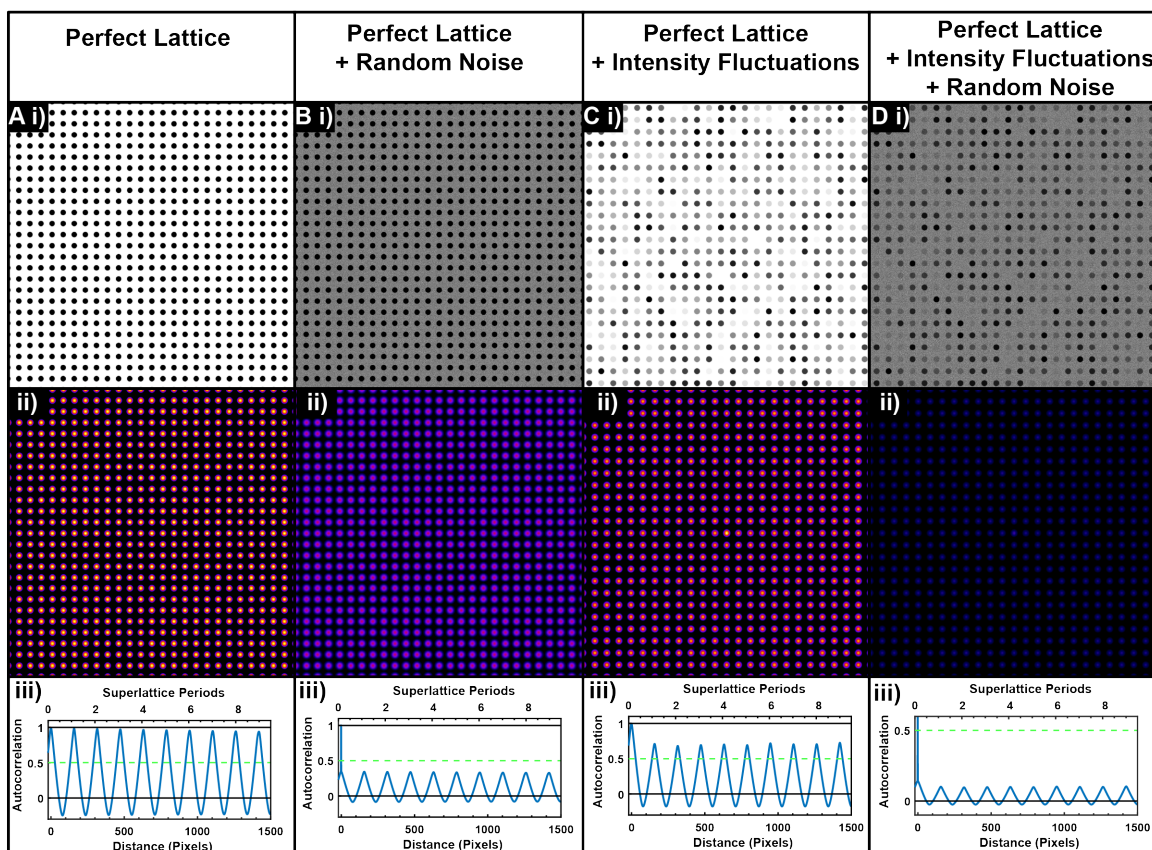


Figure A.4.5: (A) i) A perfect square lattice, ii) the 2-d autocorrelation function normalized to intensity of the zero-shift peak, and iii) a line cut of the autocorrelation along the Γ -X direction. In this case we observe a constant autocorrelation peak for all shifts that correspond to a lattice translation vector, since the images have perfect self-similarity. (B) A perfect square lattice with random noise introduced, in this case, the zero shift peak is large, but the autocorrelation amplitude is damped for all shifts since the random noise decreases the self similarity. Importantly, in the case of a perfect lattice, constant, but not unity, autocorrelation peaks are observed for all lattice translation vectors. (C) A perfect square lattice with random intensity fluctuations (to simulate diffraction contrast for perfectly on-axis particles). In this case we observe a damping of the autocorrelation peaks only after the first lattice shift, but then a constant autocorrelation amplitude. Finally in (D), we introduce particle intensity fluctuations and random noise, and in this case we see a instant decrease after the zero shift peak, and a second decrease after the first lattice vector shift to a constant. From this we choose to normalize our autocorrelation functions to a intensity of the peak of the first lattice translation, which isolates effects of random noise and particle intensity fluctuations. As such any decays in the autocorrelation amplitude are a result of nanocrystal position variations in the lattice.

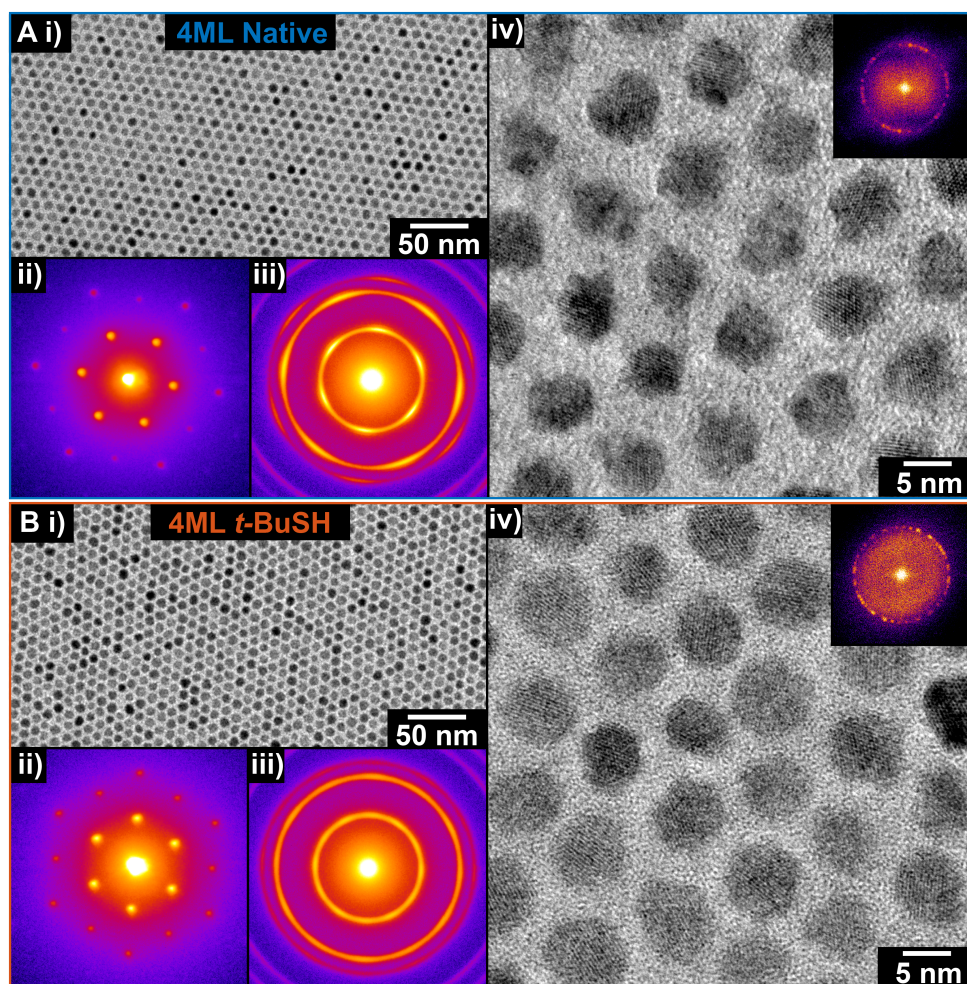


Figure A.4.6: TEM characterization of (A) assembled and (B) *t*-BuSH CdSe/CdS hexagons with 4 monolayers of shell. (i) Low magnification TEM, (ii) small angle SAED, (iii) wide angle SAED, and (iv) HRTEM with inset Fourier transform.

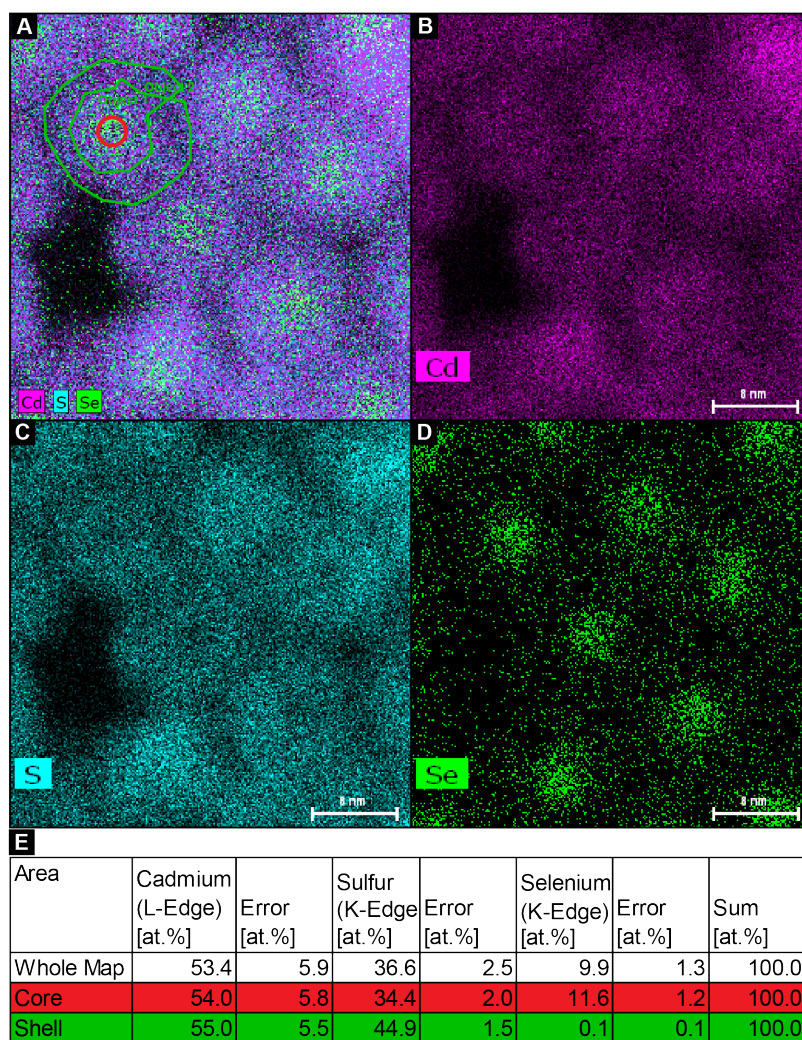


Figure A.4.7: High magnification STEM EDS maps of CdSe/CdS with 6 monolayers of SILAR grown CdS at the interface (A) HAADF, (B) cadmium, (C) sulfur, (D) and selenium maps. (E) Quantification results for the entire map, core, and shell region from and individual nanocrystal.

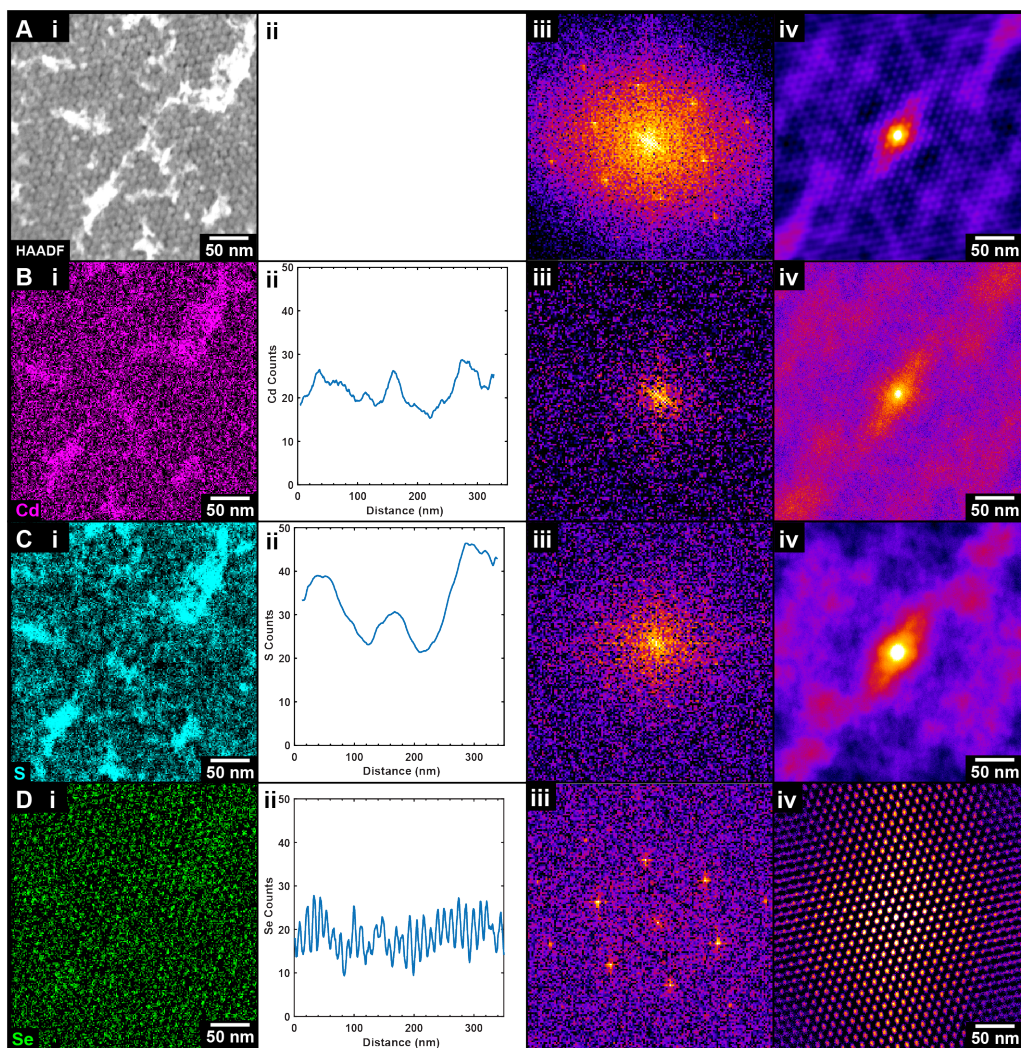


Figure A.4.8: Low magnification STEM EDS maps of CdSe/CdS with 6 monolayers of SILAR grown CdS at the interface (A) HAADF, (B) cadmium, (C) sulfur, (D) and selenium (i) maps, (ii) averaged line profiles, (iii) Fourier transforms and (iv) normalized autocorrelation functions for each respective elemental map. The $\Gamma - M$ profiles in figure 4.4 is extracted from D iv.

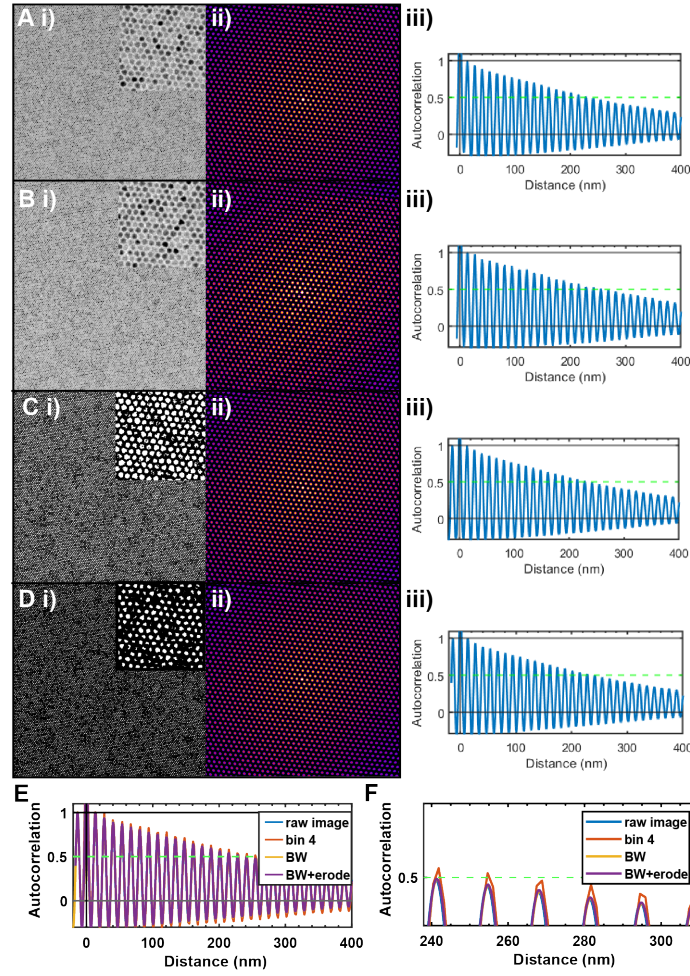


Figure A.4.9: Effect of pixel resolution and particle size on autocorrelation analysis (A) A raw TEM image of a superlattice, (B) The same image binned by 4, (C) A binarized image, (D) A binarized image after erosion (to simulate a smaller particle size) (i) images, (ii) 2-d autocorrelation function using the same contrast limits, (iii) linecuts along the Γ -M direction. In all cases, we measure an $\xi_{0.5}$ of 254 nm. (E) Autocorrelation for the 4 samples plotted on the same graph, and (F) a zoom in on the region where the amplitude crosses 0.5

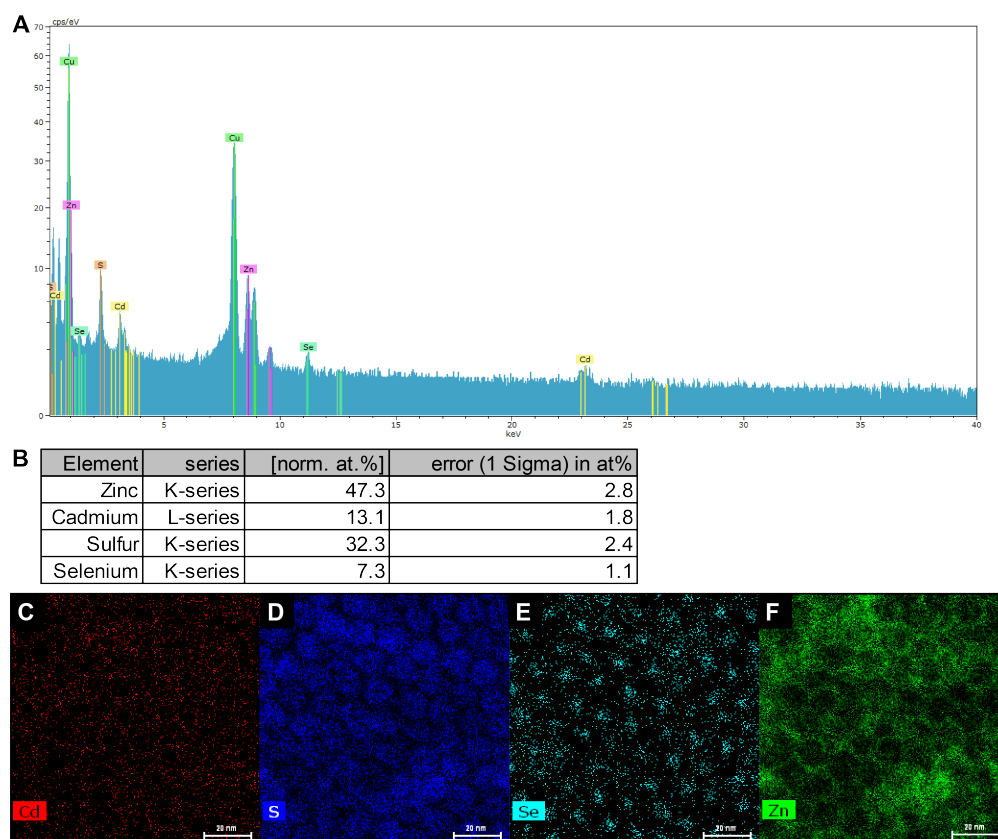


Figure A.4.10: (A) EDS spectrum for the sample (note:copper peak comes from the support grid and was not included in the quantification). (B) Results of a Cliff-Lorimer quantification of the elemental composition. (C) (D) (E) (F) elemental maps of Cd, S, Se, and Zn respectively.

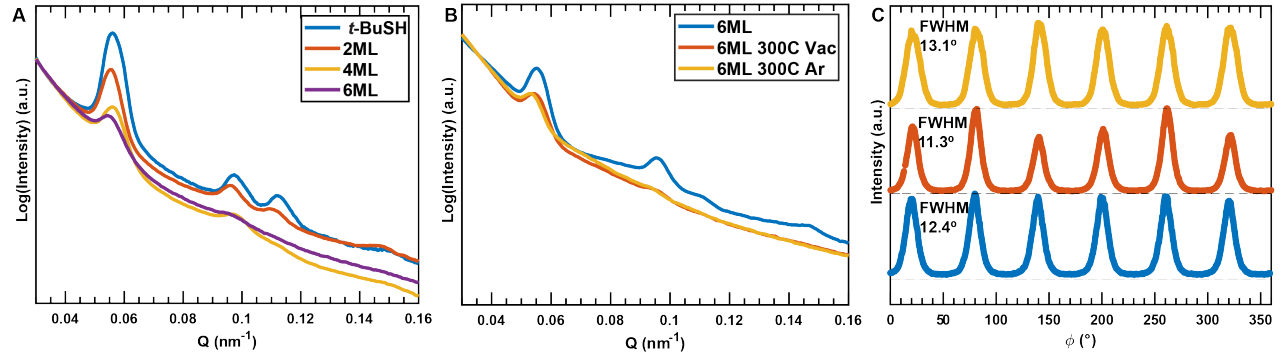


Figure A.4.11: SA-SAED of CdSe/CdS samples with different monolayers and after annealing. (A) Radially integrated small angle electron diffraction patterns for the t -BuSH treated sample and with 2, 4, and 6 monolayers of SILAR grown CdS at the interface. (B) Radially integrated small angle electron diffraction patterns for a sample with 6 monolayers of SILAR grown CdS after exposure to different annealing conditions. (C) Azimuthally integrated $\{1\bar{1}00\}$ peaks after exposure to the annealing conditions in (B).

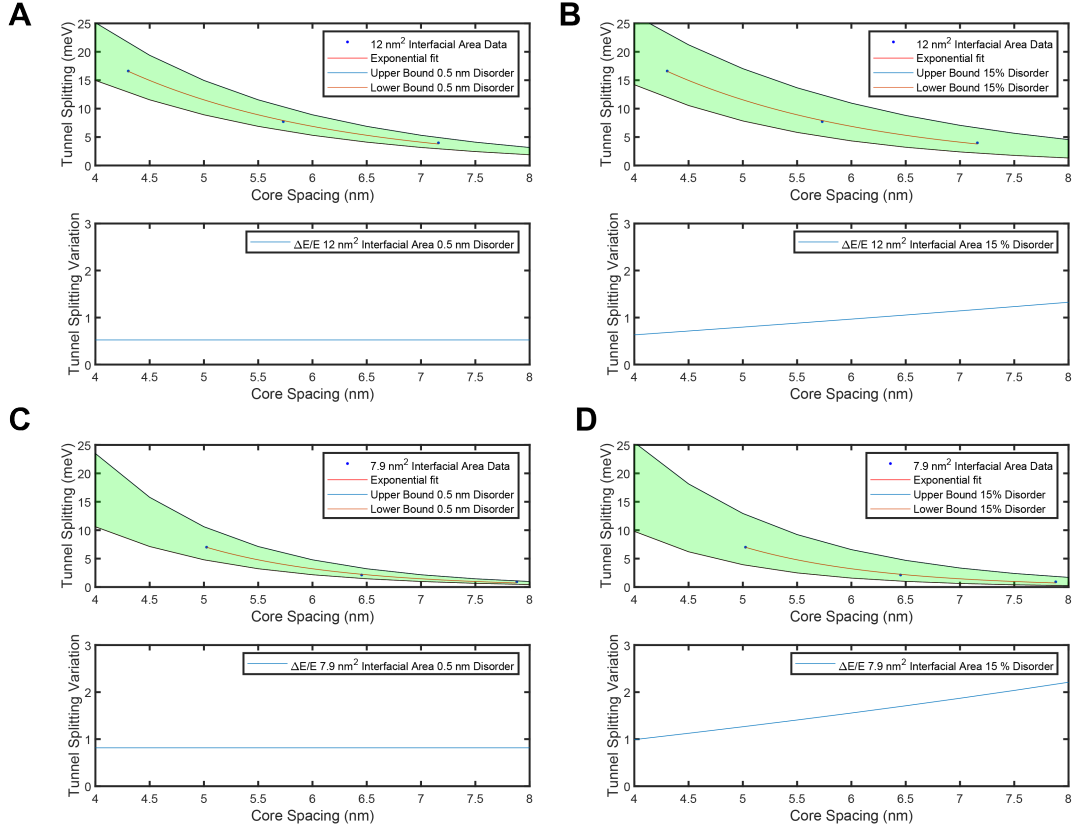


Figure A.4.12: Exponential decays were fit to the tunnel splitting for different core-core distances and interfacial areas. The variation in the coupling energy is calculated assuming a (A), (C) constant ± 0.5 nm (~ 1 atomic plane) variation for all core-core distances for 12 nm² interfacial and 7.9 nm² area. (B), (D) a $\pm 15\%$ distance variation for for a given core-core distance.

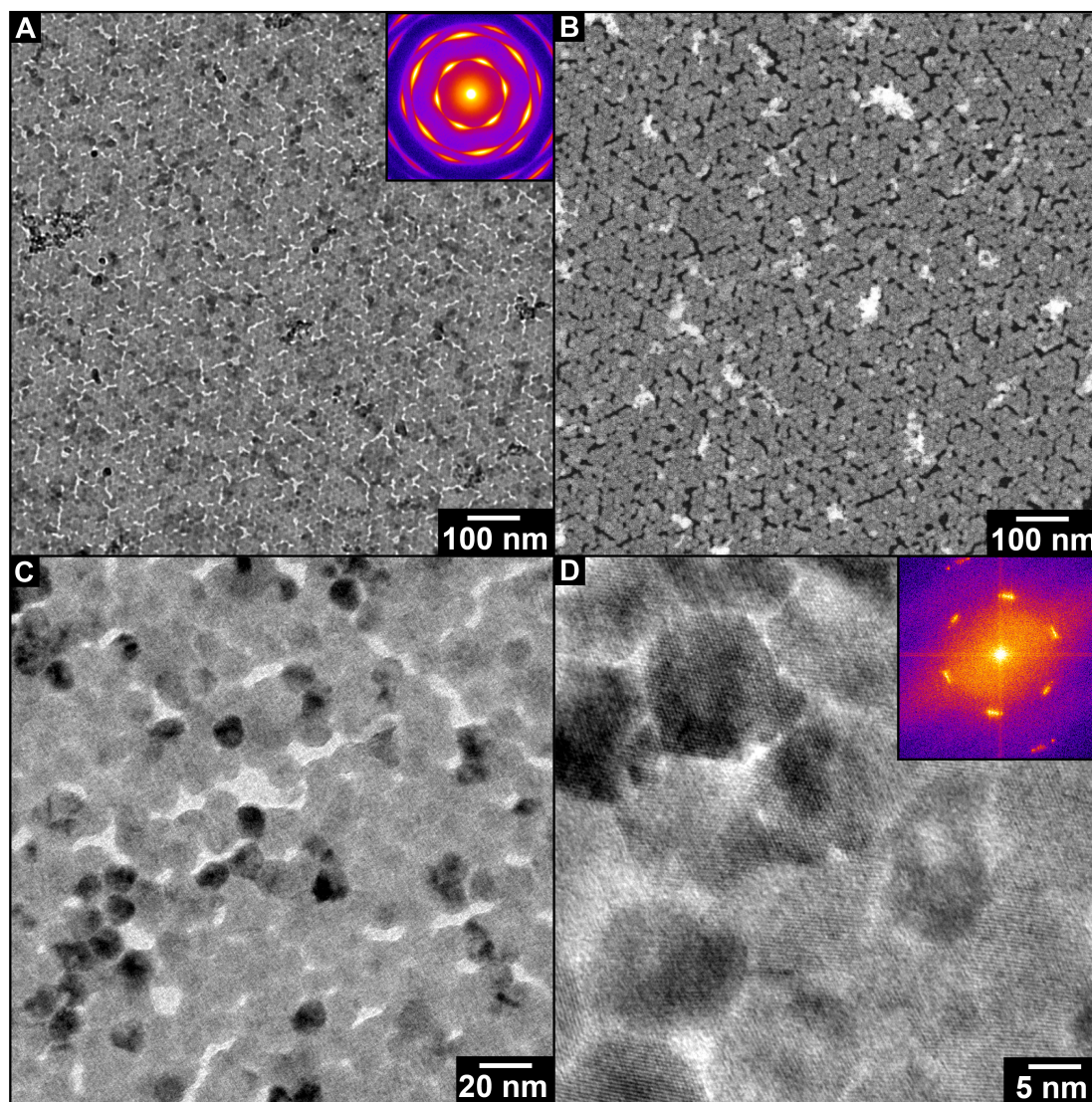


Figure A.4.13: Low magnification TEM and HHADF STEM images of a 300°C annealed CdSe/CdS sample with 6 monolayers of SILAR grown CdS at the interface. Low magnification (A) TEM with inset wide angle electron diffraction pattern, and (B) HAADF STEM image. (C) intermediate magnification bright field TEM image, and (D) HRTEM image with inset Fourier transform.

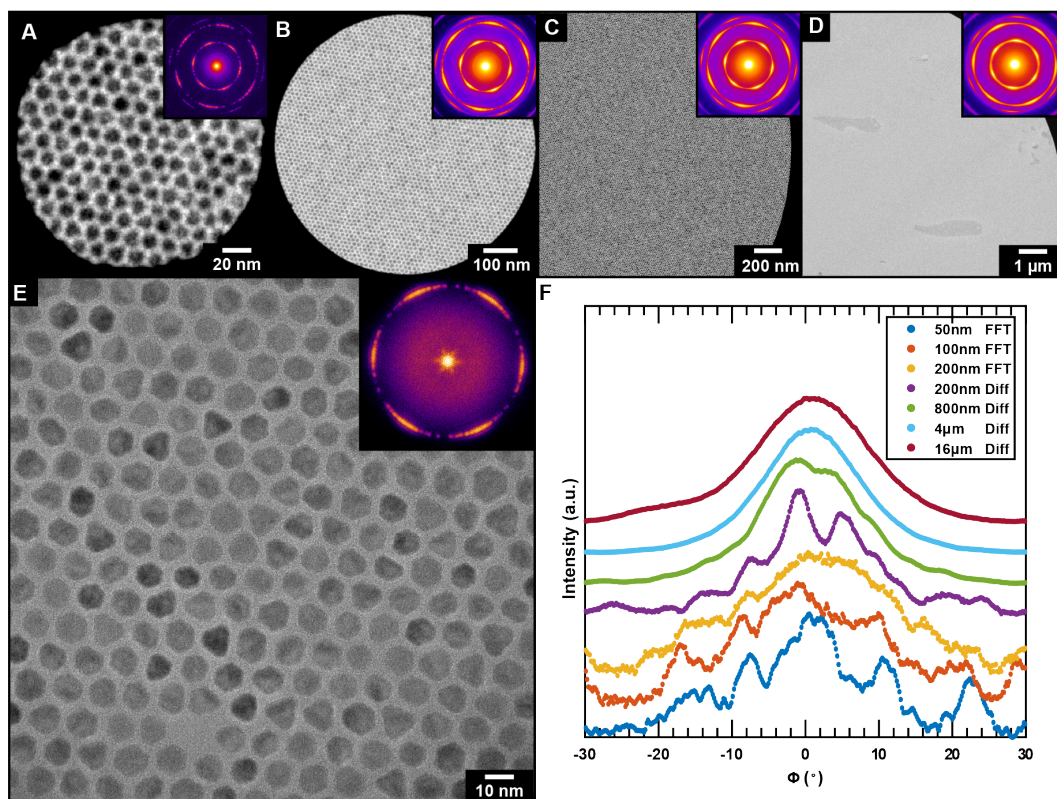


Figure A.4.14: TEM images of 6 monolayer CdSe/CdS nanocrystals through an SAED aperture and corresponding inset wide angle SAED for (A) 200 nm, (B) 200 nm, (C) 4 μm , (D) 16 μm diameter SAED aperture. (E) large field of view HRTEM image of 6 monolayer CdSe/CdS nanocrystals with inset Fourier transform from the full field of view. (F) Width of the $[1\bar{1}00]$ peak for various different areas *via* SAED and Fourier transforms of different area HRTEM images.

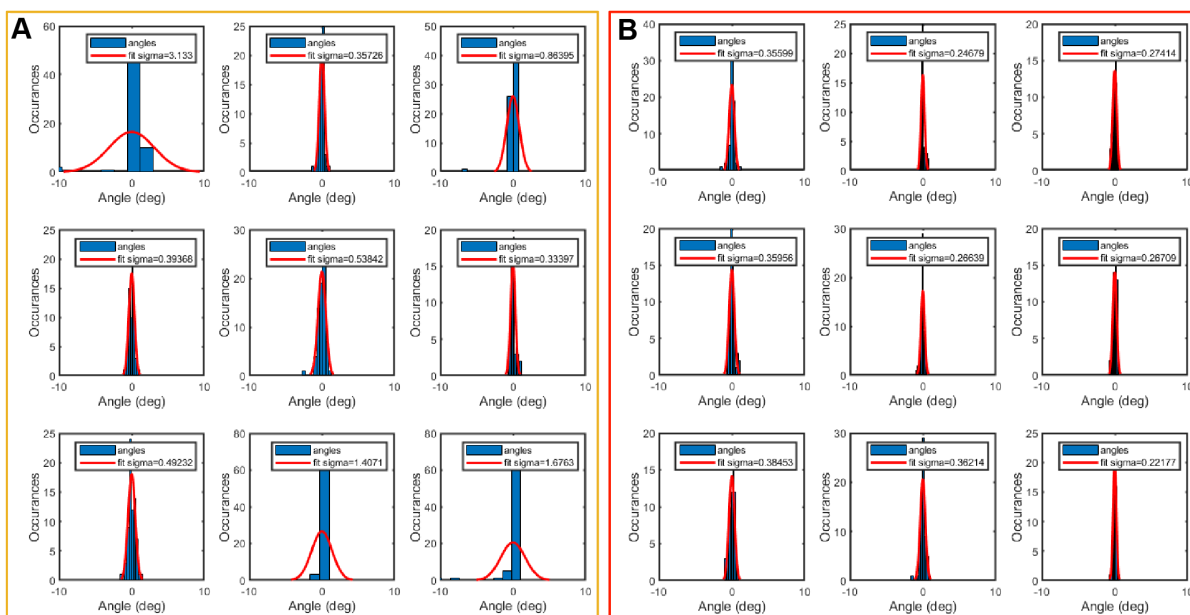


Figure A.4.15: Analysis of the standard deviations of angles between nearest neighbor nanocrystals within the same domain for (A) infilled with 6 monolayers of SILAR grown CdS and (B) after annealing at 300°C for 20 min.

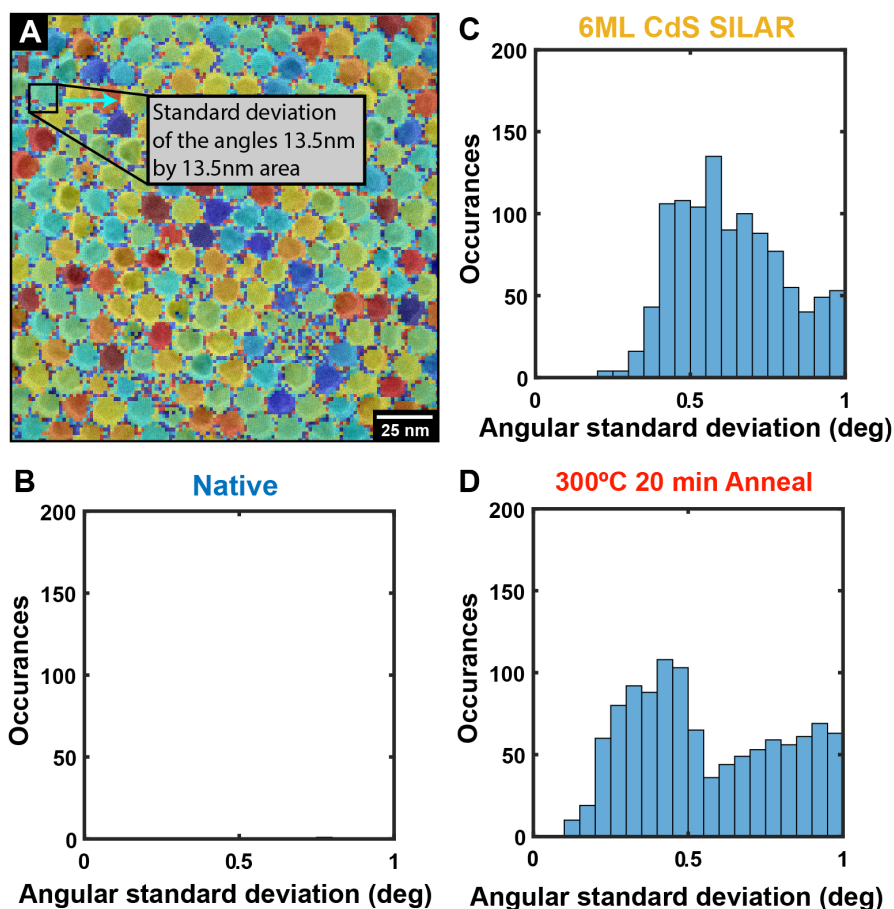


Figure A.4.16: (A) the angle map of a native assembled sample (same as Figure 4.7A) with the area where the local standard deviation of angles was calculated for a 13.5 nm by 13.5 nm area to look at the coherence of angles across nearest neighbors. (B) Histogram of the angular standard deviation for the native assembled sample. (C) the 6 monolayer of SILAR grown CdS sample and (D) after annealing the sample at 300°C for 20 min. we focus on the region of the histogram for 1 degree of deviation which is the areas within the same domain. Unsurprisingly, we observe no cases of $\approx 1^\circ$ deviation for the native sample (B) since there are no nearest neighbor angular correlations. Comparing the attached (C) and annealed sample (D), we observe that there are considerably more areas with ≈ 0.5 degree deviation, indicating better angular coherence within domains.

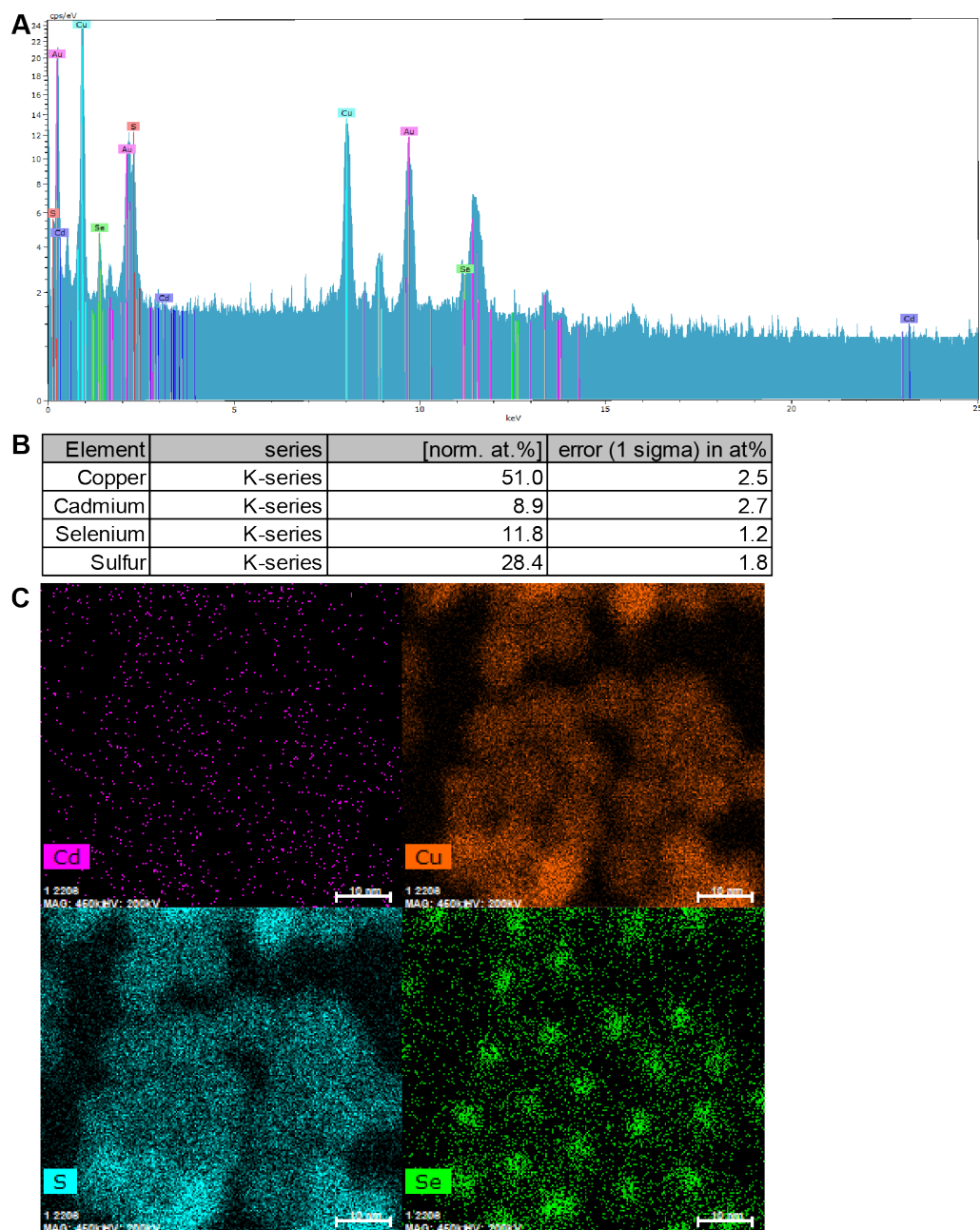


Figure A.4.17: (A) EDS spectrum from a $\text{Cu}_{2-x}\text{Se}/\text{Cu}_{2-x}\text{S}$ superlattice (B) results of a Cliff-Lorimer quantification of the elemental composition. Note: gold is present due to the TEM grid support and was not included in the quantification results. (C) Corresponding elemental maps for cadmium, copper, sulfur and selenium

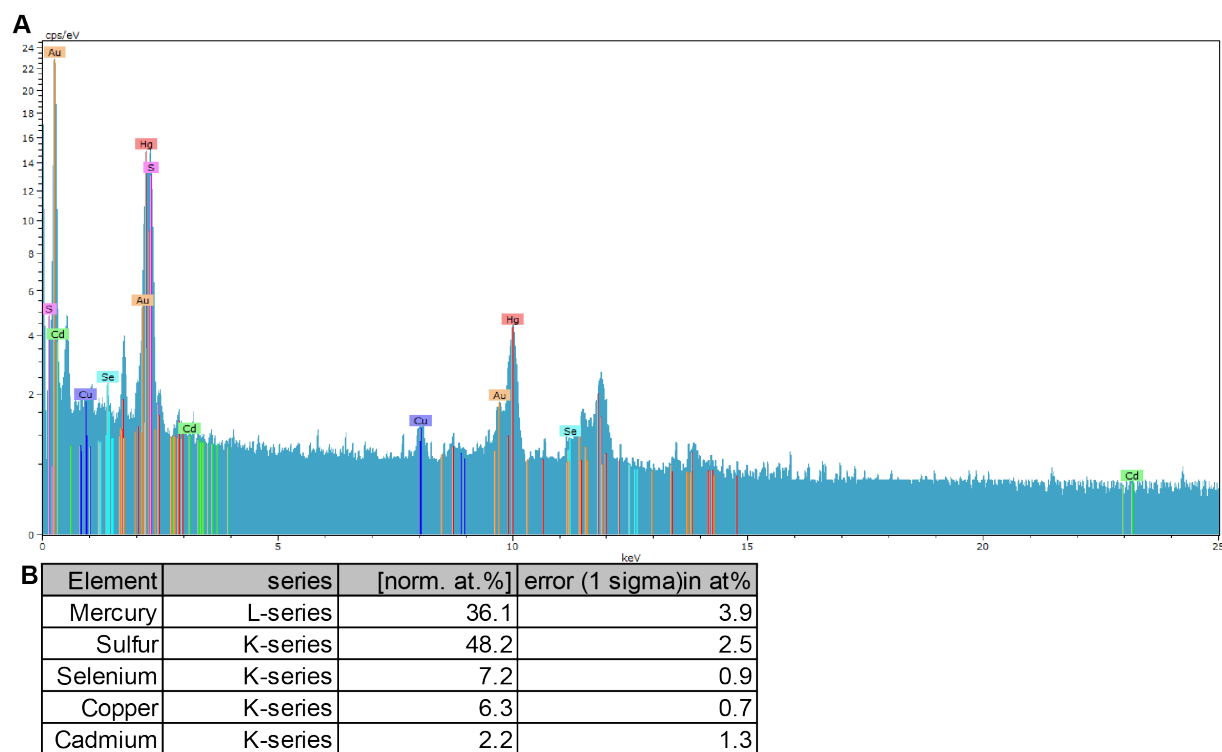


Figure A.4.18: (A) EDS spectrum from the HgSe/HgS superlattice shown in figure 4.9. (B) Results of a Cliff-Lorimer quantification of the elemental composition. Note: gold is present due to the TEM grid support and was not included in the quantification results

A.5 Chapter 5 Supplementary Figures

Appendix B

Supplementary Multimedia

B.1 Chapter 1

B.2 Chapter 2

Videos are hosted on the ACS website at DOI:10.1021/acsnano.8b00638.

Movie B.2.1: HRTEM movie of $\{100\}$ imperfectly attached PbTe nanocrystals shown in Figure 2.3. Available at DOI:10.1021/acsnano.8b00638. nn8b00638_si_001.zip, VideoS1

Movie B.2.2: HRTEM movie of $\{110\}$ imperfectly attached PbTe nanocrystals shown in Figure 2.4. Available at DOI:10.1021/acsnano.8b00638. nn8b00638_si_001.zip, VideoS2

Movie B.2.3: HRTEM movie and bandpass filtered HRTEM movie of $\{100\}$ imperfectly attached PbTe nanocrystals used to get removal time for Figure 2.7. Available at DOI:10.1021/acsnano.8b00638. nn8b00638_si_001.zip, VideoS3

Movie B.2.4: HRTEM movie and bandpass filtered HRTEM movie of $\{110\}$ imperfectly attached PbTe nanocrystals used to get removal time for Figure 2.7. Available at DOI:10.1021/acsnano.8b00638. nn8b00638_si_001.zip, VideoS4

Movie B.2.5: HRTEM movie and bandpass filtered HRTEM movie of $\{100\}$ imperfectly attached PbTe nanocrystals used to get removal time for Figure 2.7. Available at DOI:10.1021/acsnano.8b00638.nn8b00638_si_001.zip,VideoS5

B.3 Chapter 3

Videos are hosted on the ACS website at DOI:10.1021/acsnano.9b03052.

Movie B.3.1: HRTEM movie of imperfectly attached $\{1\bar{1}00\}$ terminated CdSe NCs with a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation at the interface. Available at DOI: 10.1021/acsnano.9b03052,nn9b03052_si_002.avi

Movie B.3.2: HRTEM movie of imperfectly attached $\{11\bar{2}0\}$ terminated CdSe NCs with a PSF across the entire interface. Available at DOI: 10.1021/acsnano.9b03052,nn9b03052_si_003.avi

Movie B.3.3: HRTEM movie of imperfectly attached $\{11\bar{2}0\}$ terminated CdSe NCs with a PSF across part of the interface which is terminated with a partial dislocation. Available at DOI:10.1021/acsnano.9b03052,nn9b03052_si_004.avi

Movie B.3.4: HRTEM movie of imperfectly attached $\{11\bar{2}0\}$ terminated CdSe NCs with a $b = \frac{a}{3}[2\bar{1}\bar{1}0]$ edge dislocation with a $\perp$ glide plane for removal. Available at DOI:10.1021/acsnano.9b03052,nn9b03052_si_005.avi

Movie B.3.5: HRTEM movie of imperfectly attached $\{11\bar{2}0\}$ terminated CdSe NCs with a $b = \frac{a}{3}[11\bar{2}0]$ edge dislocation with a $\parallel$ glide plane for removal. Available at DOI:10.1021/acsnano.9b03052,nn9b03052_si_006.avi

Movie B.3.6: HRTEM movie of imperfectly attached $\{11\bar{2}0\}$ terminated CdSe NCs with two edge dislocations. Available at DOI:10.1021/acsnano.9b03052,nn9b03052_si_007.avi

Movie B.3.7: HRTEM movie of imperfectly attached $\{1\bar{1}00\}$ terminated CdSe NCs with two edge dislocations. Available at DOI:10.1021/acsnano.9b03052,nn9b03052_si_008.avi

B.4 Chapter 4

B.5 Chapter 5