EXPLORING CONDENSED PHASES IN ENGINEERED SEMICONDUCTING NANOCRYSTALS

BY

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DISSERTATION

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ABSTRACT
The Jain lab employs a topotactic method called cation exchange to produce semiconductor nanocrystals (NCs) in novel morphologies, compositions, and crystallographic phases. My dissertation research focuses on the understanding of the physical properties and phase transitions of these new nanomaterials prepared by cation exchange. In Chapter 1, I describe the countless possibilities of the exploration of physicochemical properties and applications of molecularly precise semiconductor nanoclusters, a class of materials that we were able to expand with the help of cation exchange. In Chapter 2, I discuss how ultrasmall copper selenide (Cu$_{2-x}$Se) NCs prepared by cation exchange of cadmium selenide NCs exhibit a disordered cationic sub-lattice under ambient conditions. This behavior is quite unlike larger NCs or the bulk, suggesting an interesting effect of crystallite size and strain on the stability of super-ionic phases. In Chapter 3, I describe my investigations of Li-doping of Cu$_{2-x}$Se NCs and how this doping influences the crystal structure and consequently the phase transition behavior. A close-to-ambient-temperature transition from the non-superionic to superionic phase transition also appears to be present in the final lithium selenide (Li$_2$Se) NCs formed from this doping reaction. In Chapter 4, I explain on the basis of optical spectra measurements and density functional theory (DFT) calculations how HgSe NCs, prepared using cation exchange in a novel wurtzite phase, differ from their natural zinc-blende counterparts. The latter is a semi-metal, whereas the newer phase obtained from cation exchange is found to have an inverted band structure along with a finite band-gap, making it a potential 3D topological insulator. In Chapter 5, I extend the understanding of ion exchange reactions to an “anion exchange” process in zinc oxide (ZnO) NCs. As a detour from the central thesis of my dissertation, in Chapter 6, I present my work on electrodynamic simulations of optical properties
of nanostructures, which helped demonstrate that localized surface plasmons can be imaged in real space with nanometer resolution using a scanning tunneling microscope (STM) coupled to a laser.
Dedicated to my parents
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CHAPTER 1: UNIQUE PHYSICAL CHEMISTRY OF SEMICONDUCTING NANOCLUSTERS AND NANOPARTICLES

1 Reproduced with permission from Banerjee P., Jain P. K., Perspectives on the Physical Chemistry of Semiconducting Molecules-Opportunities and Challenges, to be submitted.

1.1 INTRODUCTION:

Science and technology at the nanoscale (<10^{-9} m) has played a major role in several new technologies such as, nanomedical diagnosis techniques, nanonvironmental monitoring, nanoelectronics devices, nanofabrication techniques, nanocomputing using nanotubes, etc. in the last two decades. A common underlying way in which the nanomaterials behave differently from their bulk counterparts is that most physicochemical properties do not scale linearly with size. Rather, there is a complex interplay among various factors such as the fraction of surface atoms, specific surface energy, contraction of crystal lattice parameter, coordination number, interfacial tension, chemical environment, and ligand effects. On reducing the size of semiconducting materials to the nanoscale, several properties (optical, electronic, conductivity, melting point) first undergo a drastic change, followed by the emergence of unique properties. Tunability in size, shape, surface, composition, temperature and environment all aid in the modification of the opto-electronic properties. In nanocrystals (NCs) for example, thermodynamic properties can be greatly modified from the bulk, leading to phenomena such as the depression of melting point, $T_m$, with decreasing size or the development of negative heat capacities.
1.2 NOVELTY OF SEMICONDUCTING NCs:

Containing anywhere from two-atom particles to organizations of $3 \times 10^7$ atoms, varying from 1 to 10 nm, NCs are instrumental in studying the emergence and onset of individual to collective behavior in bulk solids. Quantum dots (QDs) are a sub-class of semiconducting nanocrystal materials (consisting of elements from either of Group II-VI, III-V, I-III-VI$_2$, IV-VI, or IV) that exhibit quantum size effects in their optical spectra$^{11}$. These are thought to be the ideal semiconducting cluster. Semiconductor crystals consist of the Mott-Wannier$^{20}$ exciton, the Bohr diameter of which dictates if a nanocluster of comparable size will be quantum confined. The size effects prevalent in NCs arising from quantum confinement has given rise to many interesting size-dependent optical properties. In addition, a large percentage of the atoms in these NCs are present on the surface, increasing the reactivity of the particle. These surfaces can act as electron (hole) traps due to their imperfect nature, leading to non-linear optical effects. Field intensity enhancement$^{10}$ at the boundary of these NCs due to refractive index mismatch with the surroundings is size-dependent and can be explained by the Lorenz-Mie scattering theory$^{21}$. For a sharp size-distribution as displayed in NCs, these effects of a local field on sharp exciton resonance and its possible effects in optical switching application are interesting areas of research.

A well-known direct effect of quantum confinement in semiconducting nanomaterials is the discretization of energy levels and increase in the band-gap; primarily absorption and emission energies (Fig 1.1A and B). Due to the localization of one or both charge carriers$^{10}$, the exciton energy becomes dependent on shape and size of the nanocrystal, leading to the discretization of electronic transitions, and the addition of quantum confinement effects to the mix of phenomenon, which may influence thermodynamics and therefore phase stability and phase transitions. This also leads to the optical and physico-chemical properties tunable by the shape and size (Fig 1.1D),
leading to varied applications in diverse fields. This peculiar dependence on physical shape (Fig 1.1C) leads to emergence of properties in a new regime.

The size and shape\textsuperscript{22} of the quantum dots, which are protected with an outer coating layer of organic molecules called surfactants, can be easily controlled by the synthesis parameters (temperature, ratio of the reactants, choice of ligands) in the case of colloidal bottom-up synthesis\textsuperscript{23}. How these different factors influence the exact nature (kinetics and dynamics) and order of phase transitions on the nanoscale constitutes an open question. As an example, the effect of ligands on the morphology, electronic structure of the smallest synthesized CdSe QD, Cd\textsubscript{33}Se\textsubscript{33} cluster\textsuperscript{24} is displayed in Fig 1.2. It has already been demonstrated that in nanoscale systems, a transition displaying the characteristics of a continuous second order phase transition can maintain a discontinuous character at the microscopic level\textsuperscript{25}. Additionally, with size reduction, phase transitions tend to be less sharp and order-disorder transitions are hard to classify as first order or second order transitions\textsuperscript{13}. 
**Figure 1.1:** Illustration of the (A) Density of states (DOS) in metal and semiconducting NCs, (B) DOS in one band of a semiconductor as a function of dimension. (C) Comparison of a colloidal quantum dot and an island-like, self-assembled quantum dot epitaxially deposited on a crystalline substrate (D) Size-dependent PL colors of semiconductor QDs. Electronic structure of QDs correlated with the QD radius and resulting ‘blue shift’ due to quantum confinement as the QD size decreases. Panels (A), and (B) are reprinted with permission from ref 16. Copyright 1996 AAAS\(^{16}\). Panel (C) is reprinted with permission from ref 14. Copyright 2010 ACS Accounts of Chemical Research\(^{14}\). Panel (D) is reprinted with permission from ref 25. Copyright 2012 RSC Journal of Materials Chemistry\(^{25}\).
Figure 1.2: Effect of surface ligands on the CdSe$_{33}$ cluster$^{24}$ (A) Molecular orbitals representing typical states localized on the QD, localized on ligands, and delocalized over the QD and ligands (hybridized MOs), and their corresponding angle-averaged electronic density distributions (B) Plots of HOMO and LUMO for the bare and ligated QDs. For all QDs, both HOMO and LUMO are surface states: HOMO is mostly distributed over Se atoms on the (0001j) facet, while LUMO is spread over Cd and Se atoms on the (0001) facet. For full capping with 21 ligands, when all surface Cd atoms are passivated, the LUMO is significantly changed from the LUMO of the bare and partially passivated QDs, showing that ligands do affect surface states. Fig 2 is reprinted with permission from ref 24. Copyright 2009, JACS, ACS.
1.3 FUNDAMENTAL PROPERTIES OF QUANTUM DOTS AND MAGIC-SIZE SEMICONDUCTING NCs:

The large quantity of surface atoms in NCs make them especially sensitive to changes in the surrounding medium, thus resulting in opto-electronic properties that are size and shape dependent\textsuperscript{26–28}. Exact characterization, manipulation and optimization of the nanoscale composition, size, and shape is necessary for wide-spread technological implementation. II-VI compounds have been at the forefront of progress in semiconducting NCs. CdSe NCs\textsuperscript{29} have generated an intense research interest due to their easily tunable optoelectronic properties. Alongside experimental methods\textsuperscript{30,31} for preparation of a wide variety of NCs with different cage configurations, computational studies\textsuperscript{32,33–36} have been crucial for elucidating design principles of these solids. A simple tuning of temperature is often sufficient to give rise to NCs with variable sizes (Fig 1.3B). Semiconductor NCs have gained in popularity after the pioneering discovery of magic sized (CdSe)\textsubscript{n} NCs with \( n = 13, 33 \) and 34 by Kasuya et al\textsuperscript{30}. Magic sized NCs were identified based on their mass spectral intensity among a range of other cluster species. Several new semiconductor NCs have been reported with precise molecular formula. Mass spectrometry is often used in the exact quantitative identification such atomically precise NCs (Fig 1.3C). Owen et al\textsuperscript{37} have speculated the single crystal structures of three NCs (Cd\textsubscript{35}Se\textsubscript{20}(X)\textsubscript{30}(L)\textsubscript{30}, Cd\textsubscript{56}Se\textsubscript{35}(X)\textsubscript{42}(L)\textsubscript{42}, and Cd\textsubscript{84}Se\textsubscript{56}(X)\textsubscript{56}(L)\textsubscript{56}; \([X = \text{O}_2\text{CPh, L = H}_2\text{N-C}_4\text{H}_9]\), respectively. The preparation of (CdSe)\textsubscript{n} NCs using reverse micelles method by Kasuya et al\textsuperscript{30}, and subsequent demonstration of new forms of unique crystal structures make it a prototype for research on general cluster systems such as fullerenes\textsuperscript{49}. Demonstration of mass-selected (CdSe)\textsubscript{33} and (CdSe)\textsubscript{34} highly-stable NCs \textsuperscript{30} make it possible to attribute several physical and optoelectronic
characteristics to their cage structures (Fig 1.3A). These specific sizes are reproducible and well-characterized from their excitonic positions, with estimated diameters of approximately 1.5 nm.

**Figure 1.3:** (A) Theoretical models of the atomic structure of a (CdSe)₃₄ cluster; (B) Simplified model of CdSe MSQDs synthesized at different temperatures; (C) TOF-MS spectra of positive ions for CdSe. (D) PEG₆-thiolate coated CdSe NCs in different solvents, (E) absorption and HRTEM image of 1.6 nm NCs to show the effect of solvent in which these NCs are dispersed in. Panel (A) is reprinted with permission from ref 29. Copyright 2004, Nature publishing group. Panel (B) is reprinted with permission from ref. 38. Copyright 2014, ACS Nano Letters. Panel (C) is reprinted with permission from ref 30. Copyright 2004, Nature publishing group. Panels (D) and (E) are reprinted with permission from ref 39. Copyright 2014, RSC Adv.

Some of the NCs with specific sizes are more stable, earning the name “**magic-sized**” NCs, and containing numbers of atoms directly corresponding to the magic numbers. Magic-size cysteine-capped CdSe with diameter of 1.57 nm has been reported in aqueous solution at room-temperature. The optical properties of these NCs also depend on ligand size and distribution,
solvents (Fig 1.3D, E). Simulations carried out on the bare-NCs to understand the effect of surface ligands have pointed out that the Cd-Se bond distance is larger at the core of the quantum dot and shorter at the surface when compared to bulk values\textsuperscript{51}. Presence of ligands allows the density of states to display a clear HOMO-LUMO gap, alongside strong surface reconstructions for smaller NCs.

Although a lot of importance has been historically assigned to probing optical properties of NCs to detect VB to CB transitions, tunneling transport is often utilized to understand the electronic properties in conjunction. In NCs with strong confinements, the single-electron tunneling effects become commensurate to the size effects, when charging energy of the dot is comparable to electron level separation\textsuperscript{40}. To navigate the difficult task of connecting QDs to electrodes, scanning probe measurements are a popular method. Scanning tunneling microscopes (STM) have been utilized to measure the tunneling transport microscopy on a single NC\textsuperscript{41,42}.

1.4 PHYSICAL MODELS:

Electronic properties of semiconducting NCs\textsuperscript{43} are non-trivial to calculate since the number of atoms are greater than molecules where standard \textit{ab initio} methods apply, but small enough that lattice periodicities are non-applicable. Physical models are useful to ascertain the molecular precision in NCs arising from precisely controlled number of atoms with size dependent properties; with scope for theoretical verification before conducting experiments. Detailed insightful descriptions of the effect of the optical bandgap, oscillator strength, surface-trapped electron-hole pair and the dielectric confinement on the electronic and photophysical properties of clusters are given by Wang and Herron\textsuperscript{21}, Brus\textsuperscript{44–46}, Alivisatos\textsuperscript{16,46} and others\textsuperscript{47}. 


Different sizes of CdSe NCs have been studied to understand the correlation of band-gaps and hence optical properties with size and cage structure. A series of passivated CdSe NCs were analyzed by ab-initio methods (TDDFFT) ranging from 10 to 82 atoms to analyze of charge density states to compare with absorption spectra stemming from Mie theory (Fig 1.4A, B) Studies depicting the role played by ligands on the binding energy minimal (Fig 1.4C, D) CdSe cluster Cd$_2$Se$_2$ is useful for designing these NCs for targeted applications. DFT calculations for (CdSe)$_n$ (n=4-60) analyzing the electronic, optical, cohesive and vibrational properties are sometimes inconclusive due to large deviations of experimental data from predicted theory, hence open questions remain in this area of research.

**Figure 1.4:** (A) Lowest energy structures of (CdSe)$_n$ (n=4,6,7,8,9,10,12,15,20,25,33,45 and 60). (B) Unrelaxed and relaxed wurtzite (CdSe)$_n$ (n=13, 19 and 33), (C) Binding energy vs size, (D) Binding energy of NCs (CdSe)$_n$ (n=1-10, 13, 16 and 19) in gas, toluene and water. Panel (A) is reprinted with permission from ref 48. Copyright 2014, RSC Adv. Panel (B) is reprinted with permission from ref 32, Copyright 2011, ACS, JPCC. Panel (C) is reprinted with permission from ref 48. Copyright 2014, RSC Adv. Panel (D) is reprinted with permission from ref 49. Copyright 2015, RSC PCCP.
1.5 MOLECULAR NATURE OF CLUSTERS AND MOLECULAR CONTROL:

Clusters are often dubbed as artificial atoms because of their molecular nature, in that these are unique localized entities. These NCs exhibit degenerate level structure and discrete spectra, and lasing\textsuperscript{50}. These materials form the basis of a new artificial periodic table. The NCs and their derivatives, such as materials formed through their assembly (self-assembled materials: SAM) offer unforeseen opportunities in producing new classes of materials with custom properties. Due to their high photo-stability and size-tunable emission spectra semiconducting NCs have led to the production of bright, sensitive, biocompatible fluorophores used in cellular imaging, labeling and study of dynamic processes \textsuperscript{51-53}. Fullerenes have been applied as photovoltaics, due to the advantage their high electron affinity offers as promising self-assembled materials \textsuperscript{54-58}. Due to the high transport properties of these materials, thin film organic solar cells can be prepared from fullerenes. The small NCs corresponding to “magic numbers \textsuperscript{59,60}” have been observed to mimic the properties of rare gases, alkaline earth elements etc. Discovery of new NCs has paved the way to expanding the periodic table with concepts such as “superatoms \textsuperscript{61}”.

Reliable synthetic methods producing NCs in nearly monodisperse form in different shapes and sizes\textsuperscript{22,62,63} have provided a strong foundation for the study and utilization of these NCs in different applications. In addition to the variation of surface energy through the use of ligands, non-stoichiometric NCs\textsuperscript{64} may also be prepared by controlling the synthetic parameters such as the coordination chemistry. Several theories are proposed implying the inclusion of correlation effects in excitation spectra in these artificial atoms, including quantum\textsuperscript{65} and diffusion Monte Carlo\textsuperscript{66} methods and equation-of-motion coupled cluster theory\textsuperscript{67}.

NCs are often used as single molecule or in coupled form\textsuperscript{68} and manipulated through static or dynamic electric fields. Often, molecules of a different species may be attached\textsuperscript{69} to the NC surface
to induce significant electric fields sufficient to alter the electronic and optoelectronic properties of the NC. Interparticle spacings play an important role in charge transport in solids made from colloidal NC assembly. Arrangement of the different facets of the NCs brought about by the molecular ligands play an important role in the charge transport. More recently, the use of femto- and nanosecond broad-band transient absorption (TA) spectroscopy to control the on/off ultrafast electron transfer (ET) at QD interfaces has been reported. Moreover, low temperature measurements offer increased sensitivity to external stimuli.

1.6 EXPLORATION OF NEW CLASSES OF MATERIALS WITH UNIQUE FUNCTIONALITIES:

While molecularly precise II-VI semiconductor chalcogenide NCs with tunable size and optoelectronic properties can be easily prepared through hot-injection synthesis or other wet-preparation techniques, we are limited in scope of the classes of materials that can be accessed in cluster form. However, the use of ion exchange, specifically cation exchange in larger particles has been performed over centuries to meet expectations based on quality improvement or new functionalities. Some remarkable applications that are still relevant to date are base exchange in soils with zeolites as carriers, used in 1876 by Lemberg which was industrialized in the early 20th century in Germany. Partial or complete substitution of metal ions in the starting materials with a different species is the defining feature of cation exchange. Employment of this technique to derive new morphologies and phases in NCs is a relatively recent development. More recently, this technique has been applied to MOFs to exchange metal ions at the SBUs (secondary building units), and in semiconducting NCs (Fig 1.5).

The cation exchange pathway in each material is expected to depend on various factors such as relative orientation and density of ions, ligands passivating the surface etc. which may collectively
determine the condition and outcome of the cation exchange reaction. However, one sharply demarcating feature of cation exchange in larger aggregates such as soil where cation exchange (diadochy \(^76\)) capacity defines the extent of the reaction occurring over a timescale of years; cation exchange in NCs can take place over a period of seconds \(^77,78\).

![Diagram of cation exchange reaction](image)

**Figure 1.5:** (A) Depicts cation exchange from 4 nm CdSe to Cu\(_2\)Se NCs, \(^{121}\), bottom figure (A) Cation exchange reaction as monitored by UV-Vis spectroscopy where the well-defined exciton peak of CdSe is replaced by the band-edge of Cu\(_2\)Se. (B) HAADF-STEM images showing the preservation of morphology and size in different sizes of NCs after cation exchange reaction and (C) Histogram proving the size remains unaffected. Panel (A) is reprinted with permission from ref 78, Copyright 2013, Nature publishing group\(^{78}\). Panels (B), (C) and (D) are reprinted with permission from ref 77. Copyright 2017, Nature publishing group\(^{77}\).

Many different compounds across the periodic table may be synthesized using a one-step room-temperature fast post-synthetic cation exchange procedure, including II-VI as demonstrated in Fig 1.6, III-V, and IV-VI compounds. More interestingly, one can go beyond a single step and expand on synthesizing numerous compounds or complex mixture by employing this method the requisite number of times (Fig 1.6). This opens up a wide arena of opportunities where this method can be
utilized to design any nanocrystal or complex architecture for device applications, such as photovoltaic devices \(^7^9\), thermoelectric devices, battery materials, topological insulators etc. Extensive discussions on the mechanistic aspects of cation exchange are reported in the review article by Rivest \textit{et. al.} \(^8^0\), where guidelines are put forward to understand the process, and explanations are provided to elucidate the fast-kinetic timescales of these reactions in NCs. A wide variety of NCs have already been produced using this route, starting from magic-sized NCs (some shapes have been shown in Fig 6 to show that this process can be continued in multiple steps). \(^7^7,8^1\).

\textbf{Figure 1.6.} Cation exchange of CdSe NCs showing that the starting nanocrystal acts not only as a shape/morphology template but also a crystallographic template. All panels are reprinted with permission from ref 79. Copyright 2011, ACS Nano Letters\(^7^9\).

Of especial interest among semiconductor NCs are the chalcogenides. Copper chalcogenides for example have emerged as promising candidates for sustainable energy applications, such as
photovoltaics, switching and sensing due to environmental compatibility and low toxicity.\textsuperscript{82–88}

The unique structural and physical behavior at an ultrasmall size of the semiconductor copper selenide (Cu\textsubscript{2}Se) was probed by White and Banerjee \textsuperscript{77}. Ultrasmall Cu\textsubscript{2}Se NCs were prepared by solution-phase cation exchange of magic-sized CdSe NCs with Cu\textsuperscript{+}\textsuperscript{77}. The sub-stoichiometry, Cu\textsubscript{2-x}Se (0 ≤ x ≤ 0.25) in this material contributes hole carriers to the valence band, leading to the emergence of a localized surface plasmon resonance band (LSPR) in the near-infrared (NIR) region of the absorption spectrum.\textsuperscript{89} Fig 1.7C shows that with increasing oxidation levels, there is an increase in the peak energy $\omega_{sp}$ of the LSPR band with the increase in the free hole carrier concentration. The Cu\textsubscript{2}Se NCs synthesized here also show reversible tunability of the doping level and the LSPR.\textsuperscript{90,91} The ability to be self-doped, the NIR plasmonic nature, and active plasmonic tunability of the Cu\textsubscript{2}Se NCs can be particularly attractive for electro-optic switching. Such switching can be rapid given the ultrasmall size, which favors short nanometer-scale diffusion lengths for Cu\textsuperscript{+}. 
Figure 1.7: (A) The superstructural vacancy ordering in Cu$_2$Se NCs is depicted using HRTEM images of four representative NCs at each size: 2, 4 and 6 nm. Scale bars correspond to 5 nm. (B) Differential scanning calorimetry (DSC) thermograms for larger-size Cu$_2$Se NCs (heating and cooling) are compares to those for 2 nm Cu$_2$Se NCs. (C) The tunable LSPRs displayed by the Cu$_2$Se NCs is represented by the absorption band in the NIR region. Hole concentration is found to increase with increasing oxidation resulting in a blue-shift of the LSPR band, treatment of the oxidized NCs with the reducing agent cobaltocene results in the annihilation of the holes, characterized by a gradual red-shift and suppression of the LSPR band. Schematic of the chemical oxidation and reduction is explained via the band-diagram. (D) The compressive strain at ultrasmall size is depicted by the increase of the LO phonon mode frequency going from 6 nm to 2 nm NCs. All panels are reprinted with permission from ref 77. Copyright 2017, Nature publishing group.

Vacancy ordering below the order-disorder transition (ca. 400 K) temperature is another well-established hallmark of bulk Cu$_2$Se, which was studied in the NCs and the larger NCs using high-resolution transmission electron microscopy (HRTEM). The LT β non-superionic phase has
a defective anti-fluorite structure, wherein a fraction of the tetrahedral sites is vacant and the displaced Cu\(^+\) ions instead occupy trigonal sites. These tetrahedral vacancies as shown in Fig 1.7A in the 6 nm NCs stack every four Cu\(^+\) layers along the <111> crystallographic axis creating a super-structure with a periodicity of 6.7 Å between bright fringes, which is twice the typical lattice spacing along the <111> direction.\(^92\) As a result of vacancy ordering, the Se\(^2-\) sub-lattice is slightly distorted by few % with elongation along the stacking direction and contraction in the basal plane.\(^92\)

On the other hand, the 2 nm NCs displayed in Fig 1.7A show a complete lack of superstructure, quite unlike 6 nm NCs or bulk Cu\(_2\)Se at ambient temperature. The results may be explained by a simple size-dependent reduction in the order-disorder transition temperature T\(_c\) such that the transition temperature is below ambient for the 2 nm size and above ambient for the 6 nm case. From differential scanning calorimetry (DSC) measurements (Fig 1.7B), indeed, the (ensemble-averaged) order/disorder transition temperature T\(_c\) for the NCs was found to be below room temperature (10°C/-2°C heating/cooling), significantly depressed compared to the temperature of 413 K or 140°C reported for bulk Cu\(_2\)Se.\(^94\) To determine the residual strain in the Cu\(_2\)Se lattice, phonon scattering spectra (Fig 1.7D) were measured for NCs of all three sizes at room temperature. The A\(_1\) longitudinal optical (LO) phonon mode of Cu\(_2\)Se\(^95\) was detected in all three samples, but with a frequency \(\omega\) that increased with decreasing NC size. This mode hardening indicates the presence of a compressive strain in the NCs,\(^96\) which increases in magnitude with decreasing size. NC size tuning of phase transition temperatures is well known, but the influence of NC size and associated strain on ionic structure and transport is an open area of investigation. The findings provide insight into the role of vacancies, cation-anion co-ordination, and nature of bonding in the achievement of fast-ion conduction, which may lead to broader design principles\(^97\) beyond the specific Cu\(_2\)Se system studied here. For instance, high-pressure superionic phases have been
predicted in other materials such as ice. \textsuperscript{98} T-O-T- pathways are important in solid-state lithium ion conduction. \textsuperscript{97}

1.7 LONG-RANGE ORDERED SUPERLATTICES FROM NCs: CLUSTER-ASSEMBLED MATERIALS:

Ordered superstructures of NCs provide the opportunity to study behavior of materials that are inhomogeneous at the nanoscale, while paving the way for practical applications. Complex shapes such as branched NPs (octapods \textsuperscript{99–101}) make it hard for precise predictions based on the structures of the components alone. Magic-sized NCs containing certain characteristic number of atoms that are stable can be considered as superatoms with their unique properties. Investigation of bonding in these superatoms have revealed that they mimic properties characteristic of that of rare gases\textsuperscript{61}, alkaline rare earth elements\textsuperscript{102} etc., which can be used as artificial atoms in applications involving these classes of materials. The concept of NCs as building blocks for nanoscale assembly, superlattices with and without controlled dimensionality has been covered in an excellent review by Claridge \textit{et. al}. \textsuperscript{58}

Methods for organization into superlattices have been carried out through antisolvent precipitation, slow evaporation, DNA-mediated assembly, biphasic interfacial assembly etc. Cost effective large-scale methods giving rise to continuous films at the nanoscale with the desired control are being examined\textsuperscript{103}. Dip-coating has been popular for use in NC electronics because of the advantages in controlling thickness, NC organization, film continuity\textsuperscript{104–106} etc.

1.8 DISTINCTION WITH METAL NCs:

Among the metals, gold NCs containing anywhere from 10-300 atoms\textsuperscript{107,108} are excellent candidates to study the fundamental behavior at the nanoscale. Historically dating back to
Faraday’s time, colloidal gold nanoparticles have seen a tremendous rise in interest in modern times due to their applicability in several aspects of modern medicine, bioimaging and optoelectronic devices. Before the advent of electron microscope imaging techniques and ensuing detailed study on gold sols\textsuperscript{109}, gold particle sizes were identified by their x-ray diffraction patterns (Scherrer method\textsuperscript{110}). The discovery of the structure of the DNA made gold sols popular to biologists for use as labels in electron microscope studies. The next big milestone was the application of the Raman enhancing properties (SERS) of both gold and silver nanoparticles. The rise of nanotechnology ushered in large communities of scientists across several disciplines to research on many nanoparticles, including that of metal, semiconductor carbon nanostructures, with tremendous advances following suit.

Structure and properties of ultrasmall nanoparticles (gold and silver) with < 3 nm diameter are not well understood as well as larger plasmonic counterparts. Larger NPs exhibit size-dependent plasmonic behavior that is tunable to error limits of ~1 nm. in the ultrasmall regime, quantum size effects make them extremely sensitive down to differences at the atomic level\textsuperscript{108}. With decreasing size, the SPR blue-shifts, followed by disappearance below ~ 2nm\textsuperscript{111}. Atomic-level precision and control over the synthesis and ensuing treatment of these NCs are essential to study such systems. LSPR tunability of metal NCs depends strictly on size, shape but is not customizable unlike semiconducting materials.
Figure 1.8. Four shells in the Au$_{130}$(p-MBT)$_{50}$ nanocluster$^{112}$. Upper: top view; lower: side view. (A) central atom Au1 (green) and the 1st shell Au$_{12}$ (magenta); (B) the 2nd shell Au$_{42}$ (gray); (C) the 3rd shell Au$_{50}$ (blue); (D) the 4th shell Au$_{25}$ (orange) and S$_{50}$ (yellow). (E) Chiral surface patterns of−S−Au−S−pentagon ripples on the Au$_{105}$ kernel. Reprinted with permission from ref 112. Copyright 2015, JACS, ACS.

1.9 TECHNOLOGICAL CHALLENGES:

Although an excellent control of particle size distribution, shape, composition, crystal structure, and surface functionalization techniques in metal and semiconducting nanoparticles has been perfected over the last few decades, many aspects remain challenging to grasp to this day. The outermost “amorphous”$^{107}$ surface layer is not readily characterized using standard TEM techniques, so adhesion of organic functional layers and their interaction with the metal nanoparticle at the interface is not well understood even with SPM techniques. The excess ligands
present at the surface, residual reactants, side products, polydispersity in nanoparticles, etc., make it difficult to apply spectroscopic techniques (NMR, IR, Raman etc.) to confidently assign structure-property relationships. Thus, questions on the bonding of surfactants, and how the nanoparticle surface maintains its stability remain. Knowledge of interfacial bonding mechanisms will allow researchers to concisely engineer nanoparticle surfaces to be resistant to external unwanted stimuli (chemical environments, heat, etc.) while allowing accessibility to their functional properties directed at specific applications including catalysis. Existing literature on the effects of ligands on the morphology, electronic structure and optical response of clusters hint toward significant surface charge redistribution and polarization effects on the surface arising from the surface-ligand interactions. Shape controlled synthesis is not well understood, whether it is kinetically or thermodynamically controlled.

Growth mechanisms of nucleation are unclear, hence multiple theories have been proposed, especially that of anisotropic shape formation. In-situ techniques are critical towards monitoring the growth in real-time. Strict tuning of various parameters (high temperatures, inert atmosphere, reaction times) during NC syntheses limit the choice of materials in observing in-situ growth though electron microscopy techniques. High-energy electron beams or X-ray radiation may interreact with the materials, giving rise to altered growth conditions and therefore properties.
Figure 1.9: (A) Proposed mechanism of formation of the low temperature synthesis of magic-sized CdSe capped with TOPO. (B) (a) Absorption (black) and PL (red) spectra of toluene solutions of 46 nm long CdSe/CdS nanorods grown from 4.4 nm w-CdSe seeds. Gray line shows magnified absorption spectrum to emphasize structure of the absorption onset. Absolute PL quantum efficiency of this sample was 80%, measured at the excitation wavelength 514 nm. (b) Absorption (black) and PL (red) spectra of toluene solutions of CdSe/CdS nano-tetrapods with 24 nm CdS legs grown from 4 nm zb-CdSe seeds. Absolute PL quantum efficiency of this sample was 39%, measured at the excitation wavelength 512 nm. (c) Fluorescence decay of 4.4 nm w-CdSe NCs (black) and CdSe/CdS nanorods with different lengths: 12.2 nm (red), 24 nm (green), 36 nm (blue). (d) Fluorescence decay of 4.0 nm zb-CdSe 10 NCs (black) and CdSe/CdS nanotetrapods with arm length of 9.2 nm (red), 24 nm (green), 38 nm (blue). (e) Comparison of Absorption and PL excitation spectra for 46 nm CdSe/CdS nanorods shown in panel (a). PL intensity was integrated throughout the entire emission band. (f) Comparison of Absorption and PL excitation spectra for CdSe/CdS nano-tetrapods with 24 nm long CdS arms shown in panel (b). PL intensity was integrated throughout the entire emission band. Panel (A) is reprinted with permission from ref 113, Copyright 2012, ACS JPCC. Panel (B) is reprinted with permission from ref 114. Copyright 2007, ACS Nano Letters.

Different growth mechanisms have been put forward in the last few decades involving “burst-nucleation” growth of high concentrations of monomers (LaMer mechanism), Ostwald ripening where smaller nanoparticles dissolve in solution to allow growth into larger particles, coalescence and oriented attachment and intra-particle growth, to name a few. Growth mechanisms are material specific. Metal nanoparticles such as Au exhibit different growth mechanisms which
are dependent on the pH level of the solution. This is explained nicely in a review article by Thanh et al.\textsuperscript{119}. Mechanisms for Ag nanoparticle growth was described by Wang\textsuperscript{120} and Henglein et. al.\textsuperscript{121}. It has been conjectured by Yu et.al.\textsuperscript{122} that magic-sized nanoparticles, such as $(\text{CdSe})_{34}\textsuperscript{30,122–124}$ only undergo a nucleation step without any further growth (Fig 1.9A). Many control experiments involving plotting absorbance peaks of nanoparticles with growth time were performed to overrule the presence of Oswald ripening mechanisms. Seeded growth has been studied extensively for NCs (Fig 1.9B) to understand the design principles of nano-heterostructures with complex shapes and morphologies by changing the crystalline structure of the seed\textsuperscript{114}. The most plausible mechanism for magic-sized particles is provided below from Yu et. al.’s experiments, as validated from NMR experiments. Larger quantum dots such as PbS are often formed through Ostwald ripening as verified through UV-Visible spectroscopy to probe the change in particle size with reaction time and temperature, factors which affect the solubility. ZnO nanoparticles on the other hand, exhibit multiple stages of growth: nucleation, growth of compact and fractal aggregates and secondary nucleation; as probed by a variety of experimental techniques such as XAFS, SAXS and UV-Vis\textsuperscript{125}.

1.10 APPLICATIONS EXPLOITING THE UNIQUENESS:

Large-scale synthesis of high-quality, nearly monodisperse semiconducting NCs such as CdSe\textsuperscript{122}, CdSe/CdSe core-shell structures\textsuperscript{126}, has made it possible to employ their size-dependent properties on an industrial scale. Unique properties (luminescence, catalytic activity, magnetism) displayed by the metal NCs aid in various applications in diverse fields: catalysis\textsuperscript{127,128}, chemical sensing of biomolecules, ions, peroxides and others. Optical imaging using two-photon absorption\textsuperscript{129,130} and fluorescence properties of nanocluster offer excellent resolution. Other popular applications lie in biological imaging and light-emitting diodes.
Nanoscale photonics: Band-gap tunability of small atomically precise inorganic NCs is especially attractive for photonic device technology. Optical switching and frequency conversion elements in telecommunications and fiber optics technologies could immensely benefit from materials with tunable optical properties, such as semiconducting quantum dot NCs (CdS, PbS, GaAs, CdSe etc.)\textsuperscript{131}. These NCs could form nanometer-sized building blocks for photonic circuitry utilizing the size dependent properties arising from quantum confinement. In semiconducting cluster sizes comparable to the Bohr radius, eg., 6 nm CdS, discrete electronic states have been probed by short laser pulse to generate bound excitons, i.e., electron-hole pairs\textsuperscript{26,45,132–134}. The generated exciton gets trapped by the shallow surface sates thus giving rise to nonlinear optical absorption spectra. NCs often behave as single molecules in the sense that one trapped electron-hole pair is sufficient to bleach the entire cluster, the basic mechanism for which was laid out more than two decades ago\textsuperscript{131}. Monodispersed NCs (such as those with large absorption coefficient GaS, PbS) can help design materials which provide sharp exciton resonance bands, improving upon the precision of resonant nonlinearity measurements and transitions; while providing an improved figure of merit, biological labeling/imaging next-gen solar energy capture, conversion and storage\textsuperscript{135}. 
Sensing applications: Optical excitations from composite NCs can be probed effectively and distinguished from their isolated constituents with the knowledge of size-dependent dielectric functions\textsuperscript{137}. In the recent years, graphene quantum dots have become leading candidates in electronic, photoluminescence, electrochemical and electrochemiluminescence sensor fabrications (Fig 1.10). A review article by Sun et. al.,\textsuperscript{136} discuss these diverse applications in details, the scope of which is too broad for this article.

1.11 SUMMARY AND OUTLOOK:

These are exciting times for the nanocluster community to spearhead research in unforeseen directions using the cation exchange technique to chart new territories in semiconductor nanoparticle synthesis. New phases and morphologies present in the synthesized nanocrystals and NCs could give rise to new class of materials useful for a variety of applications\textsuperscript{138,139}. For example, a variety of chalcogenides such as Ag\textsubscript{2}Se, PbSe can be prepared as molecularly precise...
NCs and probed for different applications. A much better understanding of the ligand structure using NMR, the chemical nature and physical attributes (such as chain lengths, chirality, orientation) of ligands passivating the surfaces of nanocrystals and NCs play a crucial role in determining the functional aspects of these materials. More importantly, a better understanding of the structure using crystallography (X-ray and neutron diffraction techniques) of these molecules; bridging the gap between molecules and solids, especially in the area of catalysis, and constructing solids from precise molecular units are exciting avenues that can be pursued in materials science and condensed matter communities.

**Figure 1.11:** The intercalation potential of some electrode materials that could possibly be used for aqueous lithium-ion batteries\(^\text{138}\). Left: \(O_2/H_2\) evolution potential versus NHE for different pH in 1 M Li\(_2\)SO\(_4\) aqueous solution. Right: lithium-ion intercalation potential of various electrode materials versus NHE and Li/Li\(^+\). Theoretically, an aqueous lithium-ion battery can be assembled by combining a lower potential lithium-accepting anode and a higher potential lithium-source cathode within the \(O_2/H_2\) evolution potential range. AC, activated carbon; NASICON, materials with NASICON structure. Reprinted with permission from ref 138. Copyright 2010, Nature publishing group.
Many challenges remain to uncover the functionalities in this field however. We ask the question, what are the special attributes of these ultrasmall NCs prepared through cation exchange? Where are these properties coming from? Does the structure play the only important role in ion distribution and pathways in the crystals? What are the various physical properties and applications of these NCs as compared to their nanoparticle counterparts? What is the long-term stability for these NCs derived through ion exchange? How does the ion exchange occur?

The important question stemming from theoretical community should be effective prediction and design of these material-driven systems using a variety of electronic structure calculation methods such as DFT. This is especially useful in complex systems such as Li-ion batteries where complex materials (NASICON etc.) are used (Fig 1.11). Simple experimental characterization such as diffraction or NMR alone cannot elucidate the origin and effective application of the novel properties observed in these materials.
CHAPTER 2: ROAD TO PREPARING COPPER SELENIDE NANOCRYSTALS WITH LIQUID-LIKE CATIONIC SUB-LATTICE AT ROOM-TEMPERATURE

2 Reproduced from White S. L. (co-first), Banerjee P. (co-first), Jain P. K., Liquid-like cationic sub-lattice in copper selenide clusters, Nature Communications, 8, 14514, 2017. DOI:10.1038/ncomms14514 with permission of primary author and journal. This manuscript was also reproduced in the PhD dissertation of Sarah White.


2.1 AUTHOR CONTRIBUTIONS:

This chapter resulted from a collaboration between Sarah White, a former member and PhD alumnus of our group and me. Sarah’s dissertation work investigated in detail the Cu⁺ exchange of CdSe nanocrystals and nanoclusters and the optical and structural properties of the resulting Cu₂Se nanocrystals and nanoclusters. The nanoclusters had low colloidal stability, which made it challenging to perform cation exchange reactions on them and characterize the resulting nanocrystals. I helped identify ligand and colloidal conditions that allow the nanoclusters to be stable in the course of cation exchange. I showed using Vis-NIR optical spectrophotometry measurements that the 2-nm Cu₂Se nanoclusters exhibit reversible plasmon resonances, which can be tuned by oxidation/reduction, quite like larger Cu₂Se nanocrystals, which was known from literature including our group’s work. I also performed elemental analysis of the Cu₂Se nanocrystals using energy dispersive spectroscopy (EDS) to ensure that cation exchange from CdSe to Cu₂Se was indeed complete.

Sarah’s high-resolution electron microscopy studies indicated a clear structural difference between the lattice structure of 6-nm and 4-nm Cu₂Se nanocrystals as compared to those of 2-nm Cu₂Se nanoclusters. The former showed a super-lattice structure, which the latter lacked. Based on known literature on bulk Cu₂Se, Sarah and my advisor proposed that the 2-nm nanoclusters have a super-
ionic structure, i.e., the Cu sub-lattice is mobile, at room temperature, quite unlike bulk Cu$_2$Se which is super-ionic above ca. 140 °C. The hypothesis was verified by my differential scanning calorimetry (DSC) measurements of 2-nm Cu$_2$Se nanoclusters, which identified the phase transition temperature and compared it with that of larger size Cu$_2$Se nanoplates I synthesized.

Sarah performed X-ray diffraction studies of the crystallographic structures of all three sizes of Cu$_2$Se nanocrystals. Using structural models of the Cu$^+$ sub-lattice, my advisor deduced from these measurements that in the 2-nm nanoclusters, octahedral lattice sites have an unusually high Cu$^+$ occupancy, which he hypothesized by analogy with rocksalt crystals, may be an outcome of compressive strain in such small nanocrystals. I performed a systematic phonon spectroscopy of Cu$_2$Se nanocrystals of the three sizes, from which it was found that the 2-nm nanoclusters have significant compressive strain relative, not only to the bulk, but also to the 6-nm Cu$_2$Se nanocrystals. Thus, a compressive lattice strain could indeed be at the origin of the distinct structure and room-temperature super-ionic behavior of 2-nm Cu$_2$Se nanoclusters.

2.2 ABSTRACT:

Super-ionic solids, which exhibit ion mobilities as high as those in liquids or molten salts, have been employed as solid-state electrolytes in batteries, improved thermoelectrics, and fast-ion conductors in super-capacitors and fuel cells. Fast-ion transport in many of these solids is supported by a disordered, “liquid-like” sub-lattice of cations mobile within a rigid anionic sub-lattice, often achieved at high temperatures or pressures via a phase transition. Here we show that unlike larger nanocrystals, ultrasmall clusters of copper selenide exhibit a disordered cationic sub-lattice under ambient conditions, where Cu$^+$ ions and vacancies form an ordered superstructure similar to the bulk solid. The clusters exhibit an unusual cationic sub-lattice arrangement wherein octahedral sites, which serve as bridges for cation migration, are stabilized by compressive strain.
The room-temperature liquid-like nature of the Cu\(^+\) sub-lattice combined with the actively tunable plasmonic properties of the Cu\(_2\)Se clusters make them suitable as fast electro-optic switches.

2.3 INTRODUCTION:

Nanoscience is rife with examples of nanosized crystals displaying unique optical, electronic, chemical, or structural properties not found in their bulk counterparts. For instance, in semiconductor nanocrystals (NCs) smaller in size than the Bohr excitonic radius, quantum confinement of carriers leads to discretization of energy levels and size-dependent excitonic transition energies and band-gaps.\(^{140,141}\) Depression of solid-to-liquid melting points\(^{142,143}\) as well as solid-to-solid phase transition temperatures\(^{144–147}\) is also observed in small semiconductor and metal crystallites due to the increased contribution of surface energy to the total internal energy. An increase in interface-to-volume ratio in ionic materials, through reduction in size or nanostructuring of interfaces, has been found to reduce the formation energies of defects and thereby increase ionic transport.\(^{148,149}\) Other nanoscale size effects in the thermodynamics and kinetics of pressure-induced structural phase transitions\(^{150}\) and chemical transformations\(^{151,152}\) are also known.

We investigate the unique structural and physical behavior at an ultrasmall size of the semiconductor Cu\(_2\)Se. Cu\(_2\)Se is a solid with a peculiar ionic structure: the smaller Cu\(^+\) ions (eight or fewer per unit cell) have access to a much greater number of crystallographic sites within a rigid cage formed by the significantly larger Se\(^2-\) anions.\(^{14}\) The large number of vacant sites available for Cu\(^+\) hopping is a primary factor in the manifestation of super-ionic transport in this solid. However, in its low temperature (LT) \(\beta\) phase, the vacancies are ordered and Cu\(^+\) ions are localized at the lowest-energy interstitial sites within a lower symmetry pseudo-cubic Se\(^2-\) sub-lattice.\(^{14}\) Ionic
transport in this form is rather limited. Above ca. 400 K, there exists a high temperature (HT) α phase of Cu$_2$Se, in which the Cu$^+$ ions form a disordered, liquid-like sub-lattice. The Cu$^+$ ions are freely mobile between vacant and occupied sites within the immobile, face-centered cubic (fcc) Se$^{2-}$ sub-lattice. This mobile Cu$^+$ network supports Cu$^+$ diffusivities ($10^{-5}$-$10^{-4}$ cm$^2$ s$^{-1}$) as high as those of liquids or molten salts and resulting ionic conductivities of 1-2 Ω$^{-1}$ cm$^{-1}$ (at 670 K), three orders of magnitude larger than the room temperature value. This super-ionic behavior is promising for replacing liquid electrolytes of batteries with solid-state ion conductors, developing fast-ion conductors for fuel cells, and enhancing $zT$ values for thermoelectric transport. However, the need for high temperatures can be limiting in these applications. In other closely linked systems, high pressures can alternatively be employed to achieve a super-ionic phase.

Here we show that in the form of ultrasmall clusters, Cu$_2$Se exhibits a disordered, liquid-like Cu$^+$ sub-lattice under ambient conditions of temperature and pressure. We find that the mobile Cu$^+$ network is linked to a unique cationic sub-lattice structure in the clusters that is remarkably different not just from the bulk form of the solid but also from larger NCs due to the effect of high compressive strain in the clusters. The preparation and subsequent study of this cluster form of Cu$_2$Se is facilitated by cation exchange transformation of CdSe, which is available in the form of monodisperse, zinc blende-like clusters of ca. 2 nm size. For studying the comparative effect of crystallite size on room-temperature ionic structure, larger NCs are also prepared from size-controlled CdSe NCs using the same cation exchange method. The room-temperature super-ionic nature of Cu$_2$Se clusters, combined with their actively tunable plasmonic properties, also demonstrated here, make them candidate materials for ultrafast electro-optic switching.
2.4 SYNTHESIS AND CHARACTERIZATION OF Cu$_2$Se CLUSTERS:

Figure 2.1. Synthesis and characterization of ultrasmall Cu$_2$Se clusters. (a) The excitonic absorption spectrum of CdSe clusters (black curve) shows a narrow excitonic band at 406 nm, which upon cation exchange with Cu$^+$ ions is lost and the featureless band-edge absorption of the indirect bandgap semiconductor Cu$_2$Se appears (red spectrum). (b) HAADF-STEM images of Cu$_2$Se clusters after exchange show that cation exchange of CdSe clusters results in discrete Cu$_2$Se clusters with an average diameter of 2.1 nm ± 0.3 nm as shown by the (c) size histogram.

Ultrasmall Cu$_2$Se clusters were prepared by solution-phase cation exchange of magic-sized CdSe clusters with Cu$^+$ (see Methods). Thermodynamically stable, single-sized (ca. 2 nm) clusters of CdSe, popularized by the work of Kasuya and coworkers,\textsuperscript{17} have been known to be formed in colloidal syntheses.\textsuperscript{156–158} Their single-sized nature is manifested in their narrow 1S$_b$-1S$_c$ excitonic absorption peak at 406 nm (Fig. 2.1a), which shows lack of inhomogeneous broadening. Due to the topotactic nature of cation exchange, the anionic framework is preserved in the cation exchange process,\textsuperscript{159,160} yielding ultrasmall Cu$_2$Se clusters of similar ca. 2 nm size and fcc Se sub-lattice arrangement as the initial zinc blende CdSe template. The exchange process can be monitored by absorption spectroscopy (Fig. 2.1a). Upon addition of an excess of Cu$^+$ to a solution of CdSe
clusters, the narrow $1S_h-1S_e$ excitonic absorption peak of CdSe is replaced by a featureless, band-edge absorption of the near-infrared band-gap Cu$_2$Se. Completion of exchange to yield the Cu$_2$Se phase was verified by measurement of the elemental composition (Supplementary Fig. 2.7) by scanning transmission electron microscopy/energy dispersive spectroscopy (STEM/EDS) The Cu:Se ratio was found to be ca. 2:1, whereas the Cd signal was at the noise level of the EDS measurement, indicating little to no remnant Cd. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) of the cation exchange product showed presence of discrete Cu$_2$Se domains 2 nm in size (Fig. 2.1b & 2.1c).

![Graph](image)

**Figure 2.2.** Cu$_{2-x}$Se clusters display tunable NIR LSPRs. (a) As Cu$_2$Se clusters are oxidized by O$_2$ in air, a LSPR absorption band appears in the NIR region resulting from the creation of holes in the valence band of Cu$_2$Se. The hole concentration in the clusters increases with increasing degree of oxidation, resulting in a blue-shift of the LSPR band. (b) Treatment of the oxidized clusters with the reducing agent cobaltocene results in the annihilation of the holes, leading to a gradual red-shift and suppression of the LSPR band. (c) In the process of oxidation, the LSPR peak energy of the Cu$_2$Se clusters saturates to a value close to that for larger 6 nm Cu$_2$Se NCs. A schematic of the chemical oxidation and reduction of Cu$_2$Se clusters is shown in (d).
2.5 Cu$_2$Se CLUSTERS SUSTAIN Cu VACANCIES AND LOCALIZED SURFACE PLASMONIC RESONANCES:

The clusters, synthesized at this size for the first time, were found to exhibit a hallmark property of Cu$_2$Se. It is known that copper chalcogenides, including Cu$_2$Se, are stable in considerably Cu-deficient stoichiometries, Cu$_{2-x}$Se (0 ≤ x ≤ 0.25), and therefore can be heavily p-type doped.$^{161-165}$ The stoichiometry and associated doping level can be tuned by oxidation/reduction. Similar to larger copper chalcogenide nanostructures,$^{161-165}$ as shown here for 6 nm Cu$_2$Se NCs in Supplementary Fig. 2.2, upon exposure to O$_2$, Cu$^0$ is removed from the cluster in the form of copper oxide, creating Cu deficiency in the lattice. The sub-stoichiometry contributes hole carriers to the valence band, leading to the emergence of a localized surface plasmon resonance band (LSPR) in the near-infrared (NIR) region of the absorption spectrum (Fig. 2.2a).$^{161}$ With increasing oxidation levels, there is an increase in the peak energy $\omega_{sp}$ of the LSPR band (Fig. 2.2c), which is reflective of the increase in the free hole carrier concentration $N$ as $\omega_{sp} \propto \sqrt{N}$. In this regard the clusters show behavior similar to that of the larger 6 nm NCs, even though the oxidation kinetics appear to be slower for the 2 nm clusters (Fig. 2.2c). The LSPR peak energy of the clusters saturates to a value of 1.06 eV upon prolonged oxidation, only marginally higher than the saturation peak energy of 0.99 eV for the 6 nm Cu$_2$Se NCs and the value of 1 eV from Manna and coworkers.$^{23}$ The difference is only 7% and could be due to increased carrier confinement in the clusters, known to cause a blue-shift$^{140,166}$ or due to differences in the local medium refractive index presented by the ligand shell. The similarity of LSPR peak energies for the two sizes suggests that the saturation hole concentration in the clusters is of the same magnitude (within 14%) as that in the larger NCs and is ca. 4 x 10$^{21}$ cm$^{-3}$ as estimated before$^{161}$ for a 1 eV LSPR peak energy. The latter doping level corresponds to a stoichiometry in the range of Cu$_{1.8}$Se commonly found for this
semiconductor. The Cu$_2$Se clusters synthesized here also show reversible tunability of the doping level and the LSPR.$^{162,167}$ Upon exposure of the oxidized clusters to a reducing agent such as cobaltocene, electrons are injected back into the Cu$_{2-x}$Se clusters, the hole carriers are progressively annihilated, and the NIR LSPR band red-shifts while decreasing in absorbance (Fig. 2.2b). The LSPR band can be fully suppressed, indicating a return to the initial stoichiometric or nearly-stoichiometric form with low doping levels. The ability to be self-doped, the NIR plasmonic nature, and active plasmonic tunability of the Cu$_2$Se clusters can be particularly attractive for electro-optic switching. Such switching can be rapid given the ultrasmall size, which favors short nanometer-scale diffusion lengths for Cu$^+$. 

2.6 LACK OF VACANCY ORDERING IN Cu$_2$Se CLUSTERS:

Vacancy ordering below the order-disorder transition (ca. 400 K) temperature is another well-established hallmark of bulk Cu$_2$Se,$^{29-31}$ which we studied in the clusters and the larger NCs (Fig. 2.3) using high-resolution transmission electron microscopy (HRTEM). The unit cell structures and the Cu$^+$ sub-lattice arrangement in bulk Cu$_2$Se have been extensively studied. It is known that even in the near-stoichiometric form of Cu$_2$Se, vacant sites abound because the number of interstitial sites – 8c tetrahedral, 32f trigonal, and 4b octahedral locations per unit cell – available to the Cu$^+$ ions is considerably larger than their number. In the ideal cubic anti-fluorite structure of the solid, the Se$^{2-}$ anions occupy 4a sites forming a fcc sub-lattice with a lattice constant $a_c$ of 5.85 Å, while the Cu$^+$ cations fill all eight tetrahedral interstices within the fcc Se$^{2-}$ cage. However, in practice, the LT β non-superionic phase has a defective anti-fluorite structure, wherein a fraction of the tetrahedral sites are vacant and the displaced Cu$^+$ ions instead occupy trigonal sites.$^{29}$ Rather than arranging randomly, in the non-super-ionic phase these tetrahedral vacancies stack every four
Cu\textsuperscript{+} layers along the <111> crystallographic axis creating a super-structure with a periodicity of 
\[ \frac{a_c}{2\sqrt{3}} \times 4 = 6.7 \, \text{Å} \], which is twice the typical lattice spacing along the <111> direction.\textsuperscript{29} As a result of vacancy ordering, the Se\textsuperscript{2-} sub-lattice is slightly distorted by few % with elongation along the stacking direction and contraction in the basal plane.\textsuperscript{168}

Cu\textsuperscript{+} vacancy ordering is manifested in the form of a lattice fringe contrast pattern in HRTEM with an abnormally large 6.7 Å periodicity. In the HT super-ionic \( \alpha \)-Cu\textsubscript{2}Se phase, the Cu\textsuperscript{+} ions are mobile between filled and vacant interstitial sites and the super-structural ordering is lost. The Se\textsuperscript{2-} sub-lattice is no longer distorted and restores its cubic arrangement. In this form, regular lattice fringes corresponding to an inter-Se planar spacing of \( \frac{a_c}{\sqrt{3}} = 3.3 \, \text{Å} \) is seen along the <111> direction.\textsuperscript{29,30} Thus, vacancy ordering is a signature of the LT \( \beta \)-Cu\textsubscript{2}Se non-superionic phase.\textsuperscript{29-31} Most recently, Liu et al. used this super-structure contrast pattern in HRTEM to detect in bulk Cu\textsubscript{2}Se thermoelectric materials the transition from a non-superionic to a super-ionic, “liquid-like” Cu\textsuperscript{+} subsystem when the temperature was raised from ambient to 423 K, above the point of order-disorder transition.\textsuperscript{30}
Figure 2.3. Superstructural vacancy ordering in Cu$_2$Se NCs. HRTEM images of four representative Cu$_2$Se NCs at each size: 2 nm, 4 nm, and 6 nm regime are shown. Absorption spectra of the corresponding samples are also shown. Vacancy ordering, characterized by a double lattice spacing of 0.67 nm along <111>, is evident in most 6 nm NCs and a fraction of 4 nm NCs; whereas such ordering is absent in 2 nm NCs, where a regular lattice spacing of 0.32 nm along <111> is seen. Image analysis was performed on ca. 30 NCs at each size and the percentage of NCs displaying superstructures is listed in Table 2.1. All images used for analysis are shown in Supplementary Fig. 2.3.

In analogy to such observations on bulk Cu$_2$Se, we employed HRTEM imaging to characterize at ambient temperature the presence of tetrahedral vacancy ordering and the resulting super-structure in the Cu$_2$Se clusters and the NCs. Several NCs with high-resolution lattice patterns along <111> were analyzed (Supplementary Fig 2.3), results of which are summarized in Table 2.1.
Representative images of four NCs at each size are shown in Fig. 2.3. The 6 nm NCs (Fig. 2.3d) displayed a contrast pattern along \( <111> \) with a distance of 6.7 Å between bright fringes that represent Cu vacancy planes. This contrast pattern arising from vacancy-ordered super-structure was observed in 80% of the 6 nm NCs, suggesting the existence of these NCs in the non-superionic phase. On the other hand, the 2 nm clusters (Fig. 2.3b) displayed a complete lack of superstructure, quite unlike 6 nm NCs or bulk \( \text{Cu}_2\text{Se} \) at ambient temperature. Lattice fringes along \( <111> \) with a 3.2 Å periodicity of adjacent Se planes were seen, characteristic of the super-ionic phase with a mobile, disordered \( \text{Cu}^+ \) sub-lattice. Interestingly, at the intermediate size of 4 nm, super-structural ordering was observed in only 10% of the NCs. Thus, as the crystallite size is reduced from 6 nm to 2 nm, HRTEM shows an increase in the statistical prevalence of a disordered \( \text{Cu}^+ \) sub-lattice with no super-structural ordering. The results may be explained by a simple size-dependent reduction in the order-disorder transition temperature \( T_c \) such that the transition temperature is below ambient for the 2 nm size and above ambient for the 6 nm case. The depression of the phase transition temperature in nanosized domains of superionic solids like \( \text{Cu}_2\text{S} \), \( \text{AgI} \), and \( \text{Ag}_2\text{Se} \) has been reported previously. Invoking such an effect would imply that the 2 nm clusters are effectively in the HT α-\( \text{Cu}_2\text{Se} \) phase at ambient temperature. From differential scanning calorimetry (DSC) measurements (Supplementary Fig. 2.8), indeed, the (ensemble-averaged) order/disorder transition temperature \( T_c \) for the clusters was found to be below room temperature (10°C/-2°C heating/cooling), significantly depressed compared to the temperature of 413 K or 140°C reported for bulk \( \text{Cu}_2\text{Se} \).
2.7 UNUSUAL CATIONIC SUB-LATTICE STRUCTURE OF Cu$_2$Se CLUSTERS:

However, further characterization of the Cu$^+$ sub-lattice structure by powder x-ray diffraction (PXRD) suggests the presence of an unusual arrangement, which deviates considerably from the HT $\alpha$ phase of bulk Cu$_2$Se. We compared the PXRD patterns of 2 nm Cu$_2$Se clusters to those of 4 and 6 nm NCs (Fig 2.4a). All three patterns closely matched that of cubic Cu$_2$Se with a lattice parameter of $a_c = 5.85$ Å. However, there are notable differences as one goes from the 6 nm to the 2 nm Cu$_2$Se: (i) the intensity of the $\{200\}$ peak ($2\theta = 30.5^o$) relative to that of the $\{111\}$ peak ($2\theta = 26.4^o$) increases, and (ii) the intensity of the $\{311\}$ peak ($2\theta = 51.8^o$) decreases. As we show below, these trends arise from differences between the cationic sub-lattice arrangements of the different size NCs, while the overall cubic structure of the unit cell, dictated by the rigid Se$^{2-}$ arrangement, is mostly conserved.

We performed simulations using the program PowderCell which generates a PXRD pattern based on a structure factor calculation from unit cell parameters (Fig. 2.4b). Our simulation models employed an fcc Se sub-lattice. Known distortions from this close-packed arrangement of the anions, like those in the LT phase,$^{29}$ are minor enough to be undetectable in our PXRD data. In simulations, occupancies of the eight Cu$^+$ ions in available interstitial sites ($4b$, $8c$, $24e$, and $32f$) within the rigid fcc Se$^{2-}$ cage were varied until the simulated PXRD pattern matched the experimental one for each size. In this manner, Cu$^+$ sub-lattice structures were determined for 2 nm, 4 nm, and 6 nm Cu$_2$Se. It must be noted that site occupancies determined are statistical: they do not imply a necessarily static distribution of Cu$^+$, but reflect a dynamic average, which is why even a mobile arrangement with significant site-to-site hopping, can be characterized in such terms.
Figure 2.4. PXRD and cationic sub-structure. (a) Experimental and (b) simulated PXRD patterns of 2 nm clusters, 4 nm NCs, and 6 nm NCs. The experimental pattern for the 6 nm NCs matches that of the LT phase of Cu$_2$Se simulated on the basis of parameters from an established crystal structure. The $\{200\}$ reflection missing in the pattern of 6 nm NCs is present in the pattern of 4 nm NCs. For 2 nm clusters, the $\{311\}$ reflection is suppressed and the $\{200\}$ reflection is strong. (c) Starting from the LT Cu$_2$Se phase (black curve), the series of simulated XRD patterns show that the progressive removal of Cu$^+$ occupancy from trigonal positions and their placement in tetrahedral positions results is an increase in the intensity of the $\{200\}$ reflection. (d) Starting from a structure in which all Cu$^+$ occupancy is in tetrahedral and 24e positions (black curve), the series of simulated XRD patterns shows that the progressive removal of Cu$^+$ occupancy from 24e positions and their placement in octahedral positions results in a suppression of the $\{311\}$ reflection and an increase in the $\{200\}$ reflection intensity. Note, the peak at $2\theta = 59^\circ$ is a background reflection from the sample holder (see Supplementary Fig. 2.9).
As per simulations, the experimental PXRD pattern of 6 nm Cu$_2$Se agrees with an established structure for LT β Cu$_2$Se, in which only a third of the Cu$^+$ ions occupy 8$c$ tetrahedral positions, whereas a majority occupy 32$f$ trigonal positions. The Cu$_2$Se sub-lattice structure of 6 nm NCs is thus consistent with the presence of tetrahedral vacancies, which order in the LT phase. Comparison with occupancies of bulk Cu$_{1.8}$Se suggests that the filling of all eight tetrahedral sites in the stoichiometric solid (ideal anti-fluorite) would constitute a high-energy configuration due to Cu$^+$-Cu$^+$ repulsion. Occupation of other trigonal sites is therefore favored at lower temperatures.

As the temperature is increased, the relative occupation of the tetrahedral sites increases. In fact, in the HT phase, tetrahedral occupancy is significantly greater than trigonal site occupancy, possibly due to the increased mobility of Cu$^+$. Such an increase in tetrahedral occupancy (simulated in Fig. 2.4c) leads to the emergence of the {200} reflection and an increase in its intensity relative to the {111} intensity. In the anti-fluorite Cu$_2$Se structure, the {200} reflections from the Se planes are canceled out by {200} reflections from adjacent Cu planes, spaced from the Se planes by $a_c/4$ layers. The cancelation is most effective when the tetrahedral sites are only half filled, i.e., by four Cu$^+$ ions to compensate for four Se$^{2-}$ anions in the fcc anionic sub-lattice. When more of the tetrahedral sites are occupied by Cu$^+$, a {200} reflection originates from the Cu-Cu inter-planar arrangement with a spacing of $a_c/2$ units. When all eight tetrahedral sites are filled, the {200} reflection is the strongest. The change in the experimental PXRD in going from 6 nm to the 4 nm NCs is exactly in line with such a change in the Cu$^+$ sub-lattice. In fact, the best match for the experimental PXRD pattern of the 4 nm NCs, which shows a distinct {200} peak, is the anti-fluorite structure, wherein all or most 8$c$ tetrahedral sites are occupied and there is little to no occupancy in 32$f$ trigonal sites. Thus, the increase in tetrahedral site occupation measured by
PXRD goes hand-in-hand with the decrease in the propensity of tetrahedral vacancy ordering seen in HRTEM.

The experimental PXRD pattern for 2 nm clusters could not be reproduced using only 8c tetrahedral and 32f trigonal site occupation. In this pattern, the {111} and {200} peaks are nearly equal in intensity, which could be simulated only by placement of Cu$^+$ in 4b octahedral positions (Fig. 2.4d). The {311} peak is weak in intensity in the 2 nm clusters, which is also consistent with octahedral occupancy (Fig. 4d). Filling of octahedral sites with Cu$^+$ leads to the emergence of {200} reflections associated with Cu-Cu and Se-Cu inter-planar arrangement with spacing of $a_0$/2 units, leading to an overall {200} peak of strong intensity. On the other hand, the Cu planes arising from octahedral occupation, normal to the {311} direction, serve to cancel the {311} reflection from adjacent Se layers.

A fit to the experimental PXRD of 2 nm clusters was obtained by a structure with 28% tetrahedral occupancy, 18% octahedral occupancy, and the remaining Cu$^+$ in 24e interstitial sites (Supplementary Fig. 2.11). The significant occupancy in octahedral sites is quite striking, since these sites play an important role in the mechanism of fast-ion conduction in fcc solids, where a major mode of cation migration is along <111> through faces shared by tetrahedra and octahedra within the fcc unit cell.$^{174}$ Thus, octahedral sites (O) serve as bridging or intermediary sites for hopping between tetrahedral sites (T). But in α-Cu$_2$Se, unlike in α-CuI (another common fcc super-ionic solid),$^{175}$ the much greater number of Cu$^+$ ions per unit cell and the consequently higher Cu$^+$-Cu$^+$ repulsion renders octahedral sites energetically unfavorable. While XRD and neutron diffraction studies suggest negligible occupation of 4b octahedral sites in LT β-Cu$_2$Se phase,
occupancy is only 5% even in the HT $\alpha$-Cu$_2$Se phase, whereas it is 15% in the clusters at ambient temperature.

If it were not for the infeasibility of octahedral occupation and the consequently high activation energy for -T-O-T- migration paths, $\alpha$-Cu$_2$Se would be much more ionically conductive than $\alpha$-CuI due to twice the number of mobile cations in the former. The unusual sub-lattice structure of Cu$_2$Se clusters combines the high cation density of Cu$_2$Se and high octahedral occupation found in $\alpha$-CuI (30% occupancy at 743 K). Moreover, this combination of attributes, desirable for fast-ion transport via -T-O-T- paths, is achieved in the clusters at room temperature. The statistical site occupancies determined from PXRD and the complete lack of superstructural ordering capture a dynamic cationic sub-lattice in the clusters where Cu$^+$ ions are mobile (either via hopping or anharmonic thermal vibrations$^{172}$ over multiple tetrahedral and octahedral sites along $<111>$ -T-O-T- conduction paths, at room temperature. Such a scenario is paraphrased by the “liquid like” description of the Cu$^+$ sub-lattice. Likewise, 24e site occupancy may suggest that their role as intermediary sites in tetrahedral-to-tetrahedral site hopping along $<100>$. 

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Figure 2.5. Compressive strain at ultrasmall size. The frequency of the LO phonon mode of Cu$_2$Se increases from 6 nm to 4 nm to 2 nm Cu$_2$Se NCs, indicating that the smallest NCs are considerably more compressively strained. Raman scattering spectra used for determination of the LO phonon mode frequency are shown in Supplementary Fig 4. The LO phonon frequency plotted here is an average obtained from multiple measurements with the standard deviation represented by the error bar.

2.8 EFFECT OF SIZE-DEPENDENT STRAIN:

Whereas a combination of tetrahedral and octahedral site occupation is critical for barrier-free ion transport, these sites are weakly populated in bulk Cu$_2$Se in the absence of thermal activation. As described before, it is energetically unfavorable to fill all 8c tetrahedral sites due to significant Cu$^+$-Cu$^+$ repulsion. Octahedral occupation is even less favored due to heavy repulsion between an octahedral Cu$^+$ and its four tetrahedral Cu$^+$ neighbors. How are octahedral sites then significantly populated in 2 nm clusters at room temperature? Taking a cue from the pressure-induced phase transition of binary cubic solids from tetrahedrally co-ordinated zinc blende structures to octahedrally co-ordinated rock salt structures, it may be hypothesized that the effect of cation repulsion may be countered by high pressure or compressive strain. Since our measurements are carried out at ambient pressure (in fact, the HRTEM is performed in vacuum),
we explored the presence of compressive strain in the NCs. In order to determine the residual strain in the Cu$_2$Se lattice, phonon scattering spectra were measured for NCs of all three sizes at room temperature (Supplementary Fig. 2.4). The $A_1$ longitudinal optical (LO) phonon mode of Cu$_2$Se$^{178}$ was detected in all three samples, but with a frequency $\omega$ that increased with decreasing NC size (Fig. 2.5). This mode hardening indicates the presence of a compressive strain in the nanocrystals,$^{40}$ which increases in magnitude with decreasing size. It must, however, be acknowledged that the LO phonon frequency can shift also due to the effect of phonon confinement in small crystallites, as shown by the classic work of Richter et al.$^{41}$ The phonon confinement effect causes a red-shift of the phonon frequency, opposite in trend to the influence of compressive strain in nanocrystals. These competing effects were discussed by Scamarcio et al. in CdS$_{1-x}$Se$_x$ NCs embedded in glass,$^{42}$ where it was shown that the effect of compressive strain on the phonon frequency more than overcomes the confinement effect. Thus, the compressive strain within a nanocrystal measured using the blue-shift of the phonon frequency serves as a lower limit; the actual compressive strain may be somewhat larger in magnitude. In fact, from the $\{111\}$ peak in experimental PXRD patterns, the clusters were estimated to be compressively strained by 4.5% relative to the 6 nm NCs (Supplementary Fig. 2.10), although it must be acknowledged that the strain measured by PXRD has uncertainties due to the overlap and asymmetric broadening of peaks. Nevertheless, PXRD and phonon spectroscopy are qualitatively consistent in the finding of a compressive lattice strain in the clusters.

Such a size-dependent compressive strain in nanoparticles is a well-known effect of the high % of surface atoms of nanoparticles and their resulting propensity to undergo compression to reduce surface energy,$^{179}$ which is simply described by Gibbs-Thomson relationship:
\[
\mu(D) - \mu(\infty) = \frac{4\gamma v}{D (2.1)}
\]

where \(\mu(D)\) is the molar free energy of a NC of diameter, \(D\), \(\mu(\infty)\) is the free energy in the bulk, \(\gamma\) is the surface tension and \(v\) is the molar volume. At smaller NC sizes, the surface energy term (r.h.s. in eq. 2.1) increases. To overcome the resulting increase in free energy, the NC undergoes a volumetric compression. For colloidal NCs, the degree of compressive strain is dictated not just by the size, but also by surface faceting and the nature of surface ligands, which influence \(\gamma\): strongly passivating ligands can reduce the surface tension \(\gamma\), thereby relieving some degree of strain caused by small size. The higher compressive strain measured in the 2 nm Cu_{2}Se clusters relative to the larger NCs is a result of the smaller crystallite size of the former along with some contribution from differences in ligand passivation: the clusters are capped with trioctylphosphine (TOP), whereas the 4 and 6 nm NCs are capped with octylamine.

By using the relation\textsuperscript{180}:

\[
\frac{\Delta \omega}{\omega} = \left(1 + 3 \frac{\Delta a}{a}\right)^{-\gamma} - 1 \quad (2.2)
\]

where \(\gamma\) is the Grüneisen parameter for LO phonons assumed to have the common value of 1.1, we estimated that the compressive strain \(\frac{\Delta a}{a}\) in the 2 nm clusters is 2.4% relative to the larger 6 nm NCs. The compressed lattice in the clusters can electronically stabilize Cu\(^{+}\) occupation in the six-coordinate octahedral sites. In the bulk Cu_{2}Se lattice, a Cu\(^{+}\) occupying an octahedral site is at a distance of \(a/2\) from six Se\(^{2-}\) anions, but at a smaller distance of \(\sqrt{3}a/4\) from the other Cu\(^{+}\) ions occupying tetrahedral sites. Thus, the net dominant effect of Cu\(^{+}\)-Cu\(^{+}\) repulsion destabilizes Cu\(^{+}\) occupation of an octahedral site in Cu_{2}Se.\textsuperscript{37} In a compressed Cu_{2}Se lattice, however, the bond
distance between the octahedral Cu\(^+\) and the six-fold Se\(^2-\) neighbors is shorter, resulting in strengthened Cu-Se bonding that can potentially offset the Cu\(^+\)-Cu\(^+\) repulsion. Expressed in terms of Pauling’s rules of bonding in ionic crystals, tetrahedral co-ordination between Cu and Se is favored in the typical Cu\(_2\)Se lattice; but, octahedral co-ordination can become relatively favorable when the density is increased, as is the case for the compressed lattice (ca. 7\% smaller unit cell volume) of the clusters. Using the bulk modulus of 85 GPa of the closely related Cu\(_{1.5}\)Se\(^{43}\) as an estimate for Cu\(_2\)Se (for which a bulk modulus is not available), the compressive strain in the clusters, relative to 6 nm Cu\(_2\)Se is equivalent to the application of a 2 GPa pressure, which is similar to the magnitude of pressure at which CdSe transforms from the four-co-ordinate wurtzite/zincblende phase to the six-coordinate rocksalt phase with octahedral sites filled with cations.\(^{44}\)

Since octahedral bridging sites play a critical role in Cu\(^+\) migration in Cu\(_2\)Se, the energetic cost of octahedral occupation of Cu\(^+\) is likely to influence the activation energy, \(E_a\), of Cu\(^+\) sub-lattice disordering/melting. From phonon scattering measurements, we find that with decreasing NC size \(D\), the lattice is under an increasing degree of compressive strain, which we postulate to result in an increasing stabilization of octahedral Cu\(^+\) occupation (as manifested by the crystallographic findings) and, consequently, a decreasing activation energy, \(E_a\), for cationic disorder. Such a size-dependent \(E_a(D)\) can explain the results from HRTEM analysis (Table 2.1). Even at a specific NC size \(D\), why is it that a sub-population of the NCs is in the ordered state, while the remaining is in the disordered, super-ionic state? This is because, in nanocrystalline samples, phase transition points are not necessarily sharp; rather they may be heterogeneously broadened. Thus, even at a temperature \(T > T_c\), the (ensemble-averaged) order/disorder temperature, the ordered phase may persist in a sub-population of NCs. The % sub-population of
NCs in this frozen state, expected to vary as $e^{E_a(D)/RT}$, is indeed found to decrease with decreasing NC size, $D$ (Table 2.1). Specifically, for the 2 nm clusters, not only is the order/disorder transition temperature, $T_c$, below room temperature, but a low activation energy for cationic disorder ensures the prevalence of a molten Cu$^+$ sub-lattice across all NCs in the measured ensemble (Supplementary Fig. 2.3).

2.9 CONCLUSION:

In summary, we found that ultrasmall Cu$_2$Se clusters exhibit a mobile, “liquid-like” Cu$^+$ sub-lattice at room temperature, quite unlike larger NCs and bulk Cu$_2$Se where such a super-ionic phase is seen at significantly higher temperatures. Possibly due to the effect of compressive strain, the clusters exhibit an unusual cationic sub-lattice structure, wherein energetically unfavorable sites in the conduction pathway are stabilized. NC size tuning of phase transition temperatures is well known, but the influence of NC size and associated strain on ionic structure and transport is an open area of investigation. The findings provide insight into the role of vacancies, cation-anion co-ordination, and nature of bonding in the achievement of fast-ion conduction, which may lead to broader design principles$^{174}$ beyond the specific Cu$_2$Se system studied here. For instance, high-pressure superionic phases have been predicted in other materials such as ice.$^{181}$ -T-O-T- pathways are important in solid-state lithium ion conduction.$^{36}$

The properties of Cu$_2$Se clusters make them promising for the fabrication of nanostructured conductors for solid-state electrolytes and ionic switches, which can be operated at room temperature. However, a near-term challenge will involve the achievement of fast-ion conduction through solids comprised of the room-temperature super-ionic phase of Cu$_2$Se. The clusters will need to be assembled into mesoscopic or macroscopic solids, interfacial defects and ligands will
need to be eliminated without modification of the nanocrystalline morphology or the crystallographic phase, and the ionic conduction will need to be characterized using AC impedance measurements, an effort currently underway in our laboratory.

The actively tunable plasmonic properties of the Cu$_2$Se clusters can be exploited for electro-optic switching. Since, the switching ON/OFF of the optical resonance would rely on voltage-assisted in/out migration of a Cu$^+$ ion from the cluster, the fast-ion transport characteristics of the system can be particularly advantageous. Lindenberg and coworkers$^{182}$ have shown that in the super-ionic phase of Cu$_2$S, Cu$^+$ hopping between adjacent sites takes place on the 20 picosecond time-scale. Given that a small number of hops are sufficient for Cu$^+$ to migrate into/out of a 2 nm cluster, ultrafast operation may be possible.

2.10 METHODS:

Synthesis of 2 nm CdSe clusters. The procedure for the synthesis of CdSe clusters was adapted from Yu, K. et al.$^{158}$ Cadmium acetate (0.20 mmol, 53.3 mg) and oleic acid (0.13 mmol, 41 μL) were added to a 25 mL three-neck flask. The flask was repeatedly purged with Ar to remove O$_2$. Under Ar atmosphere, 5 g of trioctylphosphine (TOP) was added to the flask using a syringe and the reaction mixture was heated to 120 °C, and then subject to vacuum for 45 min. Then, the reaction mixture was brought to Ar atmosphere, the temperature was dropped to 100 °C, and a TOP-Se solution (0.05 mmol or 4 mg of selenium powder in 0.4 mL of TOP) was added to the flask. The temperature was raised to 120 °C and the reaction was allowed to proceed for 60 min. The solution was a light yellow color. After synthesis, the clusters were washed repeatedly with toluene and methanol and dispersed in toluene.
Synthesis of 4 nm CdSe NCs (zinc blende). The procedure for synthesis of 4 nm CdSe NCs was adapted from Yang, et al.\textsuperscript{183} Cadmium myristate (192 mg, 0.34 mmol) was added to a flask with 3.4 g, i.e. 4.3 mL of octadecene (ODE). The reaction mixture was heated to 140 °C under Ar atmosphere. The solution was then cooled to 100 °C and subject to vacuum for 30 min. The solution was then put under Ar and cooled to room temperature. A solution of TOP-Se was prepared in a glove box by dissolving 13.4 mg of Se (0.17 mmol) in 126 mg of TOP (0.34 mmol). The TOP-Se solution was injected into the reaction flask. The temperature was raised to 210 °C, which occurred over ~ 9 min. After reaching 210 °C, 48 mg of oleic acid in 0.5 mL ODE was injected into the flask to stabilize growth. Then the reaction proceeded at 210 °C for 50 min. After synthesis, the NCs were washed repeatedly with toluene and methanol and dispersed in toluene.

Synthesis of 6 nm CdSe NCs (wurtzite). The procedure for synthesis of 4 nm CdSe NCs was adapted from Carbone \textit{et al.}\textsuperscript{184} Cadmium oxide (0.06 g), octadecylphosphonic acid (0.28 g), and trioctylphosphine oxide or TOPO (3.0 g) were added to a 50 ml three-neck round-bottom flask. The flask was degassed under vacuum at 150 °C for 1.5 h. The flask was then put under Ar atmosphere and the temperature was gradually increased to 300 °C over the course of 2 h. While slowly ramping up the temperature up to 320 °C, the solution becomes optically clear. After reaching 320 °C, 1.8 mL of TOP was gradually injected into the mixture. A solution of TOP-Se was prepared in a glove-box by dissolving 0.6 g Se in 4.48 ml TOP and stirred at room temperature overnight. The temperature of the mixture in the flask was raised to 360 °C and then 0.45 mL of the TOP-Se solution was injected rapidly. After injection, the solution is heated at 360 °C for 70 sec, or until the solution is a dark red color, after which the heating mantle was removed. The NCs were washed repeatedly with toluene and methanol and dispersed in toluene.
Synthesis of 6 nm CdSe NCs (zinc blende). The procedure for synthesis of 6 nm CdSe NCs was adapted from Liu, et al.\textsuperscript{185} 78.4 mg of Se and 15 mL of octadecene (ODE) were added to 50 mL three-necked round-bottom flask. The flask was heated to 100 °C and subject to vacuum for 30 min. At the same time, 266 mg of Cd(Ac)\textsubscript{2} was added to a 25 mL round-bottom flask with 5 mL of oleic acid. The resulting solution was heated to 100 °C and subject to vacuum for 30 min. Both flasks were put under Ar again. The flask with the Cd salt was heated to 150 °C and the flask with Se was heated to 280 °C for 30 min. The Se solution turned yellow indicating the formation of a Se-ODE complex. Then the solution of Cd was quickly added to the other flask and the temperature was brought to 275 °C, after which the reaction was allowed to proceed for 40 min. After synthesis, the NCs were washed repeatedly with hexane and ethanol and redispersed in toluene.

Ligand exchange with octylamine. For 4 nm and 6 nm CdSe NCs, it was found that an initial ligand exchange of the NCs with octylamine increased colloidal stability of the Cu\textsubscript{2}Se NCs produced from cation exchange. Before cation exchange, solutions of 4 nm and 6 nm CdSe NCs dispersed in toluene were mixed with ~0.5 mL of octylamine, after which the NCs were washed with methanol and redispersed in toluene.

Exchange with Cu\textsuperscript{+}. All exchange reactions were carried out in an oxygen-free, moisture-free, Ar-filled glove box. CdSe NCs or clusters were dispersed in toluene. A solution of tetrakis(acetonitrile) copper(I) hexafluorophosphate ([((CH\textsubscript{3}CN)\textsubscript{4}Cu]PF\textsubscript{6}) in 10% v/v of methanol in acetonitrile was then added dropwise to the NC or cluster solution. The reaction mixture was stirred vigorously in the course of addition. Exchange was monitored by UV-Vis absorption spectroscopy. In exchange reactions with 2 nm CdSe clusters, the Cu\textsuperscript{+} reagent was prepared with 1.5 equivalents of TOP per equivalent of [(CH\textsubscript{3}CN)\textsubscript{4}Cu]PF\textsubscript{6} and was therefore added to the cluster.
solution in TOP-Cu⁺ form, a procedure that enhanced the colloidal stability of Cu₂Se clusters formed from exchange.

Oxidation of Cu₂Se NCs and clusters. To the 2 nm and 6 nm Cu₂Se NCs obtained from exchange, ~50 μL of oleic acid was added for aiding colloidal stability. The samples were then washed with methanol and dispersed in toluene and sonicated for 20 min. Cu₂Se NC or cluster colloids in vials were exposed to air with stirring to achieve oxidation. Small losses in solution volume resulting from evaporation over extended periods of time were counterbalanced by adding anhydrous toluene such that the solution height in the vial was maintained. Ultraviolet-visible-near-infrared (UV-Vis-NIR) spectra in the 300-2000 nm wavelength range were acquired at 1 hour intervals at the onset of the oxidation. At later stages, spectra were acquired at longer time intervals. The colloids were sonicated before every spectral acquisition and a small aliquot of the colloid was extracted and diluted in an NIR transparent cuvette (Spectrocell) to prepare the sample for UV-Vis-NIR spectroscopy. The spectral region with NIR absorption of toluene (ca. 1640-1740 nm) was removed manually from plotted spectra.

Reduction of Cu₂Se NCs and clusters. Oxidized Cu₂Se NCs and clusters were reduced using a strong electron donor, cobaltocene. A cobaltocene solution containing ~51 mg of cobaltocene in 4 ml toluene was prepared. Solution preparation and the reduction reaction were carried out inside the glovebox because cobaltocene is a strong reducing agent that reacts quite rapidly with oxygen. The cobaltocene solution was added in increments of 5 μL to 3.5 ml of the NC or cluster colloid in an NIR transparent cuvette. After each addition, the cuvette was tightly capped and the reaction mixture was allowed to stir for 40 min in the glovebox, after which the cuvette was taken out of the glovebox. A UV-Vis-NIR spectrum was acquired in the wavelength range from 300-2000 nm.
The cuvette was brought back into the glovebox immediately after each spectral acquisition. Sealing the capped cuvette with black tape further helped minimize any air exposure. The spectral region with NIR absorption of toluene (ca. 1640-1740 nm) was removed manually from plotted spectra.

STEM-EDS measurements. Elemental analysis was carried out on each of the three sizes of Cu$_2$Se NCs by scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS). Cu$_2$Se NCs for the measurements were prepared by cation exchange from zinc blende CdSe NCs. For the 4 and 6 nm CdSe NCs, prior to cation exchange, ligand exchange with octylamine was carried out to aid colloidal stability. 200 µL of octylamine was added to a solution of the CdSe NCs dispersed in toluene, followed by washing of the NCs with methanol. The amine-passivated NCs were redispersed in toluene. The 2 nm CdSe clusters were cation exchanged without any prior ligand exchange step. For cation exchange, a solution of CH$_3$CN)$_4$Cu]PF$_6$ in 10% v/v methanol in acetonitrile was added dropwise to the NC or cluster solution. The reaction mixture was stirred over the course of the addition. The exchanged NCs or clusters were cleaned by three successive methanol washing and centrifugation steps and finally redispersed in toluene. UV-Vis absorption spectra (350-1600 nm) were recorded to ensure the completion of the exchange.

STEM/EDS was performed on a JEOL 2010F instrument operating at 200 kV. Samples were prepared by drop casting NCs or clusters from solution onto ultrathin carbon 300-mesh Au grids from Ted Pella followed by repeated washing of the grid with methanol. A zero-background double-tilt holder was used for STEM/EDS measurements. EDS measurements were carried out over a wide-field (ca. 1 µm x 1 µm) of NCs using an Oxford INCA 30 mm ATW detector. Data were collected for 500-800 s and the double-tilt holder was placed at a 10° elevation to maximize
the signal. Elemental quantification was performed in the IXRF Iridium Ultra software, using the integrated intensities of the Cd L\(\alpha\) lines and the Cu and Se K\(\alpha\) lines in the EDS spectra. Atomic %s of Cu, Cd and Se, obtained from the IXRF Iridium Ultra software, were converted to atomic ratios by normalizing the Se content to 1. The Cu:Se:Cd atomic ratios are tabulated in Supplementary Fig. S7 along with EDS spectra for the three sizes.

Phonon scattering measurements. Phonon scattering spectra (intensity vs. Raman shift in the frequency range of 100-600 cm\(^{-1}\)) of Cu\(_2\)Se NC and cluster films on Si substrates were acquired at room temperature on a Horiba Raman confocal imaging microscope. The experiments were carried out using 532.07 nm laser excitation, without filters, and a high-resolution grating of 1800 g/mm blazed at 500 nm. A 50x long working distance (LWD) objective and a spectrophotometer setting of 350 cm\(^{-1}\) were employed, resulting in a spectral resolution of ca. 2 cm\(^{-1}\).

Cu\(_2\)Se samples for the measurements were prepared by cation exchange of zinblende CdSe NCs and clusters. For the 4 nm and the 6 nm zinc blende CdSe NCs, ligand exchange with octylamine was carried out to aid colloidal stability. 70 µL of octylamine was added to a solution of the NCs dispersed in toluene, followed by washing with methanol. The amine-passivated NCs were redispersed in toluene. The 2 nm CdSe clusters were cation exchanged without any prior ligand exchange step. For cation exchange, a solution of tetrakis(acetonitrile) copper(I) hexafluorophosphate ([(CH\(_3\)CN)\(_4\)Cu]PF\(_6\)) in 10% v/v methanol in acetonitrile was then added dropwise to the NC or cluster solution. The reaction mixture was stirred over the course of the addition. The exchanged NCs or clusters were washed with methanol and redispersed in hexane. UV-Vis-NIR spectra were acquired in the wavelength range from 300-2000 nm for all three sizes to determine that the exchange reaction was complete.
Prior to sample preparation, Si substrates were cleaned by sonication in methanol for 10 min, followed by drying in an oven at 120 °C for 15 min. About 40 µL of the Cu₂Se NC or cluster solution was drop cast onto the Si substrate and dried to form a thin film. For each size: 2, 4 and 6 nm, four film samples were prepared, and 1-3 spectra were acquired for each film. Only representative spectra are shown in Supplementary Fig. 6. The longitudinal optical (LO) phonon peak position was determined from each one of the multiple spectra at each size. The averaged LO phonon peak frequency is plotted against size in Fig. 5. The standard deviation of the phonon peak position is shown as the error bar for each data point.

Electron microscopy characterization. High resolution transmission electron microscopy (HRTEM) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were acquired on a JEOL 2010F operating at 200 kV. Samples were prepared by drop casting NCs or clusters from solution onto an ultrathin carbon grid followed by repeated washing of the grid with methanol. Size analysis was performed by measuring particle size along the long axis on HAADF-STEM images using the software, ImageJ. Analysis of the lattice superstructure in each sample was performed using HRTEM images.

 Powder X-ray diffraction (PXRD). PXRD patterns were collected on a Rigaku Miniflex 600 powder x-ray diffractometer operated at full power (40kV - 15 mA) with Cu Kα radiation wavelength (1.54 Å). Data was collected in reflection mode in the 2θ range of 15°-65° using a step size of 0.04° with scans running for 2-3 hrs. Samples were prepared by drop-casting NCs or clusters from solution into a thick film on a zero-background quartz substrate.

 PXRD simulations. Simulated PXRD patterns were generated using the program PowderCell, which performs a structure factor calculation using lattice parameters and atomic positions as input.
parameters. Input parameters for each simulated pattern are tabulated (Tables 2, 3, and 4). All simulated patterns include Debye-Scherer broadening corresponding to the finite crystallite size of 2 nm, 4 nm, and 6 nm, respectively.

Differential scanning calorimetry (DSC) measurements. DSC measurements were carried out on a DSC Q20 V24.10 Build 122 instrument. Prior to collection of a thermogram, each sample was subject to heating run from -30 to 200 °C. We have found that this procedure removes ligands from the NC surface (oleic acid, remnant phosphines etc.), thereby eliminating peaks related to ligand desorption that otherwise show up in the thermogram and complicate the analysis. For ensuring reproducibility, at each size, thermograms (cooling followed by heating) were measured for two separate samples. For at least one sample at each size, the DSC scan was run twice and confirmed to be repeatable.

Cu$_2$Se clusters for the measurement were prepared by cation exchange of CdSe clusters. The 2 nm CdSe clusters were cation exchanged by adding a solution of (CH$_3$CN)$_4$Cu]PF$_6$ in 10% v/v methanol in acetonitrile dropwise to the cluster solution. The reaction mixture was stirred over the course of the addition. The exchanged clusters were washed with methanol multiple times and redispersed in toluene followed by drying under Argon in a glovebox. The dried powder, weighing a few mg, was pressed into a T-Zero aluminum pan for the DSC measurements.

The larger size Cu$_2$Se NCs were prepared following the procedure of Deka et. al. After preparation, the colloidal solution was dispersed in toluene and subjected to selective centrifugation to extract NCs in the desired size range. The NCs were washed twice with ethanol and then dispersed in toluene. An absorption spectrum was acquired in the vis-NIR range (400-1600 nm) to confirm the presence of an LSPR typical of Cu$_2$Se NCs. HRTEM imaging was also
on a JEOL 2010F instrument operated at 200 kV with a 0.5-nm size beam to ensure a nanocrystalline morphology. For DSC measurements, the NC solution was centrifuged to obtain a pellet, which was then dried to obtain a few mg of solid. The solid was pressed into a T-Zero aluminum pan for DSC measurements.
2.11 SUPPORTING TABLES FOR CHAPTER 2:

Supporting Table 2.1. Percentage of NCs with superstructural vacancy ordering evident in HRTEM images. Image analysis was performed on ca. 30 NCs at each size and all images used for analysis are shown in Supplementary Fig. 3. Superstructural ordering is only observed along the <111> direction; only NCs displaying lattice fringes along this direction were considered in the analysis.

<table>
<thead>
<tr>
<th>NC diameter</th>
<th>% of NCs with superstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 nm</td>
<td>0%</td>
</tr>
<tr>
<td>4 nm</td>
<td>10%</td>
</tr>
<tr>
<td>6 nm</td>
<td>80%</td>
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Supporting Table 2.2. Crystallographic parameters for simulated diffraction patterns in Fig. 2.4b.

<table>
<thead>
<tr>
<th>6 nm – Cu₂Se</th>
<th>Space Group: Fm-3m, a = 5.85 Å</th>
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</thead>
<tbody>
<tr>
<td>Element</td>
<td>Wycoff Pos.</td>
</tr>
<tr>
<td>Se</td>
<td>4a</td>
</tr>
<tr>
<td>Cu</td>
<td>8c</td>
</tr>
<tr>
<td>Cu</td>
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</table>

<table>
<thead>
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<th>4 nm – Cu₂Se</th>
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<tbody>
<tr>
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</tr>
<tr>
<td>Cu</td>
<td>8c</td>
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</tbody>
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<table>
<thead>
<tr>
<th>2 nm – Cu₂Se</th>
<th>Space Group: Fm-3m, a = 5.85 Å</th>
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<tbody>
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<td>Element</td>
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</tr>
<tr>
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<td>4a</td>
</tr>
<tr>
<td>Cu</td>
<td>8c</td>
</tr>
<tr>
<td>Cu</td>
<td>4b</td>
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<tr>
<td>Cu</td>
<td>24e</td>
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</table>
**Supporting Table 2.3.** Crystallographic parameters for simulated diffraction patterns in Fig. 2.4c.

### 4 nm – Cu₂Se

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<th>Element</th>
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</thead>
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### 4 nm – Cu₂Se

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<th>y</th>
<th>z</th>
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### 4 nm – Cu₂Se

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<th>z</th>
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<tr>
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</tr>
<tr>
<td>Cu</td>
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**Supporting Table 2.4.** Crystallographic parameters for simulated diffraction patterns in Fig. 2.4d

<table>
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<th>2 nm – Cu₂Se</th>
<th>Space Group: Fm-3m, a = 5.85 Å</th>
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<tbody>
<tr>
<td><strong>Element</strong></td>
<td><strong>Wycoff Pos.</strong></td>
</tr>
<tr>
<td>Se</td>
<td>4a</td>
</tr>
<tr>
<td>Cu</td>
<td>8c</td>
</tr>
<tr>
<td>Cu</td>
<td>4b</td>
</tr>
<tr>
<td>Cu</td>
<td>24e</td>
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<table>
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<tr>
<th>2 nm – Cu₂Se</th>
<th>Space Group: Fm-3m, a = 5.85 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
<td><strong>Wycoff Pos.</strong></td>
</tr>
<tr>
<td>Se</td>
<td>4a</td>
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<td>Cu</td>
<td>8c</td>
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<tr>
<td>Cu</td>
<td>4b</td>
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<tr>
<td>Cu</td>
<td>24e</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>4 nm – Cu₂Se</th>
<th>Space Group: Fm-3m, a = 5.85 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
<td><strong>Wycoff Pos.</strong></td>
</tr>
<tr>
<td>Se</td>
<td>4a</td>
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</table>
Supporting Table 2.4. (cont.) Crystallographic parameters for simulated diffraction patterns in Fig. 2.4d

<p>| | | | | | |</p>
<table>
<thead>
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<td>Cu</td>
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Supporting Figure 2.1. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) of 4 nm and 6 nm Cu$_2$Se nanocrystals (NCs). Top panel shows representative HAADF-STEM images for 4 nm and 6 nm NCs obtained from cation exchange. NC sizes were estimated manually in Image J from STEM images. The diameter of the quasi-spherical NC domains was measured using the line tool. Data from ca. 40 NC domains was used to make the size histograms shown in the bottom panel and to determine average diameters. Samples were prepared by titrating solutions of 4 nm and 6 nm zincblende CdSe nanocrystals in toluene with a methanolic solution of Cu$^+$, as described in the Methods section. Exchange to Cu$_2$Se was monitored via UV-Vis absorption spectroscopy. Fully exchanged samples were precipitated with methanol, dispersed in toluene, drop-cast onto an ultrathin carbon TEM grid, and washed with methanol several times. HAADF-STEM images were acquired on a JEOL 2010F at 200 kV with a 0.5-nm size beam.
Supporting Figure 2.2. A) Ultraviolet-visible absorption spectra of 6 nm Cu$_2$Se nanocrystals (NCs) in the course of oxidation in air. Air oxidation results in the removal of Cu in the form of copper oxide, leading to formation of holes in the valence band. Hole formation is manifested in the emergence of a localized surface plasmon resonance (LSPR) band. With increasing oxidation time, the LSPR band blue-shifts, signifying an increase in the hole density. The peak energy of the LSPR eventually stabilizes to a value of 0.99 eV. B) UV-vis absorption spectra of the oxidized 6 nm Cu$_2$Se NCs in the course of titration with a solution of the reducing agent cobaltocene. Cobaltocene injects electrons into the NCs annihilating the holes in the valence band. As a result, the LSPR redshifts and decreases in intensity, signifying a decrease in the hole density. The 6 nm Cu$_2$Se NCs were prepared by the cation exchange of 6 nm wurtzite CdSe NCs.
Supporting Figure 2.3. High resolution transmission electron microscopy (HRTEM) images of several more 2 nm Cu₂Se clusters. Measured lattice spacings between {111} planes are shown for many of the clusters in the wide-field images. All scale bars correspond to 5 nm.
Supporting Figure 2.3. (cont.) High resolution transmission electron microscopy (HRTEM) images of several more 2 nm Cu₂Se clusters. Measured lattice spacings between {111} planes are shown for many of the clusters in the wide-field images. All scale bars correspond to 5 nm.
**Supporting Figure 2.4.** High resolution transmission electron microscopy (HRTEM) images of several more 4 nm Cu$_2$Se nanocrystals (NCs). Measured lattice spacings between {111} planes are shown for many of the NCs in the wide-field images. All scale bars correspond to 5 nm.
**Supporting Figure 2.5.** High resolution transmission electron microscopy (HRTEM) images of several more 6 nm Cu$_2$Se nanocrystals (NCs). Measured lattice spacings between \{111\} planes are shown for all NCs. All scale bars correspond to 5 nm.
Supporting Figure 2.6. Representative phonon scattering spectra of samples of 2 nm Cu$_2$Se clusters, 4 nm Cu$_2$Se NCs, and 6 nm Cu$_2$Se nanocrystals (NCs) in dried film form on a Si substrate. The primary band seen in each spectrum corresponds to the $A_1$ longitudinal optical (LO) phonon mode of the Cu$_2$Se lattice. The frequency of the LO mode increases with decreasing NC size due to the effect of compressive strain. This effect is plotted in Figure 5 in the main text. Spectra plotted were subject to baseline subtraction and intensity scaling to facilitate easy comparison. Cu$_2$Se clusters and NCs were prepared by cation exchange of zincblende CdSe clusters and NCs of the corresponding size.
Supporting Figure 2.7. Energy-dispersive X-ray spectroscopy (EDS) of a wide-field of a) 2 nm, b) 4 nm and c) 6 nm Cu$_2$Se nanocrystals (NCs), respectively. To the right of each spectrum is shown a low-magnification dark-field scanning transmission electron microscopy (STEM) image of the wide-field over which the EDS was measured. All STEM image scale bars correspond to 200 nm. Samples were prepared by cation exchange of 2 nm, 4 nm, and 6 nm zincblende CdSe nanocrystals in toluene with a methanolic solution of Cu$^+$, as described in the Methods section. Exchange to Cu$_2$Se was monitored via UV-Vis absorption spectrophotometry. Panel d) shows the absorption spectra for the final 2 nm, 4 nm, and 6 nm Cu$_2$Se NCs subject to EDS analysis. Following exchange, samples were precipitated with methanol, dispersed in toluene, drop-cast onto an ultrathin carbon Au-mesh TEM grid, and washed with methanol several times. STEM/EDS was performed on a JEOL 2010F instrument operated at 200 kV with a 0.5-nm size beam. Panel e) shows a table of the elemental compositions and stoichiometries for the 2 nm, 4 nm, and 6 nm Cu$_2$Se NCs as determined by EDS. The Cu:Se ratio is ca. 2:1 for all three sizes. In the EDS spectra, the Cd signal is at the noise level of the measurement. The presence of Au signals is due to the Au-mesh of the TEM grids.
Supporting Figure 2.8. Differential scanning calorimetry (DSC) thermograms for larger-size Cu$_2$Se nanocrystals (NCs) (a-cooling, b-heating) as compared to those for 2 nm Cu$_2$Se clusters (c-cooling, d-heating), respectively. Upon heating, the larger-size NCs show endothermic peaks at 134-138 °C, corresponding to the $\beta \rightarrow \alpha$ transition. Upon cooling, exothermic peaks are obtained at 125-133 °C, indicating some degree of hysteresis. The 2 nm clusters, upon heating, show an endothermic peak at 10 °C, corresponding to the $\beta \rightarrow \alpha$ transition. Upon cooling, an exothermic peak is obtained at -2 °C, indicating some degree of hysteresis. For ensuring reproducibility, at each size, thermograms were measured for two separate samples. For at least one sample at each size, the DSC scan was run twice and confirmed to be repeatable. The larger NCs were prepared as per the procedure of Deka et. al.,$^1$ precipitated with methanol, dispersed in toluene, and then drop-cast onto an ultrathin carbon TEM grid, which was washed with methanol several times prior to imaging. High resolution transmission electron microscopy (HRTEM) imaging was performed on a JEOL 2010F instrument operated at 200 kV with a 0.5-nm size beam. The inset in panel a) shows a representative HRTEM image of the larger NC sample showing NCs in the 9-16 nm size range (scale bar = 15 nm).
Supporting Figure 2.9. The peak at $2\theta = 59^\circ$ in our diffraction patterns is from the quartz sample holder, as seen from a pattern of the holder without any sample. Note in Figure 2.4a, this sample-holder peak appears to increase in intensity, relative to the sample nanocrystal (NC) diffraction peaks, as we go to smaller NC size. This is simply a result of the reduced intensity of the diffraction peaks for the smaller NC samples.
Supporting Figure 2.10. Powder X-ray diffraction (PXRD) patterns were analyzed for determination of lattice strain as a function of nanocrystal (NC) size. The experimental patterns for all three size NCs in the range from $2\theta = 24$ to $39^\circ$ were fit to multi-peak Voigt functions (two peaks for the 2 nm and 4 nm sample patterns and one peak for the 6 nm sample pattern). The peak position for the $\{111\}$ reflection, identified from the fit, is indicated for each size. The strain in the 2 nm clusters relative to the 6 nm NCs is:

$$\frac{\Delta d_{111}}{d_{111}} = -0.045 \quad (2.3)$$

which implies a compressive strain of 4.5%. A table on the right summarizes the results of the strain estimation from the $\{111\}$ peak. Note that strain may not be isotropic.
Supporting Figure 2.11. The experimental powder X-ray diffraction (PXRD) pattern for the 2 nm clusters (background removed, $2\theta = 25$-50° range) was subject to Rietveld refinement in Powder Cell using 5th order polynomial fitting. The fit ($R_p = 11.52$, $R_{wp} = 13.32$) is shown overlaying the scaled experimental pattern. The starting unit cell structure was based on parameters for the 2 nm clusters from Table 2.2. The lattice constant $a_c$, scale factor, $U$, $V$, $W$, and Cu site occupancy factors (SOFs) in $4b$ and $8c$ sites were allowed to vary. The Se SOF in $4a$ sites was set to 1 and Cu SOF in $24e$ sites was set to 0.182. The result of the fitting yielded $a_c = 5.75$ Å, SOF for $4b = 0.36$, and SOF for $8c = 0.28$, i.e., 18% Cu$^+$ occupancy in octahedral sites and 28% occupancy in tetrahedral sites with remaining in $24e$ sites. Note that there are uncertainties involved in this determination due to the low signal-to-noise ratio (S/N) of the experimental pattern of the 2 nm clusters coupled with severe peak broadening and overlap. More rigorous Rietveld analysis and structure determination will be possible using PXRD or full scattering data obtained at a synchrotron. Synchrotron data is expected to have high S/N and low X-ray fluorescence background.
CHAPTER 3: LITHIATION OF COPPER SELENIDE NANOCRYSTALS


3.1 ABSTRACT:

The search for ion-conductive solid electrolytes for Li\(^+\) batteries is an important scientific and technological challenge with economic and sustainable energy implications. In this study, nanocrystals (NCs) of the ion conductor copper selenide (Cu\(_{2-y}\)Se) were doped with Li by the process of cation exchange. Li\(_{2}\)Cu\(_{2-2x}\)Se alloy NCs were formed at intermediate stages of the reaction, which was followed by phase segregation into Li\(_2\)Se and Cu\(_2\)Se domains. Li-doped Cu\(_{2-y}\)Se NCs and Li\(_2\)Se NCs exhibit a possible SI phase at moderately elevated temperatures and warrant further ion-conductance tests. These findings may guide the design of nanostructured super-ionic electrolytes for Li\(^+\) transport.

3.2 INTRODUCTION:

Rechargeable lithium-ion batteries have been powering portable devices and power tools for a few decades.\(^{186}\) However, safety and lifetime concerns remain with this technology due to the use of a liquid electrolyte, which is flammable, leak-prone, corrosive to the electrodes, susceptible to thermal degradation, and also to Li-dendrite formation.\(^{187}\) Solid-state electrolytes offer a potential solution to these problems; but their ionic conductivity is poorer than liquids, which would mar battery charge/discharge speeds, capacities, and energy efficiencies. For this reason, the most ideal solid electrolytes are those, which exhibit superionicity, a phenomenon where the cationic sub-lattice is disordered and mobile,\(^{188}\) resulting in ionic conductivities matching those of liquid electrolytes.
Copper selenide (Cu\textsubscript{2}Se) is a classic superionic (SI) conductor,\textsuperscript{189} which is also earth abundant. The ionic conductivity in its SI state is exceptionally high for a solid: 1-2 \( \Omega^{-1}\text{cm}^{-1} \) at 670 K.\textsuperscript{93,153,190} However, like most solids in this class, the SI phase is only accessible via a phase transition at high temperatures, significantly over the safety limits specified for most consumer electronic devices. For instance, bulk Cu\textsubscript{2}Se exists in the SI phase only above ca. 140 °C.\textsuperscript{169} But, we recently found,\textsuperscript{77} in line with findings in other nanostructures,\textsuperscript{80,146,182,191–195} that Cu\textsubscript{2}Se nanocrystals (NCs) in the few-nm size range exhibit room-temperature SI behavior. As a result, nanostructured Cu\textsubscript{2}Se has potential as a solid electrolyte for Li\textsuperscript{+} batteries. As a further advance toward this goal, we show that Li can be incorporated in SI Cu\textsubscript{2}Se NCs. High mole fractions of Li can be incorporated via substitution of Cu in the NCs, eventually resulting in the formation of lithium selenide (Li\textsubscript{2}Se) NCs. Such insight may be useful in the future for designing nanostructured SI electrolytes for Li\textsuperscript{+} transport.

3.3 INCORPORATION OF Li\textsuperscript{+}:

To produce Li-doped NCs, we employed cation exchange,\textsuperscript{80,196} which is a post-synthetic template-based chemical transformation method for producing NCs in novel morphologies, compositions, and/or unconventional crystal structures.\textsuperscript{80,81,159,160,167,196–202} A LiNO\textsubscript{3} salt was added in the form of a methanolic solution to ca. 6 nm Cu\textsubscript{2}Se NCs at room temperature, with stirring. We chose this size of Cu\textsubscript{2}Se NCs, because it is small enough for the SI phase to be stable near ambient temperature,\textsuperscript{77} while being large enough for facile crystallographic characterization. In the cation exchange transformation, Cu\textsuperscript{+} in the NCs is substituted by the added Li\textsuperscript{+}, while the Se\textsuperscript{2-} anionic sub-lattice is expected to remain untransformed.\textsuperscript{77,78,159,200} The cation exchange of Cu\textsuperscript{+} by Li\textsuperscript{+} was performed in steps by controlled addition of aliquots of the Li\textsuperscript{+} precursor, until no further
replacement of Cu\(^+\) by Li\(^+\) was possible. At each stage in the titration, the NCs were characterized in terms of their structural properties, composition, and spectroscopic attributes. This allowed us to follow the progress of Li-doping and track the evolution of structure and properties of the NC lattice in the course of lithiation.

The cation exchange process from CdSe to Cu\(_2\)Se and the step-wise exchange from Cu\(_2\)Se to Li\(_{2x}\)Cu\(_{2-2x}\)Se was monitored by UV/Vis-NIR optical spectrophotometry. Upon complete cation exchange of CdSe NCs to Cu\(_2\)Se NCs under air- and moisture-free conditions (accomplished by a molar excess of the Cu\(^+\) salt), the visible-region excitonic absorption band associated with CdSe NCs is lost. The spectrum of the product shows an absorption onset in the ca. 1 eV region, corresponding to the band-gap of Cu\(_2\)Se NCs.\(^{78,81,162,165}\) The absorption spectrum is otherwise featureless. In the step-wise exchange of Cu\(^+\) in Cu\(_2\)Se NCs by Li\(^+\), the featureless absorption spectrum undergoes no major changes (Supplementary Fig. 3.1c).
Table 3.1. Elemental composition analysis at four stages of the Li-incorporation reaction determined by ICP-AES. Corresponding absorbance spectra are shown in Figure 3.1 a. Note that the Li mole fraction tabulated here represents an average over a large ensemble of NCs. The precise Li mole fraction likely varies from NC to NC.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Element</th>
<th>Mole fraction relative to Se</th>
<th>Li mole fraction $x = \frac{\text{Li}}{\text{Li} + \text{Cu}}$</th>
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</table>

We performed the exchange reaction in an alternate fashion. The starting Cu$_2$Se NCs were first oxidized, a process known$^{78,162,165}$ to result in the development of Cu vacancies in the NC lattice:

$$(\text{Cu}_2\text{Se})_n + \frac{n_y}{4}\text{O}_2 \rightarrow (\text{Cu}_{2-y}\text{Se})_n + \frac{n_y}{2}\text{Cu}_2\text{O} \text{ (oxidation and vacancy generation)} \quad (3.1)$$
where the degree of sub-stoichiometry, $y$, typically stabilizes at ca. 0.2. The formation of Cu vacancies is accompanied by the emergence of a well-defined localized surface plasmon resonance (LSPR) band in the near-infrared (NIR) region of the spectrum (Figure 3.1a). We monitored this LSPR band as the cation exchange of the Cu$_{2-y}$Se NCs with the Li$^+$ salt was performed step-wise. With increasing degree of Li-exchange, the LSPR band red-shifted and decreased in absorbance. Upon approaching the saturation degree of Li-exchange, the LSPR band was fully extinguished; only a featureless spectrum with an absorption onset in the ca. 1 eV region remained. Similar to what has been shown for Na$^+$ salts, the LiNO$_3$ salt appears to work as i) a reducing agent that removes the Cu vacancies from the NC lattice and itself undergoes oxidation:

$$(\text{Cu}_{2-y}\text{Se})_n + \frac{ny}{2}\text{Cu}_2\text{O} + ny\text{LiNO}_3 \rightarrow (\text{Cu}_2\text{Se})_n + \frac{ny}{2}\text{Li}_2\text{O} + ny\text{NO}_2 + \frac{ny}{2}\text{O}_2 \text{ (reduction and vacancy removal)} \quad (3.2)$$

and ii) also the source of Li$^+$ ions for exchange with Cu$^+$ in the NC:

$$(\text{Cu}_2\text{Se})_n + 2nx\text{LiNO}_3 \rightarrow (\text{Li}_{2x}\text{Cu}_{2-2x}\text{Se})_n + 2nx\text{CuNO}_3 \text{ (cation exchange)} \quad (3.3)$$

All further study of the Li-doping process (Supplementary Fig. 3.2-3.13) was carried out on such air-oxidized NCs because the Cu-deficient, sub-stoichiometric form (Cu$_{2-y}$Se) obtained by air exposure represents the stable chemical state of cuprous selenide in ambient atmosphere. Unlike Cu$_2$Se NCs, the air-oxidized Cu$_{2-y}$Se NCs can be expected to maintain a stable composition and characteristics in the course of measurements performed under ambient conditions.

The elemental compositions of the NCs at the four stages of the Li-exchange process were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES), the
results of which are summarized in Tables 3.1 and Supplementary Table 3.1. The molar ratio ($\chi$) of Li to total metal (Li + Cu), also referred to as the Li mole fraction, represents the degree of Li-incorporation. We obtained a limiting conversion of $\chi$=0.66, beyond which further exchange did not appear to take place (Supplementary Fig. 3.12). Such saturation in exchange conversion may signify a solubility-limited equilibrium attained between the reactant and product phases. Transmission electron microscopy (TEM) at the initial and final stages (Figures 3.1 b-e, Fig. Supplementary 3.2, and Supplementary Fig. 3.13) shows that nanocrystalline morphology and crystallinity is maintained in the exchange process. The average NC diameter appears to increase from 6.1 nm ($\chi$=0) to 7.8 nm ($\chi$=0.66).

\textbf{Figure 3.1.} Li-incorporation in Cu$_{2-y}$Se NCs by room-temperature cation exchange a) Optical Vis-NIR absorbance spectra (normalized to the maximum absorbance in the 380-1600 nm range) obtained in the course of the formation of Li-doped Cu$_2$Se NCs. The template CdSe NCs (black curve) show an exciton band in the visible region. Upon complete cation exchange to Cu$_2$Se, followed by air oxidation to Cu$_{2-y}$Se NCs, the spectrum (red curve, $\chi$=0) shows a strong LSPR absorption band in the NIR region. Upon increasing Li-incorporation in the Cu$_{2-y}$Se NCs, the LSPR band exhibits a decrease in absorbance and a red-shift. The highest exchanged sample (pink curve, $\chi$=0.66) shows a complete absence of the NIR absorption band. Note that the Li/metal molar ratio ($\chi$) indicated in the legend is based on elemental analysis (Table 3.1) of representative Li-doped Cu$_{2-y}$Se NC samples prepared using the same recipe. (b and d) Representative TEM image and (c and e) NC size-distribution for (b and c) $\chi$=0 NCs and the (d and e) $\chi$=0.66 NCs. The NC size shows an apparent increase from an average of 6.1 nm ($\chi$=0) to 7.8 nm ($\chi$=0.66). The standard deviation ($\sigma$) in the NC size is indicated by the error bar and listed along with the sample size ($n$).
3.4 STRUCTURE OF Li-DOPED NCs:

Powder X-ray diffraction (pXRD) was employed to determine the lattice structure of the NCs (Figure 3.2 and Supplementary Figs. 3.3-3.8) at four stages of the Li-exchange reaction. From pXRD, the initial Cu$_{2-y}$Se NCs are observed to possess the defect anti-fluorite structure known for bulk Cu$_2$Se$^{171,203}$ as well as for NCs$^{77}$ of 6 nm diameter. The structure consists of an *fcc* Se sub-lattice and a Cu sub-lattice with ca. 3 Cu atoms occupying the tetrahedral (8c) sites and remaining ca. 5 Cu atoms in trigonal (32f) sites. A structure factor simulation with these cation occupancies (Supplementary Fig. 3.3) showed good agreement with the experimental pXRD. If Cu atoms were all located in tetrahedral sites (rather than a fraction occupying the trigonal sites) the result would have been a significant {200} reflection, which was not observed in the experimental pXRD. The closest match with experimental peak positions, particularly the {220} reflection, was obtained at a lattice constant of 5.72 Å, marginally smaller than the value of 5.74 Å for bulk Cu$_{1.8}$Se.$^{204}$ It is known that NCs can exhibit some degree of compressive strain relative to the bulk solid.$^{77,150,205-207}$ The measured pXRD patterns (Figure 3.2 a) of the Li-doped NCs at all stages are best simulated (Figure 3.2 b) by a crystal structure consisting of a *fcc* Se sub-lattice and Li and Cu located at interstitial sites within the *fcc* cage (see crystallographic parameters listed in the Supporting Fig. 3.4-3.6). Thus, the pXRD results indicate that the Se sub-lattice maintains its *fcc* arrangement in the course of Li-doping, which is consistent with the fact that Li$_2$Se exhibits an anti-fluorite crystal structure,$^{208,209}$ similar to Cu$_2$Se.

At an intermediate degree of Li-incorporation ($x$=0.19), the NCs showed a pXRD pattern similar to that of the initial NCs. However, all reflections (\{111\}, \{220\}, and \{311\}) shifted to lower 2θ, signifying an increase in corresponding lattice spacings. Since Li$_2$Se has a lattice constant (\(a_c=6.0\) Å$^{210}$ larger than that of Cu$_2$Se, the measured pXRD pattern is best explained by the formation of a
Li$_2$Cu$_{2-x}$Se alloy. A pXRD pattern was simulated for such an alloy with an identical structure as the initial NCs but with a fraction of the trigonal Cu atoms replaced by Li atoms (Supplementary Fig. 3.4). The simulation reproduces the experimental pattern, with the best match with the experimental {220} peak position obtained with a lattice constant of 5.76 Å.

At the second intermediate stage of Li-doping ($x=0.26$), the pXRD peaks ({$111$}, {$220$}, and {$311$}) showed a further small shift to lower $2\theta$, signifying a further increase in lattice spacing approaching Li$_2$Se parameters. A lattice constant of 5.77 Å fits the observed {220} peak position well. From this lattice constant of the Li-doped NCs, relative to that of the initial Cu$_2$Se NCs, we estimate that $x=0.26$ level of Li-doping causes a volumetric expansion of the lattice by ca. 3 %. In addition, a broad peak centered at $2\theta = 32^\circ$ was found to emerge in the experimental pXRD. This peak corresponds to a {200} reflection and is associated with an increase in cationic occupancy of tetrahedral and/or octahedral sites. Thus, it appears that in addition to Cu substitution by Li, some Cu migrates from trigonal sites to vacant tetrahedral or octahedral sites. Structure factor simulation of a Li$_2$Cu$_{2-x}$Se alloy ($x=0.26$) with such a cation arrangement (Supplementary Fig. 3.5) reproduces the observed pXRD pattern.
**Figure 3.2.** Structure of NCs in the course of Li-incorporation. a) Experimental and b) simulated pXRD patterns for NCs at various stages of exchange are shown vertically stacked: $x=0$ (red curve), $x=0.19$ (blue curve), $x=0.26$ (green curve), and $x=0.66$ (pink curve). are shown in (a). For the $x=0.66$ NCs, distinct reflections corresponding to Li$_2$Se and Cu$_2$Se phases are observed, which are assigned to specific Miller {hkl} indices for Li$_2$Se (labels in magenta) and Cu$_2$Se (labels in orange) on the basis of reference patterns of bulk Li$_2$Se (ICDD # 00-047-1696) and bulk Cu$_2$Se (ICDD # 01-080-4377), respectively. The lattice constants and site occupancies of ions corresponding to the simulated patterns are provided in the SI in Supplementary Figures 3.3-3.6. Patterns in (a) and (b) are both normalized to the maximum peak intensity. The dotted black lines in panel (a) indicate peak maxima positions for the reflections of the initial Cu$_{2.3}$Se NCs. The gray tick marks in panel (b) correspond to peak maxima positions of the experimentally measured reflections to allow comparison of simulated pXRD patterns with corresponding experimental ones.

Upon reaching a Li-rich stage: $x=0.48$ (Supplementary Fig. 3.11) and particularly, $x=0.66$ (Figure 3.2), the NCs appear from pXRD patterns to have undergone drastic structural changes. In particular, the peaks for the {111}, {220}, and the {311} reflections split into two, indicating phase segregation into Cu$_2$Se and Li$_2$Se domains. An alloyed structure with $x=0.66$ fails to capture the split peaks (Supplementary Fig. 3.7). On the other hand, a linear combination of simulated patterns of Li$_2$Se and Cu$_2$Se (with weights corresponding to a 1.94:1 mole ratio, i.e., $x=0.66$) reproduces the measured pXRD pattern (Figures 3.2 and Supplementary Fig. 3.6). The cation arrangement of both Cu$_2$Se and Li$_2$Se domains was based on the initial NC structure. The lattice constant for Cu$_2$Se
domains was set to 5.72 Å similar to the initial NC structure and also in agreement with the observed peak position of the \{220\} reflection. The lattice constant for the Li$_2$Se domains was set to 6.05 Å,$^{210}$ consistent with the known bulk lattice constant of Li$_2$Se and also with the observed peak position of the Li$_2$Se \{220\} reflection.

Lattice constants of Cu$_2$Se (5.72 Å) and Li$_2$Se (6.05 Å) domains estimated from pXRD patterns suggest that Li$_2$Se has a ca. 17 % larger unit cell by volume than the initial Cu$_2$Se. Thus, Li-doping of Cu$_2$Se NCs to a mole fraction of $x$=0.66 is estimated to expand the lattice by ca. 11 %. The resulting tensile stress can be drastic enough to induce phase separation$^{211,212}$ into Cu$_2$Se and Li$_2$Se domains. In other words, the saturation level of Li-doping observed here (Supplementary Fig. 3.12) may represent a solubility limit for Li in Cu$_2$Se. Consistent with the findings from pXRD, the TEM imaging of the final stage NCs shows visual evidence of individual NCs segregated into distinct Li$_2$Se and Cu$_2$Se domains (Supplementary Fig. 3.13). Such segregation can give the appearance of an overall NC size increase (Figure 3.1 c,e).
Figure 3.3. DSC thermograms identifying the phase transition points in (a) the Cu$_2$Se NCs and (b) the most Li-exchanged NCs ($x=0.66$). Cooling and heating cycles are denoted by blue and red curves, respectively.

3.5 PHASE TRANSITION BEHAVIOR OF Li-DOPED NCs:

As per established practice,$^{77,93,190}$ differential scanning calorimetry (DSC) was used to examine the presence of an ordered-to-SI phase transition in the final Li-exchanged NCs (Figure 3.3 b and Supplementary Fig. 3.9). For the initial Cu$_2$-$y$Se NCs, the phase transition point is found to be close to room temperature, i.e., 22 °C in the heating half-cycle and 13 °C in the cooling half cycle. Although bulk Cu$_2$Se transitions to the SI form at 130-140 °C range, NCs have a significantly depressed transition temperature, as shown recently for Cu$_2$Se$^{77}$ as well as for other related SI solids, Cu$_2$S$^{144}$ and Ag$_2$Se.$^{145,170,213}$

Upon Li doping of the Cu$_2$-$y$Se NCs, the ordered-to-SI phase transition appears to shift to moderately higher temperatures (Supplementary Fig. 3.10). The transition peak is also
significantly broadened in the Li-doped NCs, which may be a manifestation of heterogeneity in the Li mole fraction across the NCs.

DSC of the final NCs shows a relatively weak ordered-to-SI phase transition at 28 °C/24 °C and a stronger transition at 68 °C/54 °C in the heating/cooling cycle. The observation of two distinct phase-transition points is possibly due to the presence of two separate chemical domains present in the product NCs, as determined by pXRD. The weaker transition may be attributed to the smaller fraction of Cu$_2$Se domains present in the mixture. These Cu$_2$Se domains are possibly lightly Li-doped, which would explain the deviation of their transition temperature from that of the initial Cu$_2$Se NCs (Figure 3.3a), consistent with the observed increase in the transition temperature upon Li doping (Supplementary Fig. 3.10). On the other hand, the stronger transition in the DSC of the final NCs originates from the higher fraction of Li$_2$Se NCs present in the product.

Conclusive assignment of the thermogram peak observed for Li$_2$Se NCs to an ordered-to-SI transition is not possible without temperature-dependent ion conductance measurements. Alternate assignments are possible, for instance, to a transition from a phase separated structure to an alloyed structure. But, the latter assignment is less probable. The Li$_2$Se and Cu$_2$Se phases are segregated into distinct domains (Supplementary Fig. 3.13). Transition to an alloyed structure would require the mixing of two lattices with a fair degree of mismatch and inter-domain cation migration. Such mixing entails thermodynamically and kinetically a more severe change as compared to the transition to a SI phase, where cations need only to be mobile within a crystalline domain and no drastic anionic rearrangement is required. The phase-segregated-structure-to-alloy transition, if one such exists, can be expected to occur at significantly higher temperatures as compared to the
ordered-to-SI transition, which is the likely assignment for the strong peak in the DSC thermogram of the final NCs (Figure 3.3 b).

3.6 CONCLUSIONS:

In conclusion, thus, a high mole fraction of Li can be incorporated into Cu$_2$-Se NCs by substitutional doping. At a saturation concentration of Li, Li$_2$Se NCs are formed by phase segregation. Both Li-doped Cu$_2$-Se NCs and Li$_2$Se NCs exhibit from thermograms a possible SI phase at moderately elevated temperatures close to the practical operating range of Li$^+$ batteries. This finding is promising for the use of this material as a solid electrolyte; however, future work needs to be undertaken to confirm the SI nature of this high-temperature phase and characterize the magnitude of the cation (Li$^+$) conductivity in this phase.

3.7 METHODS:

**Synthesis of CdSe nanocrystals (NCs).** For synthesis of 6 nm diameter CdSe NCs, a procedure adapted from Liu, et. al. was employed. Briefly, 78.4 mg of Se and 15 mL of octadecene (ODE) were added to a 50 mL three-necked round-bottom flask. The flask was heated to a temperature of 100 °C and subject to vacuum for 30 min. Alongside, 266 mg of Cd(Ac)$_2$ was added to a 25-mL round-bottom flask containing 5 mL of oleic acid. The resulting solution of the Cd$^{2+}$ salt was heated to 100 °C and subject to vacuum for 30 min. Both flasks were then put under Ar. The flask with the Cd$^{2+}$ salt solution was heated to 150 °C and the flask with Se was heated to 280 °C for 30 min. The Se solution turned yellow indicating the formation of a Se-ODE complex. Then the Cd$^{2+}$ solution was rapidly added to the other flask and the temperature was brought to 275 °C, after which the reaction was allowed to proceed for 40 min. After synthesis, the NCs were purified of
unreacted precursors by subjecting them to multiple cycles of washing (with hexane and ethanol) and centrifugation at 6000 rpm for 10 min each. Prior to the final purification step, 0.5 mL of oleic acid was added to enhance the colloidal stability of the NCs. The purified NCs were re-dispersed in toluene.

**Cation exchange and Li-incorporation in NCs.**

*Cation exchange synthesis of Cu$_2$Se NCs:* The cation exchange-based conversion of CdSe to Cu$_2$Se was carried out in an oxygen-free, moisture-free, Ar-filled glove box. To a solution of 100 μL of CdSe NCs dispersed in 3.5 mL of toluene, a solution of tetrakis (acetonitrile) copper(I) hexafluorophosphate ([((CH$_3$CN)$_4$Cu]PF$_6$) in 10% v/v of methanol in acetonitrile (i.e., 16 mg Cu$^+$ salt in 0.2 mL methanol and 2 mL acetonitrile) was added dropwise. The reaction mixture was stirred vigorously during addition, and the completion of the reaction was monitored by the complete loss of the visible region excitonic peak associated with CdSe NCs, as probed by UV-Vis absorption spectrophotometry. This solution was purified by two cycles of washing with methanol and centrifugation at 7000 rpm for 10 min each. Oleic acid (~50 μL) was added to this solution before the last purification cycle to increase colloidal stability. The final Cu$_2$Se NCs were re-dispersed in toluene and used for further analysis and/or Li-doping.

*Oxidation of Cu$_2$Se NCs.* The purified Cu$_2$Se NCs dispersed in toluene were sonicated for 10 min without heating, followed by exposure to air with stirring for 48 h or more to achieve oxidation of the Cu$_2$Se to Cu-deficient Cu$_{2.5}$Se. A UV-Vis-NIR spectrum of the oxidized NC solution in the 350–1600 nm wavelength range was acquired to ascertain the presence of a NIR localized surface plasmon resonance (LSPR) band.
Cation exchange of Cu$_{2-y}$Se NCs with Li$^+$ salt. Samples with different mole fractions ($x$) of Li-incorporation were prepared by cation exchange with a Li$^+$ salt: unexchanged, two intermediate stages, and a most exchanged. For the range of analyses described below, multiple samples at each $x$ were required. Therefore, a well-defined recipe was used to achieve a given degree ($x$) of Li-incorporation. In each case, 1.5 mL of a stock CdSe NC solution was diluted with 4 mL of toluene inside the glovebox. Cation exchange of CdSe to Cu$_2$Se was accomplished by adding drop-wise to the CdSe NC solution a solution of (CH$_3$CN)$_4$Cu[PF$_6$] in 10% v/v of methanol in acetonitrile (i.e., 200 mg Cu$^+$ salt in 0.5 mL methanol and 5 mL acetonitrile). The reaction mixture was stirred vigorously during addition, and the completion of the reaction was monitored by the complete loss of the visible region excitonic peak associated with CdSe NCs, as probed by UV-Vis absorption spectrophotometry. The Cu$_2$Se NCs obtained from cation exchange were subject to oxidation to Cu$_{2-y}$Se NCs, as described above. A UV-Vis-NIR spectrum of the Cu$_2$Se NC solution in toluene was acquired to ascertain the presence of a NIR localized surface plasmon resonance (LSPR) band. This is the initial stage sample for all Li-incorporation reactions.

For Li-incorporation, a stock solution of LiNO$_3$ in methanol (~942 mM) was freshly prepared. A specific volume of this Li$^+$ salt solution was added at room temperature with stirring to a solution of the Cu$_{2-y}$Se NCs prepared as above.

For the first intermediate stage sample, 0.5 mL of the solution was added with stirring under ambient conditions and allowed to proceed for 2 h. For the second intermediate stage sample, 3 mL of the Li$^+$ salt solution was added and a similar procedure was followed. In all cases, the resulting reaction mixture was sonicated for 15 min with no heating and then purified of leftover
metal salts by washing with methanol and centrifugation at 7000 rpm for 10 min. The resulting NC precipitate was dispersed in hexane.

For the most exchanged sample, the procedure leading up to the second intermediate stage was performed as above and the resulting NCs were purified and re-dispersed in toluene. Then, 2 mL of the Li$^+$ salt was gradually added to the NC solution, which was followed by the addition of ~100 μL of oleic acid for colloidal stability and sonication for 40 min without heating. The resulting NC solution was purified as described above and the final precipitate was dispersed in hexane. We found that further addition of Li$^+$ salt solution and/or allowing additional reaction time did not produce any further changes in the powder X-ray diffraction (pXRD) pattern (see Supplementary Fig. 3.12).

For the Li-doping of near-stoichiometric Cu$_2$Se NCs (Supplementary Fig. 1c), a similar procedure as above was followed as detailed above except the starting Cu$_2$Se NCs were unoxidized, and all subsequent reactions were performed in an air-free glovebox. Care was taken to prevent air exposure or oxidation during sonication and purification cycles.

**Elemental analysis.** Elemental compositions of the NCs at four stages of Li-incorporation (initial Cu$_{2+y}$Se, first intermediate, second intermediate, and final) were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). For each of the four cases, the reaction mixture or solution containing NCs was purified of metal salt precursors by two cycles of centrifugation and washing with toluene and methanol. The resulting NC precipitate was dried in a quartz digestion tube by flowing N$_2$ gas over the precipitate. The sample (few mg) at each of the four stages was subject to this preparation and then analyzed by ICP-AES for determination of the elemental composition. Measured weight percentages of Se, Cu, and Li were converted to atom
percentages values, from which a Li/metal molar ratio ($x$) at each of the stages was determined (Table 3.1 and Supplementary Fig. 3.1).

**X-ray diffraction analysis.** pXRD patterns were collected on a Rigaku Miniflex 600 powder X-ray diffractometer operated at full power (40 kV-15 mA) with Cu K$_\alpha$ radiation wavelength of 1.54 Å. Data was collected in reflection mode in the 2θ range of 20°–65° using a step size of 0.04° with scans running for 2–3 h. Samples were prepared by drop-casting NCs onto a quartz sample holder. Before each run, the quartz crystal was cleaned with aqua regia and DI water. Diffraction patterns were plotted in Origin Lab software and a manual baseline subtraction was performed for these patterns. No background subtraction was performed.

**High resolution transmission electron microscopy (HRTEM) imaging.** The initial Cu$_{2-x}$Se NCs and the most Li-exchanged NCs were subject to HRTEM imaging at room temperature. NC samples at different stages of Li-incorporation were prepared as described in the cation exchange section. To the NC solution, 0.3 mL of oleic acid was added for colloidal stability followed by purification of the NCs by two cycles of and washing with methanol and centrifugation at 7000 rpm for 15 min. The NC precipitate was dispersed in hexane and diluted 100-fold. The NCs were transferred onto an ultrathin carbon on lacey carbon grids as follows: the TEM grid was then held with tweezers and dipped once in the NC solution and then allowed to dry in a vacuum desiccator. HRTEM images were collected at a range of magnifications on a JEOL 2010-EFEG instrument operating at 200 kV. Size analysis was performed using the Fiji (Image J distribution) software. The diameter of each NC was measured manually. These measurements were tabulated and a histogram was generated.
**Differential scanning calorimetry (DSC).** The initial Cu$_2$ySe NCs, intermediates, and the most Li-exchanged NCs were subject to DSC measurements. NC samples at different stages of Li-incorporation were prepared as described in the cation exchange. NC samples for this measurement need to be thoroughly washed to remove surface ligands, which may otherwise present interfering signals in the DSC thermograms. The synthesized NC colloid was purified by washing with methanol and centrifugation at 7000 rpm for 10 min, followed by drying of the NC precipitate by blowing N$_2$ over it. The dried powder (few mg) was then pressed into a zero-T DSC aluminum can. The calorimetry measurements were carried out on a DSC Q20 V24.10 Build 122 instrument with a scan rate of 10 °C/min. Prior to a measurement, a full range heating cycle (from -30 to 200 °C for initial Cu$_2$ySe NCs and -50 to 300 °C for the most Li-exchanged NCs) was carried out to desorb ligands (oleic acid) from the NC surfaces, so that the measured DSC is not complicated by peaks originating from ligands. DSC thermograms were typically measured for a couple of samples at each stage. Multiple heating and cooling runs were performed to confirm reproducibility of the measured thermogram (Supplementary Fig. 3.9, 3.10).

**Structure factor simulations.** Simulated pXRD patterns were generated using the program Powder Cell, which performs a structure factor calculation using crystal symmetry, lattice constants, atomic positions, site occupancies, and Debye-Scherer broadening as input parameters. These simulations were performed with the objective of modeling the diffraction peak positions of the measured reflections for each NC sample. We did not attempt to fit relative diffraction peak intensities, because the crystallographic orientation of the NCs in the pXRD measurement, which can influence relative intensities of reflections, is uncertain. Input parameters for each simulated pXRD pattern are tabulated (Supplementary Fig. 3.3–3.7). The X-ray wavelength was set to 1.54 Å, corresponding to Cu K$_{\alpha1}$ radiation. All simulated patterns include Debye-Scherer broadening.
(peak-dependent fwhm of 1.4° at 2θ = 25°) corresponding to the finite crystallite size of 6 nm, which is the diameter of the initial NCs, and a Lorentzian peak profile. The intermediate stage NCs were modeled as alloys, with the Li/metal molar ratio set to the ICP-AES measurement results. The alloy was assumed to be homogeneous across the extent of the entire NC. For the most exchanged sample, the simulated pattern (Supplementary Fig. 3.6) was generated by a 2.3:1 weighted combination of Li₂Se and Cu₂Se domains, corresponding to the 1.94:1 molar ratio of Li₂Se to Cu₂Se, i.e., x = 0.66. An alloy with x = 0.66 was also examined, but it was not found to fit the measured pXRD (Supplementary Fig. 3.7).
3.8 SUPPORTING TABLE AND FIGURES FOR CHAPTER 3:

Supporting Table 3.1. Elemental composition analysis confirming reproducibility of the Li-doping of NCs. The procedure by which Li-doped NCs at various stages were prepared are described in the Experimental Methods section and the resulting elemental composition of the NC samples (Trial 1) is provided in Table 3.1. To confirm reproducibility of this method, a second trial (Trial 2) was performed using a similar procedure. NCs at an additional intermediate stage (third intermediate) were also prepared by the addition of 5 mL of the Li$^+$ salt solution in methanol (~942 mM) to the initial Cu$_{2-y}$Se NCs. For NC samples at each of these stages, the mole fraction, $x$, of Li was measured by ICP-AES. Comparison with the Li mole fraction for NC samples prepared in Trial 1 shows that the variation is low, as seen from the standard deviation in $x$ tabulated below.

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<th>SD in $x$</th>
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</tr>
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<tr>
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</tbody>
</table>
Supporting Figure 3.1. (a) Optical UV-Vis-NIR absorbance spectra for NCs at four stages of Li-incorporation into the oxidized Cu$_{2-y}$Se NCs. These NC samples were used for ICP-AES analysis. The absorbance spectrum of the template CdSe NCs used for the sample preparation is shown for reference. A first exciton peak around 660 nm is seen, which disappears upon cation exchange conversion to Cu$_2$Se. Oxidation of Cu$_2$Se to Cu$_{2-y}$Se results in the development of a NIR LSPR peak. Spectra are also shown for the first intermediate stage and second intermediate stages, which have progressively red-shifted LSPR peaks. Finally, the most exchanged sample has a spectrum which lacks any LSPR absorbance. (b) Optical UV-Vis-NIR absorbance spectra for initial Cu$_{2-y}$Se NC and most Li-exchanged NC samples used for DSC characterization. Note that the Li/metal ratio (x) indicated in the legend is based on elemental analysis (Table 1) of representative Li-doped Cu$_{2-y}$Se NC samples prepared using the same recipe. (c) The optical absorbance of the CdSe NCs (purple spectrum) shows the first exciton peak of 660 nm. Upon cation exchange conversion of the CdSe NCs to Cu$_2$Se NCs, the exciton peak was lost and a featureless absorption with an onset at 1000 nm was obtained. Upon doping of the unoxidized Cu$_2$Se NCs with Li (the amount of ~942 mM Li$^+$ solution added is indicated in the legend), the spectrum remains featureless. Note that the Li$^+$ salt solution by also itself has no absorbance in the spectral range. A sharp peak associated with methanol vibrational absorption observed around 1400 nm is labeled.
**Supporting Figure 3.2.** Representative HRTEM images of (a-d) initial Cu$_{2.5}$Se NCs and (e-h) most Li-exchanged NCs. The magnifications for the panels (a-c) is 750 kx, for panel (d) it is 240 kx, and for panels (e-g), it is 450 kx, and for panel (h), it is 300 kx.
Supporting Figure 3.3. (a) Comparison of experimental (baseline subtracted) and simulated pXRD patterns of the initial Cu$_{2-y}$Se (x = 0) NCs. Both patterns were normalized to their most intense peak, prior to plotting. (b) Crystallographic parameters of the Cu$_2$Se lattice used for structure factor simulations. This data corresponds to the results in Fig. 3.2.
Supporting Figure 3.4. (a) Comparison of experimental (baseline subtracted) and simulated pXRD patterns of the Li-doped (x = 0.19) Cu_{2-x}Se NCs. Both patterns were normalized to their most intense peak, prior to plotting. (b) Crystallographic parameters of the Li_{2x}Cu_{2-2x}Se alloy lattice used for structure factor simulations. This data corresponds to the results in Fig. 3.2.
Supporting Figure 3.5. (a) Comparison of experimental (baseline subtracted) and simulated pXRD patterns of the Li-doped \((x = 0.26)\) \(\text{Cu}_2\text{ySe}\) NCs. Both patterns were normalized to their most intense peak, prior to plotting. (b) Crystallographic parameters of the \(\text{Li}_{2x}\text{Cu}_{2-2x}\text{Se}\) alloy lattice used for structure factor simulations. This data corresponds to the results in Fig. 3.2.
Supporting Figure 3.6. (a) Comparison of experimental (baseline subtracted) and simulated pXRD patterns of the Li-doped (x = 0.66) Cu$_2$ySe NCs. Both patterns were normalized to their most intense peak, prior to plotting. The simulated pattern was generated by a 2.3:1 weighted combination of Li$_2$Se and Cu$_2$Se domains, corresponding to a 1.94:1 molar ratio of Li$_2$Se to Cu$_2$Se, i.e., x = 0.66. Diffraction peaks associated with Li$_2$Se and Cu$_2$Se domains are labeled. (b) Crystallographic parameters of the Li$_2$Se and Cu$_2$Se used for the structure factor simulations. This data corresponds to the results in Fig. 2. The agreement between experiment and simulation indicate that the most Li-exchanged sample has phase segregated Li$_2$Se and Cu$_2$Se domains.
Supporting Figure 3.7. (a) Comparison of experimental (baseline subtracted) and simulated pXRD patterns of the Li-doped \((x = 0.66)\) Cu_{2-y}Se NCs. Both patterns were normalized to their most intense peak, prior to plotting. (b) Crystallographic parameters of the Li_{2x}Cu_{2-2x}Se alloy lattice used for structure factor simulations. The poor agreement between experiment and simulation indicate that the most Li-exchanged sample is not an alloy.
Supporting Figure 3.8. (a) Experimental pXRD pattern of the clean quartz sample holder (with no deposited NCs) used for pXRD measurements. The pXRD of the most exchanged NCs, corresponding to experimental patterns in Supplementary Figs. 3.6 and 3.7, is plotted for comparison without normalization or background subtraction. (b) Experimental XRD pattern for the quartz holder plotted with a magnified intensity range indicating that the quartz holder itself gives a diffraction peak at $2\theta = 59^\circ$. 

Supporting Figure 3.9. DSC thermograms for (a) Cu$_2$-ySe NCs (x = 0) (top: cooling half-cycle, bottom: heating half-cycle) and (b) Li-doped NCs (x = 0.66) (top: cooling, bottom: heating). For ensuring reproducibility, thermograms are shown for two similarly prepared samples (labeled sample 1 and 2) at each composition. For each sample, the DSC scan cycle was run thrice (labeled cycle 1, 2, and 3) to confirm reproducibility of the thermogram. Thermograms from repeated cycling are shown vertically stacked. Only those peaks in the thermogram that reproducibly appear across all cycles are assigned to phase transitions in the NCs and labeled by the peak temperature. Other features are thought to be artefactual. There is a small cycle-to-cycle variation in the transition point (DSC peak location), as indicated by dashed lines. The data presented in Fig. 3.3a corresponds to the x = 0 sample 2, cycle 3 heating/cooling curves shown here. The data presented in Fig. 3.3b corresponds to the x = 0.66 sample 1, cycle 2 heating/cooling curves shown here.
Supporting Figure 3.10. DSC thermograms (top: cooling half-cycle, bottom: heating half-cycle) for Li-doped Cu$_{2-y}$Se NCs at intermediate stages: (a) $x = 0.18$ and (b) $x = 0.27$. These samples were prepared as described in the Experimental Methods and Supplementary Table 3.1 (Trial 2) and DSC characterization was performed as described in the Experimental Methods. Thermograms from repeated cycling are shown vertically stacked to demonstrate reproducibility. Major peaks in the thermogram are assigned to the ordered-to-SI phase transition in the NCs and labeled by the peak temperature. There is a small cycle-to-cycle variation in the transition point (DSC peak location).
Supporting Figure 3.11. (a) Optical Vis-NIR-range absorbance spectrum and (b) experimental (baseline subtracted) pXRD pattern of the Li-doped ($x = 0.48$) $\text{Cu}_2\text{Se}$ NCs. NCs at this additional intermediate stage were prepared as described in Supplementary Table 3.1 (Trial 2). The pXRD pattern shows distinct reflections for $\text{Li}_2\text{Se}$ and $\text{Cu}_2\text{Se}$, which are labeled. Thus, phase segregation into $\text{Li}_2\text{Se}$ and $\text{Cu}_2\text{Se}$ domains appears to begin prior to the $x = 0.66$ stage (Supplementary Fig. 3.6). However, from the strength of the $\text{Cu}_2\text{Se}$ $\{111\}$ reflection intensity relative to that of the $\text{Li}_2\text{Se}$ $\{111\}$ reflection, it is evident that the molar proportion of unconverted $\text{Cu}_2\text{Se}$ is greater at this intermediate stage as compared to that at the saturation level of conversion ($x = 0.66$). Essentially, a considerable fraction of the $\text{Cu}_2\text{Se}$ NCs have not reached the saturation level of Li-doping, as also indicated by the sustenance of the LSPR band in the absorbance spectrum. Further Li-doping of these $\text{Cu}_2\text{Se}$ NCs and formation of $\text{Li}_2\text{Se}$ domains continues up to the $x = 0.66$ stage, the saturation level of conversion, at which point the LSPR is fully extinguished (Fig. 3.1a).
Supporting Figure 3.12. An additional exchange reaction was performed to verify if $x = 0.66$ indeed represents the saturation level of Li-incorporation. In an attempt to push the equilibrium further in favor of Li-incorporation, the most exchanged NCs ($x = 0.66$), prepared as described in the Experimental Methods, were cleaned to remove released Cu$^+$. To these cleaned NCs dispersed in hexane, an additional 3.0 mL of Li$^+$ salt solution (~942 mM) was added. Further reaction was allowed to proceed for a day at room temperature, with stirring. An (a) optical Vis-NIR absorbance spectrum and (b) experimental pXRD pattern of the NCs resulting from such a procedure are shown. The pXRD pattern is similar to that for the NCs at the $x = 0.66$ stage (Supplementary Fig. 3.6) and shows the presence of remnant Cu$_2$Se (reflections of which are labeled). Thus, conversion indeed appears to be limited to a Li fraction of $x = 0.66$. 
Supporting Figure 3.13. (a) A fast-Fourier transform (FFT) of the representative HRTEM image of the final stage Li-doped NCs (x = 0.66), shown in Fig. 3.1d. The scale bar for this reciprocal-space image is 2 nm$^{-1}$. The FFT shows distinct electron diffraction spots, indicating crystallinity of the imaged grains. However, the diffraction spots are split into two, signifying segregation of the NCs into Cu$_2$Se and Li$_2$Se domains. The (radially) outer spots correspond to a d-spacing of 0.32 nm, close to the spacing for the \{111\} lattice planes of Cu$_2$Se, whereas the (radially) inner spots correspond to a d-spacing of 0.33 nm, closer to the spacing for the \{111\} lattice planes of Li$_2$Se. (b) A small region of a HRTEM image of final stage Li-doped NCs (x = 0.65), showing a pair of segregated Cu$_2$Se (marked by a red arrow) and Li$_2$Se (marked by a green arrow) domains. (c) An FFT of the region in (b) shows diffraction spots at 0.32 and 0.64 nm (marked by the red box), which correspond to \{111\} lattice planes and \{111\} super-lattice planes, respectively, of the Cu$_2$Se domain. There are also lattice spots at 0.34 nm (marked by the green box) corresponding to the Li$_2$Se domain.
CHAPTER 4: ENGINEERING NOVEL WURTZITE PHASE HGSE AS A POTENTIAL TOPOLOGICAL INSULATOR MATERIAL

4 Reproduced from Torres D. D., Banerjee P., Pamidighantam S., Jain P. K., A Non-Natural Wurtzite Polymorph of HgSe: A Potential 3D Topological Insulator, Chemistry of Materials, 29 (15), 6356-6366, 2017. DOI: 10.1021/acs.chemmater.7b01674 with permission of primary author and journal. This work will also be described in the future PhD dissertation of Daniel Dumett Torres.

4.1 AUTHOR CONTRIBUTIONS:

This chapter resulted from a collaboration between Daniel Dumett Torres, who performed all the density functional theory (DFT) studies, and me, whose experimental studies complemented the theoretical work. My study of the cation exchange of CdSe nanocrystals by Hg\textsuperscript{2+} followed up on preliminary investigations by Aaron Routzahn, based on which my advisor suggested that the wurtzite crystallographic structure does not change despite the replacement of the Cd\textsuperscript{2+} by Hg\textsuperscript{2+}. I performed a detailed experimental study of the cation exchange process. At several stages of conversion, I characterized the Hg(Cd)Se nanocrystals in terms of their crystallographic structure (using X-ray diffraction and structure factor simulations), elemental analysis, optical absorption and photoluminescence spectroscopy of the Hg-doped nanocrystals. These extensive studies verified that the Hg(Cd)Se nanocrystals formed maintain the wurtzite structure of the template. They also showed how the band-gap of the nanocrystals changes as a function of Hg-inciporporation.

Natural bulk HgSe is zincblende and a semimetal with inverted bands, which suggested that the wurtzite polymorph of Hg(Cd)Se formed in these cation exchange reactions was novel. My advisor suggested that the crystallographic anisotropy of the wurtzite polymorph could lead to the opening of a band-gap in HgSe, which along with its inverted band-structure, would imply that wurtzite HgSe is a 3D topological insulator. Daniel performed extensive DFT studies, which indeed showed that wurtzite HgSe, quite unlike zincblende HgSe, has a non-trivial band gap due to the

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crystallographic anisotropy. The non-trivial band-gap along with the inverted band structure strengthened the proposal that wurtzite HgSe is a 3D topological insulator. For resolving the influence of relativistic contributions from Hg addition, Daniel also performed band structure calculations for wurtzite Hg_xCd_{1-x}Se alloys, as a function of x. The band structure calculations predicted that in addition to wurtzite HgSe, Hg_xCd_{1-x}Se with x ≥ 0.33 would have similar topological insulator properties. Since Daniel’s simulations were performed on bulk solids, he extrapolated the calculated band-gaps to predictions for 6-nm nanocrystals, like those in my experiments, by including quantum confinement. Daniel’s simulations also predicted band-gap opening Hg_xCd_{1-x}Se alloys due to another form of anisotropy, i.e., compositional anisotropy.

4.2 ABSTRACT:

This study demonstrates the power of topotactic synthesis coupled with density functional theory (DFT) for accessing and exploring new phases of matter. Naturally occurring HgSe is a semimetal with a zero gap. Unlike this natural zincblende form of HgSe, our DFT investigations predict that wurtzite HgSe has both an inverted band structure and a band gap, making it a 3D topological insulator (TI). Calculated band structures of Hg_xCd_{1-x}Se alloys, containing strongly relativistic Hg and weakly relativistic Cd, show that band gap opening is a consequence of symmetry breaking resulting from a combination of crystal anisotropy and the scalar relativistic effect of Hg electrons. The relativistic contribution of Hg is significant enough in alloys with x ≥ 0.33 for achieving 3D TI behavior at room temperature. We experimentally realize the non-natural wurtzite form by topotactic ion exchange of wurtzite CdSe nanocrystals (NCs), which yields alloy NCs in the range x = 0 to x = 0.54 whose measured band gaps follow the predicted trend. We introduce crystal anisotropy as a new handle for expanding the classes of TI materials and also shed light on
electronic principles in nanocrystalline alloys containing relativistic metals. NCs of this new wurtzite phase can become platforms for discovery of rich topological states and properties.

4.3 INTRODUCTION:

Topological insulators (TIs) represent a novel state of matter: the bulk (3D) of a TI is electrically insulating, but the surface (2D) contains topologically protected conductive states. TI materials are receiving surging interest as platforms for discovery of exotic condensed matter phenomena, e.g., Majorana fermions, and for the utility of the spin-protected surface conduction in spintronics and quantum computing. Most materials that are intrinsically 3D topological insulators are Bi- or Sb-based, in particular selenides and tellurides of these metals. The list of materials is, however, rather small. Expansion of the class of 3D TI materials can accelerate new findings and technological applications. Mercury chalcogenides represent potential candidates due to strong spin-orbit coupling effects associated with heavy Hg. For instance, HgTe/HgCdTe quantum wells, have exhibited 2D TI properties with spin-protected 1D edge states. But intrinsic (in the absence of strain or external fields) 3D TI behavior is not known in mercury chalcogenides. For a solid to be a 3D TI, two conditions need to be met: i) A non-trivial band structure: the conduction and valence bands are inverted, which results in the helical spin-protected surface conduction states, and ii) A non-zero band gap, so that the bulk is electrically insulating. Here, we find using electronic structure simulations a non-natural polymorph of HgSe, which unlike hitherto known phases satisfies these conditions and qualifies as a 3D TI. We experimentally realize this novel crystal phase in nanocrystals (NCs) via the topotactic method of synthesis, cation exchange. HgSe, which has been studied extensively since the 1960s, has a zinc-blende crystal structure and a non-trivial, inverted band structure. However, zincblende HgSe has a zero gap and
is therefore classified as a Weyl semi-metal (similar to α–Sn and HgTe) and not a 3D TI. Our density functional theory (DFT) investigations reveal that unlike the known zinc-blende form, a non-natural wurtzite polymorph of HgSe has a finite band-gap in addition to inverted bands, making it a 3D TI. We synthesize using cation exchange this novel wurtzite polymorph in the form of Hg$_x$Cd$_{1-x}$Se alloy NCs, allowing a systematic experimental and theoretical investigation of the band-gap as a function of composition. Alloys with an Hg fraction $\geq 0.33$ fall within the room-temperature 3D TI regime. Band-gap and electronic structure trends in this alloy system show that the 3D TI is a consequence of the scalar relativistic contribution of the heavy Hg nuclei$^{236}$ combined with the crystal anisotropy of the wurtzite structure. Thus, we introduce crystal anisotropy as a new handle for controlling topological properties and also elucidate the principles behind electronic band structure tuning achieved by alloying of strongly and weakly relativistic metals in ionic solids.
Figure 4.1: Band structures and unit cell structures of zinc-blende and wurtzite HgSe. (a) Our calculated band structure of zinc-blende HgSe. (b) Our calculated band structure of wurtzite HgSe, indicating the presence of a band gap ~46 meV. In a) and b), we assigned light hole ($\Gamma_8$ lh), heavy hole ($\Gamma_8$ hh), and split off ($\Gamma_7$ SO) bands in a simplified manner based on zincblende semiconductors.\textsuperscript{237} Lower lying bands are not included. (c) Unit cell representation for the natural zinc-blende phase of HgSe in which every Hg$^{2+}$ is coordinated tetrahedrally to four Se$^{2-}$ anions through bonds of equal length. (d) Unit cell representation of the novel wurtzite phase of HgSe in which Hg and Se are tetrahedrally bonded to one another, but as shown in (e), one of the tetrahedral bonds is slightly longer than the other three, introducing a crystal anisotropy along the so-called c axis direction. For (c), (d), and (e), calculated lattice parameters and bond lengths are indicated.

4.4 CRYSTAL ANISOTROPY AND BAND GAP OPENING:

To study the effects of crystal structure on the electronic properties of HgSe, we used periodic plane-wave basis density functional theory (DFT) with spin orbit-coupling as implemented in the Quantum Espresso software suite.\textsuperscript{238} Our DFT calculations of zincblende HgSe (Fig. 4.1a) confirm that it has an inverted band structure as has been demonstrated in the past with experiment and theory.\textsuperscript{233,235,236} The band structure can be contrasted with the typical zincblende semiconductors, e.g., CdSe, wherein the lowest energy conduction band is comprised of cation s-orbitals, whereas
the highest energy valence bands, i.e., light hole ($\Gamma_{8}\text{ lh}$) and heavy hole ($\Gamma_{8}\text{ hh}$), are comprised of the anion p-orbitals. HgSe, however, has a dramatically different band structure due to the relativistic nature of the electrons of the heavy Hg. In HgSe, the band comprised of Hg s-like states is significantly lowered in energy due to the relativistic contraction of the outermost 6s-orbitals of Hg. The cation s-like band thus becomes a deeper lying valence band. The $\Gamma_{8}\text{ lh}$ and $\Gamma_{8}\text{ hh}$ bands become the lowest energy conduction and highest energy valence bands, respectively. Since these two bands are degenerate in the zincblende structure at the $\Gamma$ point, HgSe lacks a band-gap and is therefore only a topological semimetal.

Realization of TI behavior in HgSe would require a finite gap between the $\Gamma_{8}\text{ lh}$ and $\Gamma_{8}\text{ hh}$ bands at the $\Gamma$ point. Gap opening could be achieved by lifting of the degeneracy of these bands. Such degeneracy breaking is exhibited in wurtzite CdSe due to anisotropic crystal field splitting,\textsuperscript{239} therefore, we were motivated to investigate the wurtzite form of HgSe, even though such a form is not known to exist naturally. The calculated band-structure of this wurtzite polymorph is shown in Fig. 4.1b. We find that the inverted band structure is maintained in the wurtzite form with $\Gamma_{8}\text{ lh}$ and $\Gamma_{8}\text{ hh}$ bands as the conduction and valence band edges, respectively. However, these two bands are no longer equivalent in energy at the $\Gamma$ point, resulting in a non-zero band gap. The band gap is 46 meV in magnitude. As we explain below, this band-gap opening is indeed a consequence of crystal anisotropy in the wurtzite phase (Fig. 4.1e), which operates in a manner similar to the application of a uniaxial strain to zinc-blende HgSe.\textsuperscript{229,238,240}
Figure 4.2: Charge density maps for the lowest energy conduction band, $\Gamma_8$ lh, (left) and highest energy valence band, $\Gamma_8$ hh, (right) of wurtzite (top) and zincblende (bottom) HgSe. Hg$^{2+}$ and Se$^{2-}$ in the wurtzite phase are tetrahedrally coordinated like in the zinc-blende case. However, there is a key difference between the two structures: all four Hg-Se bonds are of equal length in the zinc-blende phase (Fig. 4.1c), whereas in wurtzite (Fig. 4.1d & 4.1e), the Hg-Se bond, i.e., the one along the $c$-axis of the crystal, is elongated. This small elongation breaks the degeneracy of the $\Gamma_8$ lh and $\Gamma_8$ hh bands. To understand this effect, the charge density maps for these two bands are compared in Fig. 4.2. Although both bands are comprised of linear combinations of the Se p orbitals, the charge density maps show that the $\Gamma_8$ lh band differs in symmetry from the $\Gamma_8$ hh band in both crystal phases. The $\Gamma_8$ hh band is directed along the $c$-axis (of the wurtzite crystal), whereas the $\Gamma_8$ lh band is oriented in a plane normal to this axis.

In the zinc-blende phase, the energy of the Se p orbitals is not orientation dependent due to the equivalence of the four tetrahedral bonds. The valence bands comprised of a linear combination of $p_x$, $p_y$, and $p_z$ orbitals are triply degenerate at the $\Gamma$ point in the perfect tetrahedral coordination.
of the zinc-blende phase, in the absence of spin-orbit coupling.\textsuperscript{240} Spin-orbit coupling results in the Γ\textsubscript{7} SO band being split off in energy from the Γ\textsubscript{8} hh and Γ\textsubscript{8} lh bands, but the latter two remain degenerate at the Γ point. This twofold degeneracy follows the conventional zincblende band structure,\textsuperscript{241} except that due to band inversion in zinc-blende HgSe, this twofold degeneracy occurs between the highest lying valence band (Γ\textsubscript{8} hh) and the lowest lying conduction band (Γ\textsubscript{8} lh), leading to a zero gap (Fig. 4.1a).

In the anisotropic wurtzite structure, the strength of the crystal field experienced by a Se p orbital depends on the orbital orientation. The crystal field degeneracy between the p\textsubscript{x}, p\textsubscript{y}, and p\textsubscript{z} states is broken.\textsuperscript{240} Se p-like states oriented along the elongated bond experience reduced electrostatic repulsion from cation electrons and are therefore stabilized with respect to Se p-like states of other orientations. Thus, the Γ\textsubscript{8} hh band, oriented along this elongated band, is lowered in energy relative to the Γ\textsubscript{8} lh band at the Γ point, thereby opening a gap. The crystal field splitting energy difference between the Γ\textsubscript{8} lh and Γ\textsubscript{8} hh bands corresponds to the magnitude of this band gap.

Conventional semiconductor band gaps calculated using the Perdew–Burke–Ernzerhof (PBE) functional are known to be underestimated due to self-interaction errors.\textsuperscript{242} However, crystal field splitting energy differences are computed more accurately by DFT, possibly due to cancelation of self-interaction errors. For instance, the crystal field splitting difference between the lh and hh bands in wurtzite CdSe is estimated to be 35 meV by our DFT calculations (Supplementary Fig. 4.2a), which is close to the known experimental value of 29 meV.\textsuperscript{243} The close agreement further suggests that our relaxed geometries are representative of the actual bond elongation present in the wurtzite phase. Since the band gap of wurtzite HgSe is equal to the crystal field splitting energy difference between the Γ\textsubscript{8} lh and Γ\textsubscript{8} hh bands, our calculated band gap of 46 meV can be expected to be quantitative. The calculated band gap is sufficiently larger than thermal broadening at room
temperature (25 meV), which predicts electrically insulating behavior in the bulk at room temperature. Cryogenic cooling would not be required for realizing 3D TI behavior. These predictions motivated us to synthesize this non-natural wurtzite polymorph of HgSe.

4.5 REALIZATION OF THE WURTZITE STRUCTURE IN NCS:

For our synthesis of wurtzite HgSe, we employed cation exchange, which is a method being increasingly used to produce NCs in novel shapes, morphologies, and phases. In this method, cations of a colloidal ionic NC are replaced by another cation, while the anionic sub-lattice is maintained intact, often resulting in (metastable) crystal structures dictated by the initial template rather than by equilibrium phase diagrams. We exploited this topotactic manner of synthesis by starting with wurtzite CdSe NCs as templates and exchanging the Cd$^{2+}$ ions with Hg$^{2+}$ at room-temperature. Note that CdSe NCs have been subject to exchange with Hg$^{2+}$ in the past. In the well-studied cases, the starting CdSe template was zincblende and naturally the resulting product was not wurtzite. In one study on wurtzite CdSe nanorods, although clear crystallographic evidence was missing, the product was suggested from scanning transmission electron microscopy (STEM) to contain local regions of zincblende HgSe. However, the conditions under which the exchange was performed were markedly different from our synthetic method (see Methods). Aqueous, basic conditions were employed in this past work with water-soluble mercaptopropionic acid-coated CdSe nanorods. A Hg(ClO$_4$)$_2$ salt and a large Hg/Cd ratio of 60 was employed for the exchange reaction, which was allowed to proceed for four days prior to STEM characterization. Under these conditions, the Hg distribution varied significantly across the product nanorods: although the overall exchange conversion was limited to $x = 0.1$, some regions of the nanorods were significantly Hg-enriched. Nucleation of zincblende HgSe, which requires drastic reorganization of the more rigid Se sub-lattice, occurred in the regions with
high Hg enrichment, significantly past the miscibility limit of HgSe in CdSe; however, such domains were not widespread. Summarizing current literature, there is no finding of a dominant wurtzite product in past studies of Hg$^{2+}$ exchange of CdSe.

**Figure 4.3:** Topotactic cation exchange from wurtzite CdSe to Hg$_x$Cd$_{1-x}$Se. (a) Absorbance spectra (stacked for presentation) for NCs in the course of the exchange. Inset shows an HRTEM image of the furthest exchanged NCs (scale bar = 5 nm) Dotted lines guide the eye to the emergence of the exciton peak associated with HgSe formation (the reddest peak), and the disappearance of the exciton peaks associated with CdSe in the course of the titration. (b) PL emission spectra obtained at various stages in the course of the step-wise cation exchange from CdSe to Hg$_x$Cd$_{1-x}$Se NCs. For both a) and b), the amount of Hg$^{2+}$ solution added at each stage in the titration is indicated in the legend in b). (c) PXRD patterns obtained at the initial, intermediate, and the final stages. The Hg to metal fraction, x, indicated in the legend is based on the elemental composition measured by ICP-AES and tabulated in Table 4.1. Reference reflections for bulk wurtzite CdSe (ICSD # 41825) as are indicated by red sticks. (d) Simulated PXRD patterns for wurtzite Hg$_x$Cd$_{1-x}$Se NCs for the different Hg fractions, x, corresponding to those in the experiment. Patterns in c) and d) were stacked vertically for presentation purposes.
Table 4.1. Elemental composition of initial, intermediate, and final NCs obtained by ICP-AES.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cd (mass %)</th>
<th>Hg (mass %)</th>
<th>Hg/(Hg+ Cd) atomic ratio (x)</th>
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</thead>
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<tr>
<td>CdSe</td>
<td>22.06</td>
<td>0.65</td>
<td>0.01</td>
</tr>
<tr>
<td>Int 1</td>
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<tr>
<td>Int 2</td>
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</tr>
<tr>
<td>final</td>
<td>4.86</td>
<td>10.16</td>
<td>0.54</td>
</tr>
</tbody>
</table>

The outcome of our synthesis was a series of Hg₉Cd₁₋ₓSe alloy NCs in the novel wurtzite phase, as found by detailed characterization. The transformation from CdSe to HgSe was carried out on NCs as opposed to bulk samples due to mass-transport-related bottlenecks in exchange reactions on the bulk scale.¹⁹⁸ The chemical composition of the NCs at various stages of the exchange was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results (Table 4.1) show successful replacement of Cd²⁺ with Hg²⁺. High-resolution transmission electron microscopy (HRTEM) showed that throughout the exchange process, the quasi-spherical morphology was maintained (Supplementary Fig. 4.1). The initial CdSe NCs (peak diameter ~3.6 nm) were similar in size as the final product NCs (peak diameter ~ 3.9 nm).

The powder X-ray diffraction (PXRD) pattern did not show appreciable change over the course of the exchange indicating that the wurtzite crystal structure was retained (Fig. 4.3c). PXRD simulations (Fig. 4.3d) assuming a topotactic replacement of Cd²⁺ with Hg²⁺ reproduce the experimental observations. In the experimental PXRDs, there are slight shifts in the peaks as one goes from the initial NCs to the final ones: e.g., the {102} reflection shifts from 2θ = 35.2° to 35.6° and the {110} reflection shifts from 2θ = 42.1° to 42.5°. These shifts amount only to small, ca. 1%, lattice constant changes as wurtzite CdSe NCs are transformed to wurtzite Hg₉Cd₁₋ₓSe NCs. The near-preservation of the lattice dimensions is consistent with our DFT simulations, which
show identical lattice constants (a = 4.422 Å, c = 7.264 Å) for structurally relaxed wurtzite CdSe and wurtzite HgSe cells. The finding is also consistent with the known zincblende phase of HgSe, which has a near-identical structure and lattice constant (6.085 Å) as zincblende CdSe. The similarity of the lattice structure and lattice parameters of wurtzite HgSe and wurtzite CdSe also make us favor progressive alloying rather than a shrinking CdSe core/thickening HgSe shell mechanism of exchange. However, the conclusion of topotactic formation of wurtzite Hg\(_x\)Cd\(_{1-x}\)Se stands irrespective of the mechanism.

We also followed the replacement of Cd\(^{2+}\) by Hg\(^{2+}\) in the NC lattice by UV-Vis absorbance (Fig. 4.3a) and photoluminescence (PL) emission (Fig. 4.3b) spectrophotometry. It is well known that CdSe NCs have a very well-defined optical signature which can be tuned by doping.\(^{34,53,54}\) The exchange with Hg\(^{2+}\) results in the gradual disappearance of the exciton peaks of CdSe NCs (first exciton peak at 580 nm). There is concomitant appearance of a new exciton peak (600-650 nm region) that can be associated with Hg\(_x\)Cd\(_{1-x}\)Se formation. This new exciton peak red-shifts with increasing conversion, \(x\). In PL spectra, the band centered at 600 nm, associated with band-gap emission of CdSe NCs slightly blue-shifts and decreases in intensity until it is fully extinguished. Concomitantly, a new PL band centered around 750 nm emerges and increases in intensity. This new band, which could be associated with band-gap emission of Hg\(_x\)Cd\(_{1-x}\)Se NCs, is seen to red-shift with increasing Hg conversion, \(x\). The point at which the spectra do not show any further changes was defined as the final stage. The elemental composition of the final NCs show significant residual Cd and an Hg fraction of 0.54. Even with elevated temperatures and a huge excess of the Hg\(^{2+}\) salt, complete conversion to HgSe was not observed. Thus, the exchange appears to be self-limited akin to a previous report on the cation exchange of PbSe nanocrystals to CdSe,\(^{261,262}\) which like the reaction system studied here involves cation exchange between two
divalent cations, known to be kinetically challenging. Conversion to Hg-rich compositions may require the nucleation of the stable, zincblende form of HgSe. Such nucleation would involve drastic reorganization of the rigid Se lattice and would therefore be expected to be kinetically limiting despite the availability of sufficient Hg$^{2+}$.

4.6 ALLOYING EFFECTS ON ELECTRONIC STRUCTURE:

While our synthesis successfully accessed the wurtzite phase, the incomplete exchange of Cd$^{2+}$ with Hg$^{2+}$ led us to investigate how the remaining Cd$^{2+}$ in Hg$_x$Cd$_{1-x}$Se alloy compositions influences the band structure and the band gap. In particular, we needed to determine whether or not a Hg$_x$Cd$_{1-x}$Se alloy has attributes of a 3D TI at room temperature, similar to HgSe. Systematic calculations of the electronic structures of wurtzite Hg$_x$Cd$_{1-x}$Se alloys were performed over the full range $x = 0$ to $x = 1$ (Figs. 4.4 and Supplementary Fig. 4.2).

The key trends are as follows. Wurtzite CdSe ($x = 0$) has a trivial band structure, i.e. there is no band inversion and the lowest energy $\Gamma_6$ band conduction band is comprised mainly of Cd s orbitals. As the structure is alloyed with Hg, the relativistically contracted 6s orbital of Hg contributes to the $\Gamma_6$ band and lowers it in energy (Fig. 4.4c). Already at $x = 0.25$, this relativistic contribution of Hg is large enough for the $\Gamma_6$ band to cross below the $\Gamma_8$ bands in energy, resulting in band inversion wherein the $\Gamma_8$ lh and $\Gamma_8$ hh bands take the role of the lowest energy conduction and highest energy valence bands respectively. A small band gap (6 meV) is seen at $x = 0.25$. The band structure continues to remain inverted up to HgSe and the band-gap increases at room temperature (25 meV). Thus, wurtzite Hg$_x$Cd$_{1-x}$Se alloys with 33% or greater Hg fractions have the band structure attributes of a room temperature 3D TI. Our experimentally synthesized alloy NCs with 54% Hg fall well within the 3D TI regime at room temperature (cyan region in Fig. 4.1a).
Figure 4.4: Overview of alloying trends in electronic structure of Hg$_x$Cd$_{1-x}$Se. (a) Dependence of the calculated band gap on the Hg fraction, $x$, of the alloy. The arrow marks the furthest extent to which alloying has been achieved in our Cd$^{2+}$ to Hg$^{2+}$ cation exchange experiments. The horizontal dotted line marks the magnitude of thermal broadening at room temperature, which allows demarcation of the regime of room temperature 3D TI behavior (cyan) from that of topological semi-metal behavior (red). (b) The cation (combination of Hg$^{2+}$ and Cd$^{2+}$) s orbital character contribution to the frontier bands as a function of Hg fraction, $x$. ‘SO band’ refers to the $\Gamma_7$ SO band and ‘Hole Bands’ refers to the combination of the $\Gamma_8$ lh and $\Gamma_8$ hh bands, which are treated as one for this analysis. (c) Schematic of the band structure showing inversion and then shift of the $\Gamma_6$ s-like band downward in energy as heavy Hg nuclei are incorporated into a CdSe lattice. (d) Calculated charge density maps for the $\Gamma_8$ hh band at representative compositions. At the pure CdSe and HgSe end points, the $\Gamma_6$ s-like band is well separated in energy from the $\Gamma_8$ hh band and does not donate any s character to the $\Gamma_8$ hh band. However, at intermediate compositions, such as in Hg$_{0.25}$Cd$_{0.75}$Se, significant cation s character can be observed in the Se p dominated $\Gamma_8$ hh band.
Next, we elucidate the electronic origin of the band gap trend. With increasing \( x \), the \( \Gamma_6 \) band owing to its cation s character continues to move lower in energy due to the increasing relativistic contribution of Hg. In its progressive energy downshift with increasing \( x \), the \( \Gamma_6 \) band crosses energetically with other bands in sequence. Near about \( x = 0.25 \), the \( \Gamma_6 \) band becomes similar in energy to the \( \Gamma_8 \) bands, which imparts the \( \Gamma_8 \) bands with a significant cation s-like character (Fig. 4.4b and 4.4d). As the Hg fraction is increased from \( x = 0.25 \) to \( x = 0.5 \), the \( \Gamma_6 \) band moves energetically away from the \( \Gamma_8 \) bands and approaches the deeper lying \( \Gamma_7 \) SO band. As a result, the cation s character of the \( \Gamma_8 \) bands decreases and that of the SO band increases. At \( x = 0.5 \), the \( \Gamma_6 \) band crosses the SO band, and the latter exhibits a maximum in its cation s character (Fig. 4.4b).

In HgSe, the \( \Gamma_6 \) band, comprised of the relativistically stabilized Hg 6s states, is deep within the valence band and neither the \( \Gamma_8 \) band nor the \( \Gamma_7 \) SO band have any significant cation s character and Se p character dominates. As the fraction of Cd increases and that of Hg decreases (\( x = 1 \) to \( x = 0.25 \)), the \( \Gamma_8 \) lh and \( \Gamma_8 \) hh bands increase in their cation s (isotropic) character and concomitantly decrease in their Se p character (Supplementary Fig. 4.3). As a result of the reduced directional nature of the \( \Gamma_8 \) lh and \( \Gamma_8 \) hh bands, the effect of crystal field splitting anisotropy decreases and the \( \Gamma_8 \) lh and \( \Gamma_8 \) hh bands become closer in energy at the \( \Gamma \) point, i.e., the band gap decreases. Although this effect explains the overall decrease in the bulk band gap as the Hg\(^{2+}\) fraction goes from \( x = 1 \) to \( x = 0.25 \) (Fig. 4.4a), there is an anomalous increase in the band gap when going from \( x = 0.75 \) to \( x = 0.66 \). We attribute this anomaly to a different kind of anisotropy. Unlike pure HgSe, the intermediate compositions can have an additional anisotropy resulting from the ordering of Cd\(^{2+}\) and Hg\(^{2+}\) in separate, alternating layers. The resulting compositional anisotropy can contribute to symmetry breaking (between the \( \Gamma_8 \) lh and \( \Gamma_8 \) hh bands) and enhance the magnitude of the band gap. The evidence for such an effect is found in a system with no crystallographic anisotropy, i.e.,
a zinc-blende lattice (Supplementary Fig. 4.4). In zincblende HgSe, all Se p states experience the same crystal field interaction, the lh and hh bands are degenerate, and a zero gap is calculated. But in zincblende Hg\textsubscript{x}Cd\textsubscript{1-x}Se, a small few meV band-gap can be observed due solely to this alloying-induced compositional anisotropy. The predicted band gap is maximum in magnitude near \(x = 0.5\), because a 1:1 Hg:Cd composition allows for the greatest degree of layer-wise stratification within the crystal.

Lastly, we validate our computational predictions by comparing DFT-calculated band gaps with those measured optically for the range of Hg\textsubscript{x}Cd\textsubscript{1-x}Se alloys accessed in our synthesis (Fig. 4.5). Because our synthesized materials consist of \(\sim3.5\) nm NCs, we must account for the effect of size-dependent quantum confinement and exciton binding energy on the optical gaps.\textsuperscript{16} Since the wurtzite phase of Hg\textsubscript{x}Cd\textsubscript{1-x}Se is realized for the first time here, carrier transport properties are naturally unavailable. We determined electron and hole effective masses from our band structure calculations as:

\[
m^* = \left| \frac{\hbar^2}{\frac{\partial^2 E}{\partial k^2}} \right| \quad (4.1)
\]

where \(E\) represents the band energy and \(k\) indicates the crystal momentum. We accounted for carrier confinement using the effective mass approximation\textsuperscript{263–266} and included an exciton binding energy correction in our estimation of the size-modified optical band gap, \(E_{NP\text{ gap}}\) as: \[\]
\( E_{NP\ gap} = E_{bulk\ gap} + \frac{\hbar^2}{2R^2} \left( \frac{1}{m^*_e} + \frac{1}{m^*_h} \right) - 1.786 \frac{e^2}{4\pi\varepsilon QD\varepsilon_0 R} \) (4.2)

Figure 4.5: Experimental (a) and calculated (b) band gaps for 3.5 nm NCs of varying Hg fraction. Experimental (optical) band gaps plotted here are based on peak maxima obtained from absorption (blue dots) and PL emission (red squares) spectra. Calculated band-gaps follow eq. 4.2. Table on the right-hand side provides the effective carrier masses, in terms of the free electron mass, used for NC size correction. The experimental trend agrees qualitatively with the calculated one, most notably with regard to the sharp decrease in NC band-gap about \( x = 0.25 \). However, it must be acknowledged that the match is not quantitative: the calculated NC band-gap decreases by 55\% from 3.37 eV (\( x = 0.25 \)) to 1.53 eV (\( x = 0.33 \)), whereas from PL, the NC band-gap drops by 20\% from 2.09 eV (\( x = 0.16 \)) to 1.69 eV (\( x = 0.34 \)). The quantitative discrepancy can be attributed to limitations of the calculation model. In addition to errors associated with treatment of electron correlation and self-interaction in DFT of semiconductors, there are considerable errors associated with the treatment of NC size effects. Effective masses calculated on the basis of band dispersion are not quantitative for NCs, in which well-defined bands do not exist and the use of an effective mass model can be a severe approximation. In addition, at each point in our exchange reaction, the alloy composition can be variable across the NC sample; the measured Hg fraction \( x \) represents only an average. This can lead to quantitative discrepancy with the calculated band-gap, as explained in Supplementary Fig. 4.5.

where \( E_{bulk\ gap} \) is the calculated band gap for the bulk alloy, \( m^*_e \) and \( m^*_h \) are the electron and hole effective masses, respectively and \( R \) is the NC radius, fixed at 1.75 nm. While it is difficult to obtain an exact quantitative match, there is qualitative agreement between the calculated trends and the experimentally determined ones: i) Cd-rich NC compositions, between \( x = 0 \) and \( x = 0.25 \) have band-gaps in the visible region, which increase marginally with increasing \( x \) ii) between \( x =
0.25 and $x = 0.33$, the band-gap drops sharply, and iii) sufficiently Hg-exchanged NCs ($x = 0.33$ to $x = 1.0$) have near-infrared band gaps, which decrease in magnitude gradually with increasing $x$.

Unlike the bulk band gaps which reflect the solid band structure (Fig. 4.4), NC band gaps are strongly dominated by carrier confinement effects. Therefore, to understand the trend in NC band gaps across alloy composition, one needs to examine the change in carrier properties, especially effective electron masses, which are smaller (Fig. 4.5, table) and therefore dominate the confinement effect in the NCs (eq. 4.2). With increasing Hg fraction, above $x = 0.25$, the inverted $\Gamma_6$ band moves lower in energy, leading to a decreasing Hg s contribution to the lowest energy conduction band. These changes in the orbital nature of the conduction band result in an increase in the effective electron mass and thereby a decrease in the NC band-gap with increasing Hg fraction.

4.7 CONCLUSIONS:

Thus, our DFT simulations reveal that the wurtzite polymorph of HgSe has a remarkably different electronic structure from the naturally known zincblende phase of HgSe. While zincblende HgSe is a semimetal, the wurtzite polymorph has the attributes of a 3D TI insulator including band inversion and a non-zero band-gap. Motivated by the calculations, we successfully realize this non-natural wurtzite phase by topotactic exchange of Cd$^{2+}$ in wurtzite CdSe NCs with Hg$^{2+}$. We measured band-gaps of the synthesized wurtzite Hg$_x$Cd$_{1-x}$Se alloy NCs and find a trend in agreement with our simulations. Systematic electronic structure investigations of the Hg$_x$Cd$_{1-x}$Se alloys elucidate the physical principles underlying 3D TI behavior. Band inversion is a result of the scalar relativistic effect of Hg 6s electrons on the $\Gamma_6$ band, while band gap opening is the result of symmetry breaking due to the crystalline anisotropy of the wurtzite structure. The relativistic contribution of Hg is sufficient for alloys with $x \geq 0.33$ to demonstrate attributes of 3D TIs at room

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temperature. Thus, we introduce crystal anisotropy as a new handle for tuning band topology, elucidate the important role of scalar relativistic effects, and expand the class of materials with 3D TI attributes to include mercury chalcogenides.

Direct demonstration of spin-protected conductive surface states via angle-resolved photoemission spectroscopy (ARPES) or scanning tunneling microscopy (STM) still remains to be conducted. A single crystal with low defect concentration is required for such measurements. NCs themselves may not serve the purpose: NCs do not have well-defined bands and (surface and bulk) band topology characteristics do not directly translate from bulk, semi-infinite solids to nanosized ones. However, these NCs can be employed as precursors for realizing a bulk 3D TI: surface ligands can be removed and NCs can be assembled into a mesoscopic or macroscopic super-solid, while maintaining the wurtzite phase with 3D TI property. Secondly, despite their lack of bands, which may preclude 3D TI behavior, NCs can exhibit other allied phenomena such as low-dimensional topological states – an example includes recently found 1-D spin-polarized states along step edges on the surface of a TI\textsuperscript{267} – or, previously unknown exotic phenomena. Faceting, surface curvature, ligands, crystal anisotropy, and quantum confinement can add further richness. Therefore, NCs of this wurtzite phase can become platforms for discovery of new topological states and properties.\textsuperscript{62-65}

4.8 METHODS:

Synthesis of ca. 4 nm wurtzite CdSe NCs: Wurtzite CdSe NCs of ca. 4 nm size were synthesized as per Carbone \textit{et al.}\textsuperscript{254} and also described in White \textit{et al.}\textsuperscript{19} Cadmium oxide (0.06 g), octadecylphosphonic acid (0.28 g), and trioctylphosphine oxide (3.0 g) were added to a 50-ml three-neck round-bottom flask. A solution of trioctylphosphine (TOP)-Se was prepared in a glovebox by dissolving 0.6 g Se in 4.48 ml TOP and stirring the solution at room temperature, overnight.
The reaction flask was degassed under vacuum at 150 °C for 1.5 h. The flask was then put under Ar atmosphere and the temperature was gradually increased to 300 °C over the course of 2 hours. Upon slowly ramping up the temperature further to 320 °C, the solution became optically clear. After reaching 320 °C, 1.8 mL of TOP was gradually injected into the mixture. The temperature of the mixture in the flask was raised to 360 °C and then 0.45 mL of the TOP-Se solution was injected rapidly. After injection, the solution was heated at 360 °C for 40 s, or until the solution was a bright red color, after which the heating mantle was removed. The NC colloid obtained from the synthesis was washed with toluene and methanol multiple times and finally dispersed in toluene.

Cation exchange of CdSe NCs with Hg$^{2+}$: CdSe NCs were dispersed in hexane with ligands (0.7 mL oleic acid and 0.7 mL oleylamine) added to aid colloidal stability over the course of exchange. To this NC colloid (OD$_{580}$ nm ~ 0.8) placed in a sealed quartz cuvette, a solution of 16 mg mercury acetate in 2 mL octylamine was added in few-μL aliquots with vigorous stirring, at room temperature. Cation exchange was monitored by UV-Vis absorbance and photoluminescence (PL) emission spectrophotometry. PL emission spectra were obtained with a 450-nm excitation wavelength. The intermediates were chosen from the UV-Vis absorbance data: the stage at which the exciton peak corresponding to HgSe just began to emerge was labeled as intermediate 1 (I1). A second stage at which a clear exciton peak from HgSe was seen in co-existence with a weak CdSe exciton was labeled as intermediate 2 (I2). I1 and I2 correspond to specific points in the titration after 12 μL and 20 μL of the Hg$^{2+}$ solution are added, respectively.

Electron microscopy characterization: High resolution transmission electron microscopy (HRTEM) images were acquired on a JEOL 2010 EF-FEG operating at 200 kV. Samples were prepared by drop casting a NC solution onto an ultrathin carbon grid followed by washing of the
grid with methanol. The sample-coated grids were then desiccated under vacuum overnight to volatilize excess ligands. NC size analysis was performed on HRTEM images using the software, Fiji. Sizes of the quasi-spherical NCs were determined manually.

Elemental composition analysis: Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used for determination of the elemental compositions of the NCs at different stages: the initial CdSe NCs, intermediates I1 and I2, and the final product NCs. For preparation of each sample for ICP-AES, the NC colloid in hexane was purified by three cycles of washing in methanol and centrifugation. The final centrifuged pellet was subsequently dried in a quartz digestion tube by flowing N$_2$ gas. Approximately, 8 mg of the initial CdSe NCs, 7 mg each of the intermediates, and 12 mg of the final exchanged sample were subject to ICP-AES and Cd, Hg, and Se weight percentages were measured. The elemental composition is tabulated in Table 4.1.

PXRD characterization: Samples for PXRD measurements were prepared by drop-casting NCs from colloidal solution into a thick film on a zero-background quartz substrate. PXRD patterns were collected on a Rigaku Miniflex 600 powder x-ray diffractometer operated at full power (40 kV - 15 mA) with Cu K$_\alpha$ radiation with an X-ray wavelength of 1.54 Å. Diffraction was collected in reflection mode in the $2\theta = 20^\circ$-$75^\circ$ range using a step size of 0.04°. Diffraction patterns were plotted in Origin Lab software and a baseline subtraction was performed to emphasize the diffraction peaks. Reference reflections for the wurtzite phase of CdSe (ICSD # 41825) are shown for comparison in Fig. 4.3c.

PXRD simulations: The software Powder Cell was used to simulate PXRD patterns (20 range of 20-75°) by performing a structure factor calculation using lattice parameters, atomic positions, and site occupancies as input parameters. A space group of 186 (P6$_3$mc) was used for the unit cell and lattice parameters known for bulk wurtzite CdSe ($a = 4.29$ Å and $c = 7.01$ Å) were employed. The
site occupancies of Cd and Hg ions in the wurtzite lattice were varied to obtain patterns for a range of alloys with Hg fraction, $x$, ranging from 0 to 0.56, corresponding to the compositions observed in the experimental synthesis. All simulated patterns incorporated Debye-Scherer broadening ($\text{fwhm} = 2.5^\circ$ at $2\theta = 35^\circ$) corresponding to a crystallite size of 3.5 nm. Simulated patterns were then stacked vertically in the order of increasing $x$ in Fig. 4.3d.

Parameter and pseudopotential usage: All electronic structure and band structure calculations were performed with plane-wave-basis periodic DFT using the Quantum Espresso$^{238}$ software suite. Unless otherwise stated, calculations were performed on bulk wurtzite and zincblende forms of HgSe, CdSe, and Hg$_x$Cd$_{1-x}$Se alloys using the PBE functional.$^{66}$ For all PBE calculations, Norm-conserving Vanderbilt pseudopotentials with spin-orbit coupling, generated using D. R. Hamman’s ONCVPSP code,$^{67,68}$ were utilized in the final band structure and charge density calculations. The code and input data were both obtained from the publicly available database at quantum-simulation.org. The fully relativistic norm-conserving pseudopotentials used in our final electronic structure calculations were obtained by using the data files that are provided along with the SG15 ONCV potentials as input for the oncypspr.x code. The input corresponded to the scalar relativistic pseudopotentials Cd_ONCV_PBE-1.0.UPF, Hg_ONCV_PBE-1.0.UPF, and Se_ONCV_PBE-1.1.UPF.

A kinetic energy-cutoff of 100 Ry. was used along with automatically generated Monkhorst-Pack $k$-point grids in our calculations. The $k$-point grid size varied with the size of the crystal basis needed to define each alloy. Alloys with compositions that deviate from 1:1 Hg:Cd ratio require larger numbers of unit cells for structural definition but can be calculated with smaller $k$-point grids as summarized in the table below.
The k-point grid dimension is reduced in the direction along which calculation cell is elongated. Convergence tests were performed, as summarized in Supplementary Table 4.1 to validate the choice of both the cutoff and grid size parameters. Some of the alloys utilized much larger grids than those needed for convergence simply out of caution at early stages of the study. Marzari-Vanderbilt smearing of 0.0019 Ry., which corresponds to room temperature, was used for the electron occupations in all the band structure calculations.

**Table 4.2. Summary of parameters used for crystal basis**

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<th>System</th>
<th># of atoms</th>
<th># of unit cells</th>
<th>k-point grid</th>
<th>Total energy (eV atom⁻¹)</th>
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<td>1</td>
<td>6x6x4</td>
<td>-2243.946348</td>
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<tr>
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<td>1</td>
<td>10x10x10</td>
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</tr>
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</table>
Crystal definition: The unit cell geometry of the wurtzite phase of HgSe was obtained by the relaxation of a starting HgSe unit cell constructed by replacing Cd$^{2+}$ cations in a wurtzite CdSe unit cell with Hg$^{2+}$ cations. This approach was necessitated by the lack of available structural parameters for wurtzite HgSe as this material has not been realized in the bulk. Moreover, our XRD experiments confirm that the lattice parameters of the Hg-containing solids obtained from cation exchange do not differ significantly from those of the initial CdSe template. The relaxation calculations were performed with the scalar relativistic norm-conserving pseudopotentials Hg.pbe-d-hgh.UPF and Se.pbe-hgh.UPF obtained from the Quantum Espresso pseudopotential vault. The zincblende HgSe unit cell geometry was obtained by an initial definition of zincblende HgSe using zincblende CdSe lattice parameters followed by a geometry relaxation performed with the scalar Hg.pbe-d-hgh.UPF and Se.pbe-hgh.UPF pseudopotentials. The resulting zincblende HgSe unit cell showed a lattice constant of 6.26 Å, which matches the experimental known value.

Calculations of the wurtzite CdSe band structure were also performed for comparison. In the relaxed geometry of wurtzite HgSe, Hg$^{2+}$ was replaced with Cd$^{2+}$ and relaxation was performed using fully relativistic Cd and Se ONCV pseudopotentials. Since no further structural change resulted from this relaxation, the CdSe geometry defined in this manner was employed.

The geometries of the wurtzite Hg$_x$Cd$_{1-x}$Se alloys were defined using a two-step procedure. First, an initial unit cell geometry of wurtzite Hg$_{0.5}$Cd$_{0.5}$Se was defined using the lattice parameters of wurtzite CdSe. This Hg$_{0.5}$Cd$_{0.5}$Se unit cell was subject to relaxation. This relaxed unit cell was used to define the geometry for all alloys Hg$_x$Cd$_{1-x}$Se without any additional relaxation. Cd$^{2+}$ and Hg$^{2+}$ cations were placed in an alternating fashion within the cells to achieve as even a distribution as possible. Zincblende Hg$_x$Cd$_{1-x}$Se alloys were defined using the relaxed zincblende HgSe unit
cell geometry without further relaxation. All relaxations were conducted using the default values in the CELL and IONS namelists of the PWSCF input.

Band structure and effective mass calculations: Band structures were plotted along \( L \rightarrow \Gamma \rightarrow K \) high symmetry lines for the wurtzite structures and along the \( L \rightarrow \Gamma \rightarrow X \) high symmetry lines for the zincblende structures. The energy v.s. k-point plots were obtained by following up the initial PWSCF ‘scf’ calculation with a ‘bands’ calculation specified along the high symmetry lines. The Quantum Espresso post processing code bands.x was then used to print the energy v.s. k-point bands data.

Effective electron and hole masses were calculated for wurtzite structures from band structure plots in Origin Lab software. k-points were first converted into inverse real-space coordinates. A 1000-point B-spline interpolation of the band structure data was performed separately along two different high symmetry lines: \(-L \rightarrow \Gamma \rightarrow L\) and \(-K \rightarrow \Gamma \rightarrow K\). The second derivative of the energy with respect to \( k \) was then calculated by a finite difference method as:

\[
E'(k) = \frac{0.5(E(k + \Delta k) - E(k))}{\Delta k} + \frac{0.5(E(k) - E(k - \Delta k))}{\Delta k}
\]

\[
E''(k) = \frac{0.5(E'(k + \Delta k) - E'(k))}{\Delta k} + \frac{0.5(E'(k) - E'(k - \Delta k))}{\Delta k}
\]

where \( \Delta k \) is the k-point spacing. The second derivative at the \( \Gamma \) point was obtained by averaging over a finite range about the \( \Gamma \) point. This range was kept smaller than 10% of the full k-point range. Effective carrier masses used to calculate the size-modified band gaps are averages of the effective masses calculated about \( \Gamma \) along the two high symmetry lines.

Calculation of NC band gaps: Values for the NC optical band gap were calculated (eq. 4.2) by accounting for quantum confinement and exciton binding.\(^7\) Bulk high-frequency dielectric
constants for CdSe ($\varepsilon_{CdSe} = 6.32$)$^{71}$ and HgSe ($\varepsilon_{HgSe} = 17$)$^{72}$ were obtained from literature. For the alloys, high-frequency dielectric constants were estimated for different Hg fraction $x$ as:

$$\varepsilon_{alloy} = \varepsilon_{HgSe} \ast (x) + \varepsilon_{CdSe} \ast (1-x) \quad (4.6)$$

NC dielectric constants were approximated from the bulk values as in literature.$^{73}$

$$\varepsilon_{NC} = 1 + (\varepsilon_{bulk} - 1)/\left[1 + \left(7.5\text{Å} / D_{NC}\right)^{1.2}\right] \quad (4.7)$$

The bulk band gap of wurtzite CdSe was obtained from a separate hybrid functional PBE0 calculation with a 6x6x6 Monkhorst-Pack grid and 100 Ry. plane-wave basis cut-off. Cd.pbe-d-hgh.UPF and Se.pbe-hgh.UPF pseudopotentials from the Quantum Espresso vault were used. This calculation yielded a band gap of 1.763 eV in good agreement with the experimental value. A hybrid functional calculation was employed only for CdSe as it has a conventional semiconductor band gap, known to be underestimated by the PBE functional.$^{242}$ The other Hg$_x$Cd$_{1-x}$Se alloys are predicted to have inverted band structures with band gaps that originate from crystal splitting, as mentioned in the main text. Thus, hybrid functionals were not needed to ensure the accuracy of the alloy band gaps. It must be noted that the unit cell geometry employed for the PBE0 calculation differed slightly from that of all other cells, since it was produced by a separate PBE variable cell relaxation starting from the ideal wurtzite parameters.$^{69}$ A 100Ry. cutoff and a 20x20x20 Monkhorst-Pack k-point grid was used for this relaxation. The Cd.pbe-d-hgh.UPF and Se.pbe-hgh.UPF pseudopotentials obtained from the Quantum Espresso vault were employed. The relaxed CdSe cell did not deviate far from the ideal structure and did not differ significantly from the other relaxed wurtzite cells.
The effective hole and electron masses for CdSe and all alloys were obtained from non-hybrid PBE functional band structure calculations.

Band orbital character calculations: Orbital character contributions were obtained by integrating projected density of states (PDOS) data at the Γ point for each alloy species using the trapezoid method. The k-resolved PDOS data itself was obtained with the Quantum Espresso projwfc.x code using an energy grid spacing of 0.001 eV. PDOS data was generated for the s, p, and d atomic states of each individual Cd, Hg, and Se atom in the calculation cell. The PDOS was summed across all atoms of an element to obtain the total s, p, and d atomic state contribution for each element: Cd, Hg, or Se. Final orbital character contributions were obtained by integrating the element-wise PDOS in an energy range corresponding to either the Γ7 SO band or the hole bands. The integration ranges were obtained by inspecting the base of the DOS peaks making sure that the range covered the whole peak. The Γ8 lh and Γ8 hh bands were not distinguished due to the significant overlap of their DOS peaks and orbital character contributions are calculated for them jointly and identified as the ‘holes’ bands. The orbital character contribution is the fraction of the total Γ7 SO band or hole band peak area contributed by s,p, or, d atomic states of the three elements.

Charge density map generation: Charge density maps were obtained via post-processing with the Quantum Espresso pp.x code and subsequently visualized with the XCrySDen visualization program. Isosurface values that allowed for the best visualization of key charge distribution features and orbital character were used to generate maps.
Supporting Figure 4.1. High-resolution transmission electron (HRTEM) images of representative nanocrystals (NCs) of (a) the initial CdSe, (b) intermediate 1, (c) intermediate 2, and (d) the final product. (e) and (f) panels show the NC size distribution at the beginning and end of the cation exchange reaction, respectively. Size histograms were subject to a normal distribution fit in Origin Lab software to determine the peak size of the distribution, which was $3.6 \pm 0.3 \text{ (sd)}$ nm for the initial NCs and $3.9 \pm 0.2 \text{ (sd)}$ nm for the final NCs. The apparent increase in NC size cannot be attributed to attachment of additional material, e.g., an overcoat of Hg$^{2+}$, because the apparent radius increase (0.15 nm) is considerably smaller than a monolayer thickness (ca. 0.3 nm). Secondly, the apparent size increase is within the uncertainty represented by the standard deviation (sd) in the measured NC diameter; thus we may conclude that NC size is preserved in the exchange reaction.
Supporting Figure 4.2. Band structures plotted around the Γ point, showing the energy gap, for a range of HgCd\textsubscript{x}Se\textsubscript{1-x} alloys: (a) wurtzite CdSe, (b) wurtzite HgSe, (c) wurtzite Hg\textsubscript{0.25}Cd\textsubscript{0.75}Se, (d) wurtzite Hg\textsubscript{0.33}Cd\textsubscript{0.66}Se, (e) wurtzite Hg\textsubscript{0.5}Cd\textsubscript{0.5}Se, (f) wurtzite Hg\textsubscript{0.66}Cd\textsubscript{0.33}Se, (g) wurtzite Hg\textsubscript{0.75}Cd\textsubscript{0.25}Se, (h) zinc-blende HgSe, (i) zinc-blende Hg\textsubscript{0.25}Cd\textsubscript{0.75}Se, (j) zinc-blende Hg\textsubscript{0.5}Cd\textsubscript{0.5}Se, and (k) zinc-blende Hg\textsubscript{0.75}Cd\textsubscript{0.25}Se.
Supporting Figure 4.2 (cont.) Band structures plotted around the Γ point, showing the energy gap, for a range of HgₙCd₁₋ₙSe alloys: (a) wurtzite CdSe, (b) wurtzite HgSe, (c) wurtzite Hg₀.₂₅Cd₀.₇₅Se, (d) wurtzite Hg₀.₃₃Cd₀.₆₆Se, (e) wurtzite Hg₀.₅Cd₀.₅Se, (f) wurtzite Hg₀.₆₆Cd₀.₃₄Se, (g) wurtzite Hg₀.₇₅Cd₀.₂₅Se, (h) zinc-blende HgSe, (i) zinc-blende Hg₀.₂₅Cd₀.₇₅Se, (j) zinc-blende Hg₀.₅Cd₀.₅Se, (k) zinc-blende Hg₀.₇₅Cd₀.₂₅Se.
Supporting Figure 4.3. Inverse correlation between (a) Se p character and (b) cation s character in the high lying valence bands. In particular, the dip in the (dominant) Se p character of the valence bands at $x = 0.5$ coincides with the peak in the cation s character contribution.
Supporting Figure 4.4. Cation layering can induce anisotropy and open up a band gap even in the zinc-blende phase for intermediate Hg$_x$Cd$_{1-x}$Se structures. (a) Left panel shows schematic of compositional anisotropy resulting from segregation of Cd cations (grey) and Hg cations (purple) in different layers. Se anions are shown in yellow. The right panel shows the anisotropy of the DFT-calculated charge density for the $\Gamma_8$ hh band of layered Hg$_2$Cd$_2$Se$_4$. (b) The latter type of compositional anisotropy has a similar effect as the anisotropy resulting from bond elongation: the degeneracy between the light and heavy hole bands is lifted and a band gap is opened. The band gap realized in this manner has the largest magnitude at 50% exchange, the composition at which the crystal can be comprised of Cd-only layers alternating with Hg-only layers, which represents maximum compositional anisotropy.
Supporting Figure 4.5. In the course of conversion, it should not be assumed that the Hg fraction, \( x \), is the same for every NC in the sample, i.e., a compositionally homogeneous distribution. It is more likely that the Hg fraction at each point in the conversion is variable from NC to NC, i.e., a compositionally heterogeneous distribution. We modeled an exchange reaction which proceeds in such a compositionally heterogeneous manner. At each conversion point, defined by an average Hg fraction, \( \bar{x} \), we considered the Hg fraction of the NC ensemble to be Poisson distributed about this average, \( \bar{x} \).

(a) At each conversion point, defined by the average Hg fraction, \( \bar{x} \), the ensemble PL spectrum of the compositionally heterogeneous NC sample was modeled by averaging the PL contribution over the variable composition, with a Poisson distribution weighting. Note that the PL contribution of each NC to the ensemble spectrum was determined by its specific Hg fraction, \( x \). The PL band position was set by the DFT-calculated NC band-gap for that Hg fraction, \( x \) (Figure 4.5b). Note that the precise wavelength positions of the calculated (ensemble-averaged) PL bands deviate quantitatively from those of the experimental PL bands due to limitations of the calculation model.
Supporting Figure 4.5 (cont.) However, the simulated ensemble PL spectra show all the qualitative trends in our experimental PL data (Figure 4.3b). From $\bar{x} = 0$ to $\bar{x} = 0.25$, the PL peak maximum, which is in the visible wavelength region, exhibits a small blue-shift and a reduction in intensity. From $\bar{x} = 0.25$ to $\bar{x} = 0.35$, there is a drastic change in the PL spectrum. At $\bar{x} = 0.3$, a PL emission band emerges in the near-infrared region (NIR) in co-existence with the visible-region PL band. At $\bar{x} = 0.35$, a the NIR PL band becomes dominant, whereas the one in the visible region is nearly extinguished. Above $\bar{x} = 0.35$, the PL band continues to red-shift gradually and increase in intensity with increasing conversion. Most notably, the simulation captures the coexistence of the visible and NIR PL emission bands (at $\bar{x} = 0.3$), which is seen in the experimental PL spectrum at an intermediate point in the exchange (Figure 4.3b). Since the simulation does not consider phase segregation at the individual NC-level, the experimental observation of co-existing emission bands cannot necessarily be assigned to NCs consisting of phase segregated CdSe and HgSe domains. Rather a mixture of Cd-rich NCs and Hg-rich NCs, considered in the simulation, reproduces the experimental observation of co-existence of the two emission bands at intermediate conversion.

(b) When NC band gaps are estimated on the basis of PL maxima of the ensemble spectra of the compositionally heterogeneous distribution (red data points extracted from panel Supplementary Figure 4.5a), they deviate either negligibly or by only a marginal degree from the ideal NC band gaps that were not subject to such compositional heterogeneity (black data points from Figure 4.5b). Thus, the use of experimental PL spectra for determination of the NC band-gap as a function of the Hg fraction (Figure 4.5a) is justified despite the presence of compositional heterogeneity present in the NC ensemble.
Supporting Table 4.1. Summary of convergence test results for crucial topological insulator (TI) properties: the band gap energy and the inverted band energy. (a) The calculated band gap does not change by more than half a meV (~1%) when either the kinetic energy cutoff magnitude or the k-point grid size is increased. Thus, the calculated band gap is well converged with respect to the kinetic energy-cutoff and the k-point grid size. (b) The calculated energy difference between the inverted band and highest energy valence band at the Γ point, termed the inverted band energy, is also well converged with respect to the k-point grid size and the kinetic energy-cutoff. The calculated inverted band energy changes only by half a meV (~0.05%) when either the kinetic energy cutoff magnitude or the k-point grid size is increased.

a) Convergence of the calculated band gap with respect to the plane wave energy-cutoff and k-point grid.

b) Convergence of the calculated inverted band energy with respect to the plane wave energy-cutoff and k-point grid.

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CHAPTER 5: MECHANISM OF SULFIDATION OF SMALL ZINC OXIDE NANOPARTICLES

5 Reproduced with permission from Banerjee P., Jain P. K., Mechanism of sulfidation of small ZnO nanoparticles, RSC Advances, 8, 34476-34482, 2018. DOI: 10.1039/C8RA06949B.

5.1 ABSTRACT:

ZnO has industrial utility as a solid sorbent for the removal of polluting sulfur compounds from petroleum-based fuels. Small ZnO nanoparticles may be more effective in terms of sorption capacity and ease of sulfidation as compared to bulk ZnO. Motivated by this promise, here, we study the sulfidation of ZnO NPs and uncover the solid-state mechanism of the process by crystallographic and optical absorbance characterization. The wurtzite-structure ZnO NPs undergo complete sulfidation to yield ZnS NPs with a drastically different zincblende structure. However, in the early stages, the ZnO NP lattice undergoes only substitutional doping by sulfur, while retaining its wurtzite structure. Above a threshold sulfur-doping level of 30 mol%, separate zincblende ZnS grains nucleate, which grow at the expense of the ZnO NPs, finally yielding ZnS NPs. Thus, the full oxide to sulfide transformation cannot be viewed simply as a topotactic place-exchange of anions. The product ZnS NPs formed by nucleation-growth share neither the crystallographic structure nor the size of the initial ZnO NPs. The reaction mechanism may inform the future design of nanostructured ZnO sorbents.

5.2 INTRODUCTION:

Zinc oxide (ZnO) nanoparticles (NPs), due to their cost-effectiveness and biodegradability, have a multitude of applications including coatings and pigments, catalysis,
energy storage, and environmental remediation. ZnO NPs have particular appeal as sorbents for scavenging polluting sulfur compounds such as mercaptans and hydrogen sulfide (H$_2$S) from petroleum-based fuels: $\text{ZnO + H}_2\text{S} \rightarrow \text{ZnS + H}_2\text{O}$. Lattice O$^{2-}$ in the ZnO is replaced with S$^{2-}$ scavenged from the pollutant. Bulk powders of ZnO have already been used for adsorptive removal of H$_2$S, but NPs have specific advantages. With smaller grain sizes, mass transport limitations are lifted. Whereas sulfidation is limited to the surface of bulk ZnO, with NPs, the entire mass of ZnO can undergo sulfidation, enabling high sorbent capacity. Volume and morphology changes resulting from restructuring of the solid can also be more easily accommodated with NPs, allowing regenerable use of the sorbent. Finally, the high specific surface area of NPs allows more enhanced kinetics of the sulfidation reaction, potentially facilitating much lower desulfurization temperatures as compared to the conventional operating temperatures of 650–800 °C.

In this context, small few-nm size ZnO NPs can be expected to be particularly promising, but it is important to understand the manner in which these NPs undergo sulfidation. The structural mechanism of the sulfidation process may have critical differences compared to bulk ZnO powders or even larger NPs of tens of nm in size and may therefore influence sorbent design. In a seminal study, Park et al. studied the sulfidation of hexagonal-shaped 14 nm ZnO nanocrystals (NCs) at high temperature (235 °C) using hexamethyldisilathiane. The reaction was found to involve the anion exchange of O$^{2-}$ with S$^{2-}$ in the NC lattice. The overall shape and crystallography of ZnS NCs was templated by the initial ZnO NCs. However, due to the faster outward diffusion of Zn$^{2+}$ as compared to the inward diffusion of S$^{2-}$, the exchange reaction was accompanied by a nanoscale Kirkendall phenomenon, as a result of which the ZnS NCs formed were hollow.
Here, we track the step-wise sulfidation of smaller (ca. 5 nm) ZnO NPs using optical spectroscopy and X-ray crystallography. Prior to the onset of sulfidation, O$^2$- in wurtzite ZnO NPs undergoes substitutional doping with S$^2$- without any major change in its structure. Upon reaching a critical concentration of sulfur doping, separate zincblende ZnS grains form and grow into ZnS NPs. Thus, the sulfidation of these small ZnO NPs studied here is not simply a topotactic or templated place exchange of anions; rather the nucleation and growth of a separate ZnS crystallite is involved in the latter stages.

5.3 METHODS:

Synthesis of ZnO NPs. The synthesis of 4 nm ZnO NPs was based on a procedure from Kamat and coworkers$^{298}$ with some changes. Briefly, 0.05 M of zinc acetate dihydrate (1.095 g) was added to 50 mL of ethanol in a 100 mL three-necked round-bottom flask. The flask was put under Ar, heated to 80 °C, and refluxed for 2 h followed by gradual cooling down to room-temperature over the course of 1.5 h. The zinc precursor solution (0.05 M) was stored in a desiccator and was used for a period up to three months from the preparation date. Whenever needed, a batch of the ZnO NP colloid was prepared by the hydrolysis of the zinc precursor using lithium hydroxide (LiOH) powder. Typically, 20 mg of LiOH was added directly to 3 mL of the precursor solution diluted with 12 mL of ethanol. The resulting reaction mixture was sonicated for 20 min without heating. The resulting colloid solution was washed by adding an equal volume of acetone and centrifuging at 10 000 rpm for 20 min. The precipitated colloid was redispersed in 25 mL of ethanol. The colloid was allowed to stand for 5 h or more to allow NP growth to stabilize before sulfidation studies or other measurements. The ZnO colloid was typically used up to a week from its preparation.
Sulfidation of ZnO NPs. The conversion from ZnO to ZnS NPs was carried out at a temperature of 45 °C. We started with a colloid of ZnO NPs dispersed in ethanol (at a concentration which yields an absorbance of ~1 at the ZnO excitonic peak maximum). The colloid was transferred to a 20 mL glass vial immersed in a water bath set at 45 °C. To this colloid, a solution of sodium sulfide (Na₂S) in ethanol (3.1 mg mL⁻¹) was added in aliquots of 10 mL with vigorous stirring. After each addition, the reaction was allowed to approach completion by waiting a duration of 40 min, after which ~3.5 mL of the colloid was transferred to a quartz spectrophotometry cuvette and a UV-vis extinction spectrum in the range of 220–600 nm was measured. After the measurement, the colloid was returned to the reaction vial. The reaction appeared to reach saturation upon the addition of 11.9 mmol of S²⁻, at which point no further change in the excitonic features in the absorbance spectrum were observed.

At various stages of sulfidation, the NPs were subject to other characterization described below. For this, the colloid subject was subject to sulfidation in steps, as described above, up to a specific stage identified by the total molar amount of S²⁻ added. The colloid was then purified from excess reagents and salts by washing with acetone and centrifugation at 10 000 rpm for 20 min. The precipitated colloid was redispersed in ethanol for further characterization.

pXRD. Powder X-ray diffraction (pXRD) patterns were collected for NPs at multiple stages of sulfidation. The diffraction measurements were conducted on a Rigaku Miniflex 600 powder X-ray diffractometer operated at full power (40 kV to 15 mA) with Cu Ka radiation wavelength (1.54 Å). Data was collected in reflection mode in the 2θ range of 20°–75° using a step size of 0.04°, with scan times lasting for 2–3 h. pXRD samples were prepared by drop-casting NPs from a colloid dispersed in ethanol into a thick film on a zero-background quartz substrate. Before each run, the
quartz substrate was cleaned by rinsing in aqua regia and DI water. Diffraction patterns were plotted in Origin Lab software and manual baseline subtraction was performed for each of the patterns.

Elemental analysis. The elemental composition of the NPs, specifically the molar ratio of S : Zn, was determined at three stages: the initial ZnO NPs before sulfidation, the intermediate stage obtained by the addition of 1.99 mmol of S\(^2\)-, and the final ZnS NPs achieved by the addition of 11.9 mmol of S\(^2\)- to the ZnO NPs. These samples were each purified of reagents and salts twice by washing with acetone and centrifugation. The washed precipitate was subsequently dried in quartz digestion tubes by flowing N\(_2\) gas. Samples were subject to inductively-coupled plasma atomic emission spectroscopy (ICP-AES) measurements, the results of which are presented in Table 5.1.

**Table 5.1: Elemental composition of the NPs at key stages in the sulfidation.**

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<th>Stage</th>
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<td>Initial (ZnO)</td>
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<td>Intermediate (1.99 µmol of S(^2)- added)</td>
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<tr>
<td>Final (ZnS)</td>
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Electron microscopy. The initial ZnO NPs and final ZnS NPs were subject to TEM imaging. For ZnO NPs, 6 mL of ZnO colloid prepared as described above was treated with 0.3 mL of oleic acid and washed with 6 mL of acetone followed by centrifugation at 10 000 rpm for 20 min. Then the precipitated colloid was dispersed in ethanol. About 50 mL of the diluted ZnO NP colloid was drop cast onto an ultrathin carbon grid, which was then allowed to dry in a vacuum desiccator. ZnS NPs were prepared by complete sulfidation of 6 mL of ZnO colloid accomplished, as described above, by addition of S\(^2\)-. The ZnS NP colloid was treated with 0.3 mL of oleic acid and washed with 6 mL of acetone followed by centrifugation at 10 000 rpm for 20 min. Then the
precipitated colloid was dispersed in ethanol. The TEM grid, held by tweezers was dipped into the colloid once and then allowed to dry in a vacuum desiccator. TEM imaging was performed on a JEOL 2010-EFFEG instrument operating at 200 kV. NP size analysis was performed using the Fiji software. The diameter of each NP identified in a representative image was determined manually along three arbitrary directions across the NP and averaged.

Structure factor simulations. For the initial ZnO and the early-stage sulfur-doped ZnO NCs, pXRD patterns were simulated using the program PowderCell. The program performs a structure factor calculation using crystal symmetry, lattice parameters, atomic positions, site occupancies and Debye–Scherer broadening as input parameters. Input parameters for each simulated pattern are presented in Table 5.2. The X-ray wavelength was set to 1.54 °A corresponding to Cu Kα1 radiation. The starting model was ZnO in a wurtzite lattice, characterized by the space group P63mmc. The O and the Zn atoms were placed in the 2b Wycoff positions. The lattice parameters were set to 3.247 °A and 5.179 °A along the a and the c crystallographic directions, respectively, which provided the closest fit to the peak positions of the experimentally measured pXRD reflections of the wurtzite ZnO NPs. These lattice parameters, while close to the known parameters of bulk ZnO (a = 3.250 °A and c = 5.204 °A), are marginally smaller, which may be explained by a small degree of compressive strain in the NPs. A peak-dependent Debye–Scherer broadening (FWHM) of 0.79° was applied at a 2θ of 20°, along with a Lorentzian peak profile. The pXRD pattern simulated with these parameters matched the experimental pattern of the initial ZnO NPs, especially in terms of the {002}:{101} peak intensity ratio. For sulfur-doped ZnO NCs, the structure was modeled by substitution of a fraction of the O2− by S2− in the 2b Wycoff positions. Four different S/Zn molar ratios of 0.1, 0.11, 0.24, and 0.29 were tested, simulated pXRD patterns
of which matched experimental patterns (in terms of the \{002\}:\{101\} peak intensity ratio) of the NPs at added S\textsuperscript{2-} amount of 0.4, 0.79, 1.99, and 2.78 mmol, respectively.

**Table 5.2:** Crystallographic parameters for structure factor simulations shown in Fig. 5.2b and d.

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5.4 optical characterization of ZNO NPS and various intermediates:

The ZnO NPs, synthesized following a known procedure\textsuperscript{298}, had an average size of 4.7 nm (Fig. 5.1a and b) as found from TEM and a wurtzite structure as shown by their pXRD pattern (Fig. 5.2a, dark purple curve). The NPs were subject to sulfidation with Na\textsubscript{2}S in ethanol at 45 °C. The
sulfidation was performed as a titration, wherein molar aliquots of Na$_2$S were added in a stepwise manner. Upon cumulative addition of 11.9 mmol of Na$_2$S or S$^2$-, the ZnO NPs underwent complete sulfidation. This is evidenced by the complete loss of diffraction peaks of wurtzite ZnO and the appearance of the {111} and {220} reflections of zincblende ZnS in the pXRD pattern (Fig. 5.2a, brown curve). In the elemental analysis (Table 5.1) of the final-stage NPs, a S/Zn molar of ca. 1 was measured, which supports the complete sulfidation of ZnO NPs to form ZnS. TEM showed ZnS NPs with an average size of 2.7 nm, significantly smaller than the size of the starting ZnO NPs. The smaller grain size of the ZnS is also reflected in the greater Debye–Scherer broadening of the pXRD peaks of the final-stage ZnS NPs (Fig. 5.2a, brown curve) as compared to those of the starting ZnO NPs (Fig. 5.2a, dark purple curve). From the Debye–Scherer broadening of the {111} peak ($2\theta = 29^\circ$, FWHM = 3.79$^\circ$) of the final ZnS NPs, we estimated the NP size $D$:

$$D = \frac{0.94\lambda}{\text{FWHM in radians x } \cos \theta} \quad (5.1)$$

to be 22.6 Å or 2.3 nm. $\lambda$ is the incident X-ray wavelength of 1.54 Å. The size estimated from pXRD is close to the one estimated by TEM (Fig. 5.1d).

At each step of the titration, the NP colloid was characterized by UV-vis extinction spectrophotometry (Fig. 5.1e) and pXRD (Fig. 5.2a), which shed light on the manner of sulfidation. The starting ZnO NPs exhibited an extinction spectrum with an exciton peak around 3.66 eV. This excitonic peak reflects the band-gap of these NPs, which is smaller than the bulk value$^{300}$ of 3.37 eV due to the effect of quantum confinement.
Figure 5.1: (a) Representative TEM image of the synthesized ZnO NPs, (b) histogram of NP diameter for n = 120 NPs showing an average of 4.7 nm with a standard deviation (s) of 0.5 nm. (c) Representative TEM image of the synthesized ZnS NPs, (d) histogram of NP diameter for n = 40 NPs showing an average of 2.7 nm with a standard deviation (s) of 0.6 nm. (e) Absorbance spectra (normalized from 0 to 1 in the 270–380 nm range) of the colloid at various stages of ZnO NP sulfidation, in terms of the moles of Na₂S added. The exciton peak positions of the initial ZnO NPs and the final ZnS NPs are marked by the vertical dotted lines. (f) The ZnO NP and the ZnS NP exciton peak energies in eV plotted as a function of the moles of Na₂S added. The exciton peak energies were extracted from the absorbance spectra in (e), which were first subject to manual baseline subtraction, without which it is difficult to discern from the plotted spectra the broad and weak ZnS exciton peak at the early stages of sulfidation.

With the sequential addition of S²⁻ in the range of 0–1.99 mmol, the ZnO excitonic peak shifted to lower energies (Fig. 5.1f). This shift cannot be attributed to the formation of ZnS. ZnS has a higher band-gap than ZnO,³⁰¹ so ZnS formation would have resulted in a shift to higher energies. Moreover, pXRD showed that, in the 0–1.99 mmol range of added S²⁻, the NPs maintain their wurtzite ZnO structure (Fig. 5.2a) and no diffraction peaks related to ZnS are observed. However, elemental analysis of the NPs obtained by treatment with 1.99 mmol of S²⁻ revealed a S/Zn molar ratio of 0.27 (Table 1). Thus, the ZnO NPs appear to be significantly sulfur-doped. Such sulfur doping can explain the red-shift of the exciton peak. Zinc oxysulfides, ZnO₁₋ₓSₓ, with x = 0–0.3
are known to have a lower band gap than ZnO due to the effect of band-bowing.\textsuperscript{301} If the sulfur-doping were to be limited to an outer shell of each NP, the resulting intermediate-stage NPs would consist of a shrunken ZnO core surrounded by a ZnS shell. Such NPs would exhibit a blue-shifted ZnO exciton peak as compared to the exciton peak of the initial ZnO NPs. On the other hand, we observe a red-shift of the ZnO exciton peak at the early stages in the sulfidation (Fig. 5.1f, bottom panel), which is consistent with the attainment of an oxysulfide composition.\textsuperscript{301} In other words, the sulfur-doping extends across the NP lattice.

5.5 STRUCTURAL STUDIES USING XRD AND STRUCTURE FACTOR SIMULATIONS:

Further confirmation of and insight into the sulfur-doping of the ZnO NPs at the early stages of the sulfidation (0–2.78 mmol of $S^{2-}$) is obtained from a closer analysis of the pXRD findings.

We performed pXRD simulations (Fig. 5.2d) of sulfur-doped ZnO lattices, where a fraction of the $O^2-$ anions were replaced by $S^{2-}$, without any other modification of the wurtzite structure. The simulated pXRD patterns of sulfur-doped ZnO resemble the simulated pattern for wurtzite ZnO (Fig. 5.2d). However, there is one difference: the ratio of the \{002\}:{\{111\} peak intensity is higher for the sulfur-doped ZnO NPs as compared to the undoped ZnO NPs. Larger the $S/Zn$ molar ratio (Fig. 5.2d), greater is the ratio of the \{002\}:{\{111\} peak intensity. This computed trend matches with the trend observed in the experimental pXRD, as shown in Fig. 5.2b. Thus, the pXRD analysis confirms that at the early stages of the sulfidation, the ZnO NPs undergo substitutional doping by sulfur. Simulations predict that NPs subject to 1.99 mmol $S^{2-}$ have a $S/Zn$ molar ratio of 0.24, which is close to the elemental analysis findings (Table 5.1).
Figure 5.2: (a) Experimental pXRD patterns (baseline subtracted) are shown for NPs at various stages of the sulfidation transformation from wurtzite ZnO to zincblende ZnS, indicated by the moles of Na₂S added. Peaks are assigned to major reflections, as labeled by the \( \{hkl\} \) Miller plane notation, with wurtzite ZnO reflections shown by purple sticks and zincblende ZnS ones by brown sticks. (b) The \( \{002\} : \{101\} \) peak intensity ratio from experimental patterns (black data points) and from simulations (red data points) plotted at the early stages of sulfidation. Lines are meant to guide the eye. (c) A magnified view of the experimental pXRD patterns plotted to highlight the peak reflection changes occurring in the early stages of sulfidation: 0, 0.4, 0.79, 1.99, and 2.78 mmol of S²⁻. The color legend is the same as that of (a). (d) Simulated pXRD patterns for NCs at early stages of sulfidation, plotted with the same magnified view as that in (c). The legend specifies the molar ratio of S/Zn used in the pXRD simulation. The crystallographic parameters used for the pXRD simulations at each stage are tabulated in Table 5.2. All patterns are shown vertically stacked and major reflections are labeled by the \( \{hkl\} \) Miller plane notation.

At the point of 2.78 mmol added S²⁻, a broad absorption peak emerged at higher energies, i.e., 4.6 eV. This peak can be attributed to newly formed ZnS NPs. After all, ZnS is known to have a higher band-gap than ZnO. Upon further addition of S²⁻, the newly emerged excitonic peak increased
in absorbance and shifted to lower energies (Fig. 5.1e and f). Alongside, the ZnO exciton peak decreased in strength until it was fully extinguished. These spectral trends can be explained by the following manner of sulfidation. A small ZnS domain nucleates from the heavily sulfur-doped ZnO NPs. The considerably higher excitonic peak energy of 4.6 eV relative to the bulk ZnO band-gap$^{302}$ of 3.72 eV suggests that the nucleated domain is ultrasmall. As more S$^{2-}$ becomes available, the ZnS domains grow further, which is manifested in the red-shift of the ZnS excitonic peak and increase in its absorbance (Fig. 5.1e and f). Concomitantly, the ZnO domains, which serve as the source of Zn, shrink in volume, which is reflected in a small blue-shift of the ZnO excitonic peak along with a decrease in its absorbance beyond 3.57 mmol added S$^{2-}$. Eventually, the ZnO excitonic peak was fully extinguished. The final ZnS NPs exhibited a spectrum with a single excitonic peak at 3.94 eV, corresponding to small NPs.

The pXRD results provide further support to the above described mechanism of sulfidation in the post-doping stages. At 4.37 mmol of added S$^{2-}$, a broad peak appeared at the position corresponding to the major {111} reflection of zincblende ZnS, which serves as a structural indicator of ZnS nucleation. This diffraction peak grew in relative intensity and also narrowed with increasing addition of S$^{2-}$, which would be consistent with a growth in ZnS domains. Alongside, with increasing addition of S$^{2-}$, the wurtzite ZnO diffraction peaks became gradually weaker in relative intensity, until they were fully extinguished. The final pXRD pattern is indicative of NPs in a single ZnS phase, as also confirmed by the elemental analysis (Table 5.1). The final ZnS NPs appear to have a broader size dispersion (Fig. 5.1d, standard deviation of 22%) as compared to that of the initial ZnO NPs (Fig. 5.1b, standard deviation of 11%). The final NPs are formed by sulfur-doping of ZnO NPs followed by nucleation and growth of separate ZnS domains, a process expected to be replete with inherent heterogeneities.
5.6 CONCLUSION:

Figure 5.3: Pictorial depiction of the atomistic mechanism of sulfidation. Zn atoms are shown in yellow, O in green, and S in red. The structures were generated in Vesta software. The ZnO crystallite was based on a wurtzite (W) P63mmc unit cell containing 2592 atoms. The sulfur-doped crystallite was made by replacing some of the O atoms by S atoms. The ZnS crystallite is based on zincblende (ZB) F43m structure containing 1963 atoms. The morphologies and shapes of the final ZnS NPs formed by the nucleation-growth mechanism do not bear a topotaxial relationship with the initial ZnO NPs.

The scheme in Fig. 5.3 summarizes the mechanism of sulfidation that is drawn from the results taken as a whole. The sulfidation of ZnO NPs is preceded by a stage where the NPs undergo substitutional doping by S$^{2-}$. The wurtzite ZnO lattice remains otherwise unmodified in its structure. Above a concentration of ca. 30 mol% S$^{2-}$ dopants, ZnS nucleates from the ZnO. The threshold concentration probably corresponds to the solubility limit of S$^{2-}$ in ZnO. As more S$^{2-}$ becomes available, ZnS domains grow by supply of Zn$^{2+}$ from ZnO. The O$^{2-}$ diffuses into solution. Thus, the complete phase transformation of the NPs from ZnO to ZnS cannot be considered simply as a topotactic exchange of anions in analogy to cation exchange reactions.$^{77,80,81,160,167,197–200,246,303–305}$ Rather the post-doping stage sulfidation is more akin to a dissolution–reprecipitation process known in mineralogy,$^{305}$ although the reprecipitation (nucleation-growth of ZnS) may occur in interfacial contact with the sulfur-doped ZnO NPs. The ZnS NPs formed from the nucleation-growth process share neither the crystallographic structure nor the morphology or size
of the initial ZnO NPs. In topotactic sulfidation, the differences between the equilibrium unit cells of ZnO and ZnS would result in lattice strain and stress; in sulfidation occurring via the reprecipitation-like mechanism found here, such stresses and any resulting thermodynamic or kinetic bottlenecks in the solid-state transformation would be relieved. This mechanism of sulfidation must be taken into consideration when developing small ZnO NP-based sorbents for uptake of sulfur compounds from fuels. The major restructuring involved in going from the oxide to the sulfide can have major implications for the engineering design and operation of NP-based sorbent columns.
CHAPTER 6: SIMULATION OF OPTICAL PROPERTIES AND NEAR-FIELD EXCITATION MAPS OF PLASMONIC NANOSTRUCTURES USING THE OPEN-SOURCE nanoDDSCAT+ TOOL


6.1 AUTHOR CONTRIBUTIONS:

This chapter resulted from a collaboration between the Gruebele group (experimental studies) and the Jain group (computational simulations). Huy Nguyen and Duc Nguyen in Martin Gruebele’s lab imaged the surfaces of photoexcited Au nanoislands using a method called single-molecule absorption scanning tunneling microscopy (SMA-STM) developed in the Gruebele group. As a team we speculated whether these SMA-STM images captured plasmonic fields generated on the Au nanoislands by photoexcitation, a hypothesis that my electrodynamic simulations set out to test. Using the nanoDDSCAT toolkit developed by the Jain group, I simulated the optical spectra and near-field profiles for representative nanoisland assemblies, which were modeled on those found in the experiments. The near-field maps observed under light excitation agreed with those imaged by SMA-STM, supporting our hypothesis. With Prof. Jain’s advice, I performed an extensive set of simulations to predict how the spatial profile of the near-field is modified when the excitation wavelength or incident polarization are tuned. These predictions motivated further experiments by Huy Nguyen, the results of which further solidified the close correspondence between near-field maps and SMA-STM images of Au nanoislands.
6.2 ABSTRACT:

An optically modulated scanning tunneling microscopy technique developed for measurement of single-molecule optical absorption is used here to image the light absorption by individual Au nanoislands and Au nanostructures. The technique is shown to spatially map, with nanometer resolution, localized surface plasmons (LSPs) excited within the nanoislands. Electrodynamic simulations demonstrate the correspondence of the measured images to plasmonic near-field intensity maps. The optical STM imaging technique captures the wavelength, polarization, and geometry dependence of the LSP resonances and their corresponding near-fields. Thus, we introduce a tool for real-space, nanometer-scale visualization of optical energy absorption, transport, and dissipation in complex plasmonic nanostructures.

6.3 INTRODUCTION:

The plasmonic scattering and absorption of noble metal nanoparticles (NPs)\textsuperscript{306} have found promise in applications ranging from photonics\textsuperscript{307,308} to biomedical sciences.\textsuperscript{309–315} As a result, the size-, shape-, and configuration-tunable absorption and scattering spectra of plasmonic NPs have been characterized in ample detail using spectroscopy, both at the ensemble and single-nanoparticle levels.\textsuperscript{316–320} In addition to these brilliant far-field spectroscopic properties, the excitation of a localized surface plasmon (LSP) on a NP is known to result in electric near-fields enhanced orders-of-magnitude relative to the incident field.\textsuperscript{321} These near-fields have utility in surface-enhanced spectroscopies, most notably surface-enhanced Raman scattering (SERS),\textsuperscript{322–325} enhancement of light absorption in photovoltaics,\textsuperscript{326–335} Purcell enhancement of light emission,\textsuperscript{336–338} and plasmonic catalysis\textsuperscript{339–343} and hot electron photochemistry.\textsuperscript{344,345}
However, the near-field properties of plasmonic NPs are harder to measure and therefore investigated more routinely using theoretical methods and electrodynamic simulations. Experimental methods such as electron energy loss spectroscopy (EELS) and scanning tunneling microscopy tip-enhanced Raman spectroscopy (STM-TERS) have now been advanced to a level where LSPs can be imaged in the near-field. Imaging tools with clear capability for the real-space nanometer-resolved visualization of LSP excitations can promote deeper understanding of photonic and energy transport processes in complex nanostructures.

Here, we demonstrate such a capability with a method known as single-molecule absorption spectroscopy detected by scanning tunneling microscopy (SMA–STM). SMA–STM is used to spatially map the light absorption of Au nanoisland assemblies. The SMA–STM map mirrors the spatial profile of the LSP near-field excited within the assembly, as demonstrated by electrodynamic simulations. While SMA–STM imaging of Pt clusters and PbS semiconductor quantum dots was reported by us in the past, here, we present the first account of real-space imaging of LSPs on a metal nanostructure surface by SMA–STM. The method is further capable of imaging the light absorption of complex Au nanostructures, where we observe intricate LSP spatial patterns that are tunable by change of the excitation wavelength and polarization.
Figure 6.1. (a) Schematic of the SMA–STM experiment: a modulated near-infrared laser beam with original polarization (p-polarization) oriented parallel to the optical table (shown in blue) passes through a half-wave plate (resulting in s-polarization) and is focused onto a transparent sapphire substrate cut for a TIR geometry. The wedge allows for plasmonic coupling with the Au nanoislands (red discs) formed on the Pt-Au thin film surface. The light absorption of the NPs induces a change in the tunneling current when the tip raster-scans over them. The change in tunneling current caused by photoexcitation is then detected by a lock-in amplifier. (b) Setup used for simulations, with p and s polarizations indicated.

6.4 SETTING UP THE EXPERIMENTS:

Au nanoislands (termed as such due to their morphology) are deposited on a PtAu layer on the side opposite to the substrate. As shown in Fig. 6.1, an incident laser illuminates the sample from the rear in a total-internal-reflection (TIR) Kretschmann configuration achieved by machining a wedge into a sapphire substrate. This rear illumination allows for the generation of LSPs at the Au surface and minimizes thermal perturbation at the STM tip–sample junction. The sample surface is scanned by the STM tip in the presence of the laser beam. To enhance detection sensitivity, the laser is amplitude-modulated. As the laser absorption modulates the electron density of the Au nanoislands, the resulting modulation in the tunneling current is detected by a lock-in amplifier, yielding the SMA–STM image (grayscale in figures). The SMA–STM image
maps with sub-NP resolution where the Au nanoislands are electronically (photo)excited by the laser light.\textsuperscript{355,360} We demonstrate that these SMA–STM images correspond to near-field maps of LSPs excited on the Au nanoislands. The average tunneling current is detected simultaneously to yield a topographic image (orange color scale in figures).

6.5 OBSERVATION OF LSPs ON Au NANOISLANDS:

We scanned the STM tip over a three-Au nanoisland assembly (whose topography is shown in Fig. 6.2a) under 700-nm p-polarized light excitation. The resulting SMA–STM image is shown in Fig. 6.2d. As we have established in the past,\textsuperscript{354-357,359,361} darker regions in such images correspond to locations of larger tunneling current modulation, which are effectively locations of higher light absorption, relative to the substrate absorption. Fig. 6.2d shows that the tunneling current modulation level is different for each nanoisland. Nanoisland 1 has the largest reduction in tunneling current upon illumination (image locally darker than background). On the other hand, for nanoisland 2, the tunneling current is actually enhanced (image locally brighter than background). Nanoisland 3 represents a situation intermediate to the former two cases.
Figure 6.2. Assembly of three Au NPs near a grain boundary showing (a) the topography of the surface plotted in an orange color intensity map, with the darkest regions representing the deepest features; (b) top-down view of the model of the assembly used in DDA simulations. The thickness of the nanoislands used in the simulation model were based on topographic height information from STM (#1 = 18 nm horizontally and 18 nm vertically, height of 2 nm above substrate, #2 = 21 nm horizontally and 25 nm vertically, height of 4 nm above substrate, #3 = 17 nm horizontally and 26 nm vertically with a height of 5 nm above the substrate). The assembly was supported on a rectangular Au slab (70 nm x 70 nm with 10 nm thickness) placed on a rectangular Pt slab (70 nm x 70 nm with 5 nm thickness); (c) a line profile (blue line in a) over particle 1, indicates that the NP is a nanodisc of aspect ratio (diameter/height) of ~10 (d) the SMA–STM signal (current modulation) map in gray scale under p-polarized TIR excitation by a 700-nm laser with an intensity of 2500 mW/mm². Darker colors in the map denote stronger absorption. The horizontal bright lines in (a) and the change in contrast 40% from the bottom in (d) are due to a tip change during the scan. (e) DDA-simulated electric field intensity for the assembly in (b) under p-polarized excitation and 700 nm wavelength. The arrow shows the projection of the polarization in the plane of the sample. A rainbow color scale shows the magnitude of the field intensity, with blue being the low and red being the highest; and (f) DDA-simulated absorption spectra for the assembly under p- and the s-polarized excitation. The STM scanning condition is 1.2 V, 5 pA. Scale bar: 20 nm in panels a, b, and d.

We hypothesized that the SMA–STM method images photoexcitation of LSPs within the Au nanoislands. LSP excitation of the Au nanoisland can promote electrons to excited states in the
vacant sp band above the Au Fermi level. Such a process would block tunneling through the previously empty states, which would be manifested in a lower tunneling current under photoexcitation. A nanoisland with an LSP resonance overlapping with the 700 nm excitation wavelength will absorb light more strongly as compared to the PtAu substrate, which itself has broad absorption across the near-infrared (NIR) region (Fig. 6.1) Such a nanoisland would exhibit a negative SMA–STM signal. This is the case of nanoisland 1. Conversely, a nanoisland may have an LSP resonance completely offset from the excitation wavelength. Such a nanoisland would absorb light less strongly than the PtAu substrate and consequently exhibit a positive SMA–STM signal. Nanoisland 2 represents this latter scenario.

To test our formulated hypothesis, electrodynamic simulations of plasmonic near-fields were performed using the discrete dipole approximation (DDA) method. The DDA-calculated near-field map for a reconstructed model of the experimental nanoisland assembly (under 700 nm, p-polarized light excitation) is shown in Fig. 6.2e. The calculated map qualitatively models the experimental SMA–STM image: nanoisland 1 exhibits the highest field intensity, nanoislands 2 and 3 exhibit smaller field intensities.

Although there is qualitative agreement, the simulated electric field distribution and the experimental SMA–STM signal contrast do not match quantitatively. The details of the electric field distribution are sensitive to subtle features of the target structure, which are impossible to ascertain with absolute precision from a top-view STM perspective. Since structural uncertainties are inherent in such a scenario, we approximated the nanostructure geometry by an assembly of idealized cylinders, a procedure that is amenable to consistent application and reproducibility. These approximations in the target structure are the likely cause of the quantitative discrepancy.
The lack of inclusion of quantum effects and the absence of a TIR excitation geometry in the simulations may be other sources of discrepancy. Notwithstanding the quantitative discrepancies, the simulations clearly demonstrate that the SMA–STM images map the degree of light absorption and the resulting near-field of the plasmon-excited nanoislands.

**Figure 6.3.** Imaging the absorption of the two Au nanoislands at various wavelengths in the NIR region. The gray images are the experimental SMA–STM maps (with subtracted background) under p-polarized light excitation of different wavelengths, (a:950 nm, c:900 nm, e:850 nm, g:810 nm, i:790 nm, k:770 nm, m:740 nm respectively). The corresponding DDA simulated near-field intensity maps obtained under p-polarized light excitation (b:950 nm, d:900 nm, f:850 nm, h:810 nm, j:790 nm, l:770 nm, n:740 nm respectively) are plotted on a colored rainbow scale. The orange image (Fig. 3o) is the STM topographic image of the nanostructure of interest. The STM scanning conditions are 1.5 V, 10 pA. The power densities of the laser at these wavelengths are 3,000±500 mW/mm². Scale bars: 20 nm.
6.6 WAVELENGTH-SCANNED SMA-STM IMAGING OF LSPs:

Following this proof-of-concept demonstration of SMA–STM imaging of an LSP excitation on a model nanostructure geometry, we employ the method for real-space mapping of the light absorption of an irregularly shaped nanostructure. Such a heterogeneous, complex nanostructured surface poses a real test of the utility of the SMA–STM technique for drawing insights into the spatiotemporal mechanisms of light absorption and energy transport. The nanostructure consisted of two Au nanoislands (labeled 1 and 2) enclosing a grain boundary, as shown by the STM topographic image (Fig. 6.3o and Supplementary Fig. 6.2a), four select line profiles taken across the topography (Supplementary Fig. 6.2b), and a perspective view of the topography (Supplementary Fig. 6.2c). There are additional nanoislands between the two numbered nanoislands, but these are found to exhibit considerably lower absorption signal in the experiment as compared to the labeled nanoislands, as also confirmed by the simulation.

As further validation of our methodology, we performed SMA–STM imaging of this nanostructure as a function of the excitation wavelength. In the past, we had been instrumentally limited to single-wavelength SMA–STM imaging. We now have the ability to measure SMA–STM images at a range of wavelengths across the near-infrared (NIR) region. Employing this ability, we measured the spectral profile (action spectrum) of the SMA–STM signal and examined whether this profile corresponds to the LSP spectrum of the nanostructure (Fig. 6.3). We obtained SMA–STM images for a range of excitation laser wavelengths (Fig. 6.3) varied from 740 nm to 950 nm in increments of 30–50 nm. Finally, the excitation was switched back in steps to 740 nm, to confirm reproducibility of the imaging (Supplementary Fig. 6.3). The excitation was p-polarized.
Figure 6.4. Dependence of plasmonic behavior on polarization of light. (a, c, and e), left: SMA–STM images (80 nm x 90 nm) of two nanoislands interacting with p-, sp- (45° between s and p), and s-polarized laser excitation of 850 nm wavelength, respectively; (b, d, and f) right: corresponding DDA-calculated near-field intensity maps under 850 nm excitation with the corresponding polarizations; (g) DDA-calculated absorption spectra of the reconstructed geometry for p-, sp-, and s-polarized excitation.
As indicated in Fig. 6.3a and c, we observe little to no absorption signals at 950 and 900 nm from either nanoisland 1 or 2. When the excitation energy is increased, we observe an increase in absorption signal from nanoislands 1 and 2. The maximum absorption appears at the excitation wavelength of 850 nm (Fig. 6.3e), followed by a progressive decrease in the signal as we move to shorter wavelengths (Fig. 6.3g, i, k, m). However, the two nanoislands behave differently: the absorption of nanoisland 2 drops off sharply as the wavelength is tuned away from 850 nm to lower wavelengths. On the other hand, the absorption signal of nanoisland 1 remains fairly strong down to 740 nm and only shows a gradual decrease when the excitation wavelength is tuned step-wise from 850 nm to 740 nm. In this wavelength dependent study, the laser power density is maintained at 3,000 ± 500 mW/mm². Although the power density is not constant, its variation does not account for the large change in the SMA–STM signal contrast seen as a result of wavelength variation.

For DDA simulations, we coarsely reconstructed the geometry of the nanoislands enclosing the grain boundary (Supplementary Fig. 6.2d, e), based on the experimental topography data. Near-field intensity maps over the target surface were calculated for p-polarized light excitation of the different wavelengths employed in experiment. An absorption spectrum over this wavelength range was also simulated for the model geometry (Fig. 6.4g, black curve). This simulated spectrum of the nanostructure captures the wavelength-dependent absorption signal observed in the experiment. The spectrum is characterized by a broad LSP resonance band with a peak near 800 nm. The absorption efficiency at 950 nm is small but intermediate at 740 nm.
The DDA-simulated near-field maps capture qualitatively the observed variation as a function of excitation wavelength. The weakest near-field intensity is observed at 950 nm (Fig. 6.3b). Both nanoislands exhibit strong absorption at 850 nm. But there are differences between the experimental trend and the simulated one. The near-field strength varies much more gradually as a function of excitation wavelength, when compared to the experiment. In addition, the experiment shows stronger absorption on nanoisland 1, in general; whereas the simulations show a stronger near-field intensity on nanoisland 2, in general. As discussed earlier in the Letter, these discrepancies result from the use of an idealized, coarse geometric representation of the complex grain boundary/nanoisland structure imaged by SMA–STM. In addition, the presence of the STM tip can lead to some perturbation of the spatial and spectral characteristics of the LSPs. For instance, the applied tip bias can cause a field-induced Stark shift of the LSP frequency.\textsuperscript{362,363} This shift depends on factors such as the dielectric characteristics of the tip, the tip-sample distance, and the applied voltage. Field-gradients at the tip can contribute to further modulation of the LSP spectrum. In fact, the small discrepancy observed between the absorption wavelength maximum of 850 nm measured by SMA–STM (Fig. 6.3e) and the simulated LSP resonance maximum of ca. 800 nm (Fig. 6.4g, p-polarization) may, in part, be due to a tip bias-induced LSP shift. However, these effects are quite complex, difficult to incorporate in our simulations, and deserving of further study.

6.7 OBSERVATION OF POLARIZATION DEPENDENCE OF LSP:

In addition to wavelength dependence, such an anisotropic nanostructure should also exhibit a polarization-dependent LSP response (Fig. 6.4). Using a zero-order half-wave plate, we changed the polarization direction of the excitation laser from p (parallel to optical table and plane of
incidence) to sp (linear combination of 50% s and 50% p polarizations) to s (perpendicular to optical table and plane of incidence) and then back to p-polarization as shown in Supplementary Fig. 6.4. SMA–STM images were collected for each polarization direction, while the excitation wavelength was fixed at 850 nm. Fig. 6.4a,c,e, (left column) shows the polarization dependence: on both nanoislands, there is a systematic decrease in the SMA–STM signal as we transition from p to s polarization via the intermediate sp case. The trend indicates a lower absorption, i.e., a weaker LSP excitation under s-polarized excitation. This experimental observation agrees with the near-field intensity maps (Fig. 6.4b,d,f, right column) and absorption spectra (Fig. 6.4g) for the nanostructure simulated as the function of the excitation polarization. Simulations indeed show a decrease in the absorption efficiency and a drop in the near-field intensity (of both nanoislands) when the polarization is changed from p to s.

6.8 CONCLUSION:

We provide a proof-of-concept use of STM for real-space, nanometer-resolution imaging of the light absorption and electric near-fields of complex plasmonic nanostructures. The STM imaging technique captures the wavelength, polarization, and geometry-dependence of the LSP resonances. The direct visualization made possible by this imaging approach may allow previously unattainable insights into nanoscale mechanisms of light-matter coupling, interfacial energy transport, and relaxation processes in nano-assemblies, including surface-supported photocatalysts, light-emitting films, and photovoltaic devices.
6.9 MATERIALS AND METHODS:

STM setup. Experiments are performed using a homebuilt horizontal STM with a base pressure\(^{364}\) of \(\leq 10^{-8}\) Pa and electrochemically etched Pt:Ir (80:20) tips. The STM operates in constant current mode, set to 5 pA for the data in Fig. 2, and 10 pA in Figs. 3, 4, and S1, a setting that was previously shown not to affect the optical absorption signal.\(^{354}\) A bias of 1.2–1.5 V is applied to the sample, whereas the tip is grounded.

Substrate preparation. The substrate is a transparent, conductive hybrid film of 5-nm Pt (bottom) and 10-nm Au (top) deposited onto c-plane sapphire by electron beam evaporation of 99.99% pure metal pellets. The temperatures of film growth are 600–700 °C for Pt and 300–400 °C for the top Au layer. The Au growth temperature range controls the grain size of the Au film, which remains un-alloyed with the Pt support layer.\(^{365}\) Au nanoislands form at the grain boundaries in various aspect ratios. Multiple STM scans were performed to look for Au nanoislands with onset of absorption within the tunability range of our laser. For better conductivity between the delicate film and the STM sample holder, colloidal silver paint from Ted Pella Inc. is applied on top of the film at the two edges of the sample. The sample undergoes a 12 h degassing at 120 °C prior to STM imaging at room temperature.

SMA–STM setup. Fig. 6.1 shows the schematic of the SMA–STM experiment. Laser excitation is incident on the back of a transparent sapphire substrate machined to have a TIR geometry, which allows for plasmonic coupling of the laser into the Au nanoislands on the surface. This geometry also reduces direct photoexcitation and heating of the tip. The incidence angle was 143° with respect to the normal of the flat surface of the sample, and the propagation vector is parallel to the floor. The STM tip scans left to right on the sample surface at a rate of ~3 ms/pixel, and the SMA–
STM images are typically 400 pixels x 400 pixels. The laser is amplitude-modulated at 2.2 kHz by a mechanical chopper wheel, giving ~6 cycles/scanning pixel. Plasmonic light absorption by Au nanoislands causes a change in tunneling current when the STM tip raster-scans over the nanoisland. This SMA–STM absorption signal is detected as current modulation using a lock-in amplifier (SR830) that is locked to the chopping frequency and set to a time constant of 3 ms. With Pt:Ir tips, the optical field amplitude enhancement is estimated to be ~30 (thus ~1000 for intensity enhancement). For wavelength- and polarization-dependent scans, the same tunneling current and bias voltage is maintained to eliminate trends originating from tip-induced effects. We simultaneously collect the average tunneling current for the topographic image (orange color scale), and the tunneling current modulation (gray scale) during SMA–STM imaging. The tunneling current modulation image is plotted with background subtraction. The background is obtained by fitting a first-order polynomial in the two lateral dimensions. The final image is obtained by subtracting pixel-by-pixel this background from the original image. The detection technique is characterized in great detail in past papers. Laser power is ~6 mW with a spot size of 0.002 mm². The laser is tunable from 690–1040 nm with a bandwidth of 10 nm (full-width-half-maximum or FWHM). The laser field is polarized parallel to the plane of incidence (p-polarization) and can be incrementally rotated using a half-wave plate to obtain a s-polarization (perpendicular to the plane of incidence) configuration.

Discrete dipole approximation (DDA). We model the interaction between light and Au nanostructures by the discrete dipole approximation (DDA) method. The DDA method entails a full electrodynamic treatment, which includes finite-size retardation effects and higher order multipolar excitations. The DDA method (version 7.3) was implemented by use of the open source nanoDDSCAT+ tool (version 2.1x; doi: 10.4231/D3KH0F08T) available on nanoHUB. The
models for the Au nanoislands atop the Au/Pt substrate were generated using open-source Blender software included in the nanoDDSCAT+ toolkit. Au nanoislands were modeled as nanodiscs with sharp edges and a thickness approximately based on the topographic height profile information obtained from STM. The assembly was supported on a rectangular Au slab placed on a rectangular Pt slab. Dimensions for each component in the model (rounded to the nearest integer nm) are described in the corresponding figures.

The object file generated by Blender was converted to a shape file by use of the DDACONVERT tool, wherein the 3D structure is constructed from a cubic array of dipoles with a density of 1 dipole/nm. The assembly sits in a surrounding medium of refractive index of 1.0, corresponding to vacuum. The bulk experimental dielectric functions of Au and Pt from Johnson and Christy are available as a library option in nanoDDSCAT+ and were used without further correction. The final step in this workflow comprises of the DDSCAT tool, which takes the shape file as one of the inputs (the other input parameters are described below) and calculates the optical spectra and the electric field intensity maps.

The light excitation was in the form of a plane wave, with its propagation direction (k vector) at an incidence angle of 143° with respect to the normal going into front side of the metal film surface and in an orthogonal plane of the film surface. This configuration mimics the incident excitation in the experiment. Target structures were excited with a plane-wave beam of a specific wavelength. The incident wave was polarized along the s, the sp, or p polarization directions (see simulation geometry shown in Fig. 6.1b). Electric field intensity maps were obtained from near-field calculations for specific light excitation conditions (wavelength and polarization). The macroscopic field intensity $|E|^2$ at each grid-point of a volume surrounding the target structure was
obtained relative to the incident field intensity $|E_0|^2$, with the latter set to a value of 1. Near-field enhancements ($|E|^2/|E_0|^2$) were plotted over the surface of the target, visualized using the open source application ParaView. For Fig. 6.2, the field profile is shown over the surface contour of the assembly. For Figs. 6.3 and 6.4, the field profile is shown across a planar section clipped at a depth of 1-2 nm from the front surface of the assembly facing the reader.

Absorption spectra (absorption efficiency vs. wavelength) obtained from simulations are shown. A spline curve was used to connect the data points.
Supporting Figure 6.1. Transmittance spectrum of a representative PtAu substrate over the UV–vis–NIR wavelength region, as measured on a Varian–Cary 5G spectrometer at normal incidence. The transmittance spectrum of the sapphire substrate is shown for comparison. The PtAu substrate exhibits broad light absorption across the NIR wavelength region.
Supporting Figure 6.2. (a) A topographic image of a Au-grain boundary enclosed by nanoislands, two of which are labeled as 1 and 2. The topography is plotted on an orange color intensity profile, with the darkest regions representing the deepest features; (b) Line profiles (horizontal and vertical) over nanoisland 1 and 2; (c) angled perspective of the image in (a); (d) the reconstructed geometry used in DDA simulations shown in a top-down view. This model was generated by using 11 nanoislands to enclose a 6 nm-deep trough (grain boundary). The structure is supported on a rectangular Au slab (91 x 89 nm with a thickness of 7 nm), which itself is placed on a rectangular Pt slab (91 x 89 nm with a thickness of 3 nm). (e) shows an angled perspective of the extended structure.
Supporting Figure 6.3. To ensure the reproducibility of the wavelength-dependence observed in Fig. 6.3, the excitation wavelength was tuned back from long to short in steps, the results of which are shown here: (b) 850 nm, (c) 810 nm, (d) 790 nm, (e) 770 nm, and (f) 740 nm, respectively. (a) shows for comparison the forward scan from Fig. 6.3 obtained at 850 nm. The gray images are the experimental SMA–STM maps under p-polarized light excitation of different wavelengths in the NIR region. Note the Au islands in (b) seem stretched due to more significant tip heating at longer wavelength. The STM scanning conditions are 1.5 V, 10 pA. The power densities of the laser at these wavelengths are 3,000 ± 500 mW/mm². All images are 100 nm x 100 nm.
Supporting Figure 6.4. To ensure the reproducibility of the wavelength-dependence observed in Fig. 6.3, the excitation wavelength was tuned back from long to short in steps, the results of which are shown here: (b) 850 nm, (c) 810 nm, (d) 790 nm, (e) 770 nm, and (f) 740 nm, respectively. (a) shows for comparison the forward scan from Fig. 6.3 obtained at 850 nm. The gray images are the experimental SMA–STM maps under p-polarized light excitation of different wavelengths in the NIR region. Note the Au islands in (b) seem stretched due to more significant tip heating at longer wavelength. The STM scanning conditions are 1.5 V, 10 pA. The power densities of the laser at these wavelengths are $3,000 \pm 500$ mW/mm$^2$. All images are 100 nm x 100 nm.
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APPENDIX A: JOINT-SIMULATION EXPERIMENTAL STUDY ON THE
POLARIZATION-DEPENDENT SURFACE-ENHANCED RAMAN SCATTERING
(SERS) ON NANORATTLES, IN COLLABORATION WITH THE SINGAMANENI
GROUP

Polarization-Dependent Surface-Enhanced Raman Scattering Activity of Anisotropic Plasmonic Nanorattles

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Supporting Information

ABSTRACT: Plasmonic nanorattles composed of solid plasmonic core and porous and hollow plasmonic shell are a novel class of nanostructures that are highly attractive for surface-enhanced Raman scattering (SERS)-based chemical and biological sensing and bioimaging. In this report, we demonstrate the polarization-dependent SERS activity of cuboidal plasmonic nanorattles composed of a solid gold nanorod core and porous and hollow cuboidal shell. Plasmonic coupling between the gold nanorod core and porous and hollow cuboidal shell of the nanorattles results in a large electromagnetic (EM) enhancement at the interior of the nanorattles. Owing to the presence of internal electromagnetic hotspots, the polarization dependence of the plasmonic nanorattles was found to be markedly different compared to that of solid AuNR@Ag nanocuboids. Similar to most conventional anisotropic solid nanostructures, the AuNR@Ag nanocuboids exhibited a polarization-dependent SERS activity that is dominated by the sharp corners and edges. Conversely, the internal electromagnetic hotspot formed between the AuNR and porous shell of cuboidal nanorattle dominates the SERS activity of the anisotropic nanorattles. The results further our understanding of the SERS activity of this promising class of hollow nanostructures with internal electromagnetic hotspots and provide guidelines for the design of highly efficient SERS substrates based on these nanostructures.

INTRODUCTION

Surface-enhanced Raman scattering (SERS), which involves the large enhancement of Raman scattering from molecules adsorbed on or in close proximity to the surface of metal nanostructures, is considered to be highly promising for chemical and biological sensing, environmental monitoring, forensics, and bioimaging. Over the past decade, remarkable progress has been made in the synthesis of size- and shape-controlled plasmonic nanostructures with a significant fraction of them designed for SERS applications. Assemblies of plasmonic nanostructures with nanoscale gaps, locations of electromagnetic hotspots, exhibit large enhancement of the electromagnetic field and are identified to be responsible for intense SERS, including single molecule SERS. It has been demonstrated that the contribution of a relatively small number of electromagnetic hotspots (63 out of 10⁶ active sites) can be quite significant (~25%) in the overall SERS signal, underscoring the importance of electromagnetic hotspots in the design of SERS substrates and tags. Despite significant efforts focusing on achieving controlled assembly of plasmonic nanostructures, scalable methods that yield nanoparticle assemblies with highly uniform, isotropic, and stable SERS enhancement remain challenging. Therefore, it is highly desirable to design and synthesize plasmonic nanostructures with inherent electromagnetic hotspots, which eliminate the need for the assembled or lightly aggregated nanostructures.

Porous or hollow metal nanostructures are attracting significant attention due to their unique optical properties such as tunable localized surface plasmon resonance (LSPR) throughout the visible and part of the near-infrared spectrum and the ability to hold and deliver cargo with an external trigger such as light or ultrasound. These nanocuboids have been extensively investigated for various applications including imaging, therapy, and sensing. Among the various synthetic methods, galvanic replacement reaction serves as an effective and versatile method to produce bi- or trimetallic hollow nanostructures with the ability to control the size, shape, morphology, composition, porosity, and surface functionality of the resulting nanostructures. Recently, we have demonstrated that plasmonic nanorattles composed of Au core and porous Au–Ag shell provide significantly higher SERS enhancement owing to the electromagnetic hotspot formed between the core and shell. The porous outer shell lends itself for facile diffusion of analytes into the electromagnetic hotspots within the nanostructures. Cuboidal nanorattles

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comprised of gold nanorod (AuNR) cores and porous cuboidal Ag–Au shells are a particularly promising class of nanostructures for SERS. We have recently demonstrated that the electromagnetic field between the core and shell exhibits a dramatic increase as the gap between the core and shell is reduced.\textsuperscript{[21]}

SERS activity of any anisotropic nanostructure or assembly of nanostructures depends on the polarization of the excitation source with respect to the orientation of the nanostructure or assembly. Polarization-dependent SERS activity of various nanostructures, including Au nanoparticles,\textsuperscript{[22,23]} Ag nanocubes,\textsuperscript{[24]} Ag nanobars and nanorods,\textsuperscript{[25,26,27]} 7 dimers,\textsuperscript{[25,28,29]} and single and coupled nanowires, has been reported.\textsuperscript{[25,29] To the best of our knowledge, polarization-dependent SERS activity of anisotropic nanorattles with internal electromagnetic hotspots has not been reported. In this work, we present the polarization-dependent SERS activity of an individual cuboidal plasmonic nanorattle and its solid cuboidal AuNR@Ag nanocuboid. Significantly, the polarization-dependent SERS activity of solid nanocuboid was found to be markedly different from that of the cuboidal nanorattle with the nanoantenna effect (i.e., enhanced electromagnetic field at the sharp corners and edges of the nanorattle) dominating the former nanorattle and internal hotspots (i.e., enhanced electromagnetic field due to the coupling of AuNR core and porous shell) dominating the latter. Computational simulations based on the finite-difference time-domain (FDTD) method also corroborate our experimental findings.

## EXPERIMENTAL SECTION

### Materials
Gold chloride (HAuCl\textsubscript{4}), sodium borohydride (NaBH\textsubscript{4}), silver nitrate (AgNO\textsubscript{3}), ascorbic acid, cetyltrimethylammonium bromide (CTAB), and 2-naphthalenethiol (2-NT) were purchased from Sigma-Aldrich. Hexadecyltrimethylammonium chloride (CTAC) was purchased from Tokyo Chemical Industry (TCI). All the chemicals were used as received without further purification.

### Synthesis of Au Nanorods
Au nanorods were synthesized by using the seed-mediated method. Seed solution was synthesized by adding 0.6 mL of an ice-cold NaBH\textsubscript{4} (10 mM) solution into 0.25 mL of HAuCl\textsubscript{4} (10 mM) and 0.75 mL of CTAB (0.1 M) solution under vigorous stirring at room temperature. The color of the seed solution changed from yellow to brown. The growth solution was prepared by mixing 5 mL of HAuCl\textsubscript{4} (10 mM), 95 mL of CTAB (0.1 M), 1 mL of AgNO\textsubscript{3} (10 mM), and 0.55 mL of ascorbic acid (0.1 M), consecutively. The solution was homogenized by gentle stirring until the solution became colorless. Then, 0.12 mL of freshly prepared seed solution was added to the colorless solution and kept undisturbed in the dark for 14 h. Prior to use, the AuNR solution was centrifuged twice at 8000 rpm for 10 min to remove excess CTAB and redispersed in Nanopure water.

### Synthesis of AuNR@Ag Nanocuboids
A 2 mL twice-centrifuged AuNR solution and 4 mL of CTAC (20 mM) were mixed at 60 °C under stirring for 20 min. 5 mL of AgNO\textsubscript{3} (2 mM), 2.5 mL of CTAC (80 mM), and 2.5 mL of ascorbic acid (0.1 M) were added under stirring at 60 °C for 4 h. Subsequently, the AuNR@Ag nanocuboid solution was cooled by immersing the reaction vial in ice-cold water.

### Synthesis of Au Nanorattles
Au nanorattles were synthesized by transforming the Ag shell of AuNR@Ag nanocuboids into a porous shell of Au using the galvanic replacement reaction. The synthesized AuNR@Ag nanocuboids were centrifuged (8000 rpm, 10 min) and redispersed in CTAC solution (50 mM), followed by heating at 90 °C for 5 min under magnetic stirring. An aqueous solution of HAuCl\textsubscript{4} (0.5 mM) was injected into the solution of AuNR@Ag nanocuboids at a rate of 0.5 mL/min under magnetic stirring until a blue solution appeared.

### Characterization
Extinction spectra were collected using a Shimadzu UV-1800 UV–vis spectrophotometer. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2100F field emission instrument. Scanning electron microscopy (SEM) images were obtained on a FEI Nova NanoSEM 2300 at an acceleration voltage of 5 kV.

### Dark-Field Scattering Spectroscopy
Dark-field scattering spectroscopy was performed using an inverted optical microscope equipped with a dark-field condenser and a grating spectrometer. Samples were prepared as follows. Coverslips and glass slides were cleaned by heating them in 2 M KOH for 30 min, followed by washing with deionized water. Significantly, the polarization-dependent SERS activity of solid nanocuboid was found to be markedly different from that of the cuboidal nanorattle with the nanoantenna effect (i.e., enhanced electromagnetic field at the sharp corners and edges of the nanorattle) dominating the former nanorattle and internal hotspots (i.e., enhanced electromagnetic field due to the coupling of AuNR core and porous shell) dominating the latter. Computational simulations based on the finite-difference time-domain (FDTD) method also corroborate our experimental findings.

### Results and Discussion

\begin{equation}
\text{scattering spectrum} = \text{(raw data – background)} / \text{lamp spectrum}
\end{equation}

Spectra were collected with the spectrophotometer centered at two different wavelengths, 540 and 660 nm. The spectra were merged to obtain spectra in the full range from 400 to 800 nm.

### Discrete Dipole Approximation (DDA) Simulations

The DDA method was used for simulating the scattering spectra of the AuNR@Ag nanocuboids. The DDA method numerically solves Maxwell’s equations for one or a series of arbitrarily shaped objects by discretizing each object into a cubic array of N polarizable point dipoles and self-consistently solving for the polarization of each dipole interacting with the...\textsuperscript{[25,29]}

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incident electromagnetic field and all other $N - 1$ dipoles. The DDisCAT code (version 7.3) was implemented by use of the open source nanoDDISCAT+ tool (version 2.0.6) available on nanoHUB. The AuNR@Ag nanocuboid target with was generated using the Blender module within nanoDDISCAT+. The configuration of the target along with dimensions is shown in the inset of Figure 54. The corners of the target structure were appropriately bevelled using options available in Blender. The generated target geometry, which had an effective radius of 37.4 nm, was then converted into a cubic grid of virtual dipoles, the input for the DDA simulation. An interdipole spacing of 1 nm was employed.

Simulated spectra of AuNR@Ag nanocuboid were obtained in two different media. In the first case, the nanostructure was placed in a surrounding medium with a refractive index (RI) of 1.33, corresponding to water. In the second case, a medium of RI 1.96, corresponding to the placement of the nanostructure on a Si substrate, was used. The mixed medium RI in the latter case was calculated on the basis of the contact area between the NS and the surrounding medium. The area of the face of the nanostructure in contact with the Si substrate was calculated to be $4757 \text{nm}^2$; the total external surface area of the nanostructure being $23.458 \text{nm}^2$. The fraction of area $\phi$ in contact with Si substrate was thus 0.19. The RI of air was taken to be 1, and that of Si was assumed to have a constant value of 4, the reported value at 580 nm in the middle of the visible region. The imaginary part of the RI for Si, which is small, was neglected. The mixed medium RI is estimated as

$$\text{eff RI} = (\phi \text{RI}_\text{Si} + (1 - \phi) \text{RI}_\text{Air})^{1/2}$$

which yields a value of 1.96, which was used in the simulations. The bulk experimental dielectric functions of Au and Ag (available as a library option in nanoDDISCAT+) from Johnson and Christy were utilized without any corrections. Extinction spectra (extinction efficiency vs wavelength) in the 300–1000 nm wavelength range were obtained from each simulation. The nanostructure was excited with a plane wave traveling along the vertical direction (relative to the inset in Figure 54) and polarized either along the long axis or the short axis of the nanorod. Spectra were simulated with these orientations, and the directivity of the nanostructure was observed, were added to obtain a “polarization-averaged” spectrum.

**SERS Spectra Measurements.** Polarization-dependent SERS spectra from an individual anisotropic nanostructure were collected using a Renishaw inVia confocal Raman spectrometer. Nanostructures deposited on a silicon substrate was exposed to 10 mW 2-NT solution in ethanol and rinsed with ethanol. The sample was mounted on a rotation stage, and the specific nanostructures were identified using dark-field microscopy and spatially correlated to SEM images obtained before exposure to 2-NT solution. Spectra were collected using 785 nm laser excitation, which was focused on the sample using a 50x objective. A 60 s exposure time was set. The laser power was measured to be $\sim 0.7 \text{mW}$. For SERS spectra collected in aqueous medium, measurements were preformed by adding 10 $\mu$L of 2-NT (10 mM in ethanol) to 100 $\mu$L of the Au nanorod solution. The sample was mounted on a rotation stage, and the specific nanostructures were identified using dark-field microscopy and spatially correlated to SEM images obtained before exposure to 2-NT solution. Spectra were collected using 785 nm laser excitation, which was focused on the sample using a 20x objective. A 30 s exposure time was used in this case.

**Finite-Difference Time-Domain (FDTD) Simulations.** Modeling of the electromagnetic field distribution around the AuNR@Ag nanocuboid and the Au nanorattle was performed using three-dimensional finite-difference time-domain (FDTD) method implemented by the commercially available software, EM Explorer. The Au nanorattle structure was simulated with dimensions of 89.3 nm × 66.6 nm × 60.6 nm and a wall thickness of 6.5 nm. The AuNR@Ag nanocuboid was simulated with dimensions of 83.9 nm × 56.7 nm × 56.7 nm and corners truncated with spheres of 24 nm diameter. The AuNR core in both cases had a length of 49.9 nm and a diameter of 14.4 nm. The simulation domain was 150 nm × 150 nm × 150 nm. A high-resolution simulation was run at the extinction wavelength ($\lambda = 785 \text{ nm}$) and the Stokes-shifted wavelength ($\lambda = 880 \text{ nm}$) corresponding to a Raman shift of $\sim 1380 \text{ cm}^{-1}$ using an incident plane wave linearly polarized at various angles with respect to the long-axis direction of the anisotropic nanostructure. The complex refractive index of Au was set to $n = 0.18 + i 4.96$ and 0.21 + i 5.88, corresponding to the values for bulk Au at 785 and 880 nm, respectively. The refractive index of surrounding medium was set to a value of 1.00 for air. The field intensities for both 785 and 880 nm excitation ($E_{x}(p)^2$ and $E_{z}(p)^2$) were determined.

**RESULTS AND DISCUSSION**

Anisotropic plasmonic nanorattles were synthesized using a two-step method involving the formation of a thin Ag shell on Au nanorods (AuNRs) followed by a galvanic replacement reaction (Figure 1). Galvanic replacement reaction performed by the addition of a Au precursor, i.e., HAuCl₄, to a solution of AuNR@Ag nanocuboids results in the transformation of the Ag shell into a hollow and porous Au–Ag shell. The plasmon coupling between the core (AuNR) and the cuboidal Ag–Au shell results in internal electromagnetic hotspots, which are accessible to the analytes of interest due to the porous nature of the cuboidal shell.

AuNRs employed as cores were synthesized using a seed-mediated method using cetyltrimethylammonium bromide (CTAB) as a stabilizing agent (see Experimental Section for details). AuNRs were found to be monodisperse with a length of 49.9 ± 0.3 nm and a diameter of 14.4 ± 1.5 nm, estimated from a particle count > 100 in transmission electron microscopy (TEM) images (Figure 2A). A thin Ag shell is formed on the AuNR by introducing the AuNR into a growth solution composed of silver nitrate (AgNO₃) as an Ag precursor, ascorbic acid as a reducing agent, and hexadecyltrimethylammonium chloride (CTAC) as a stabilizing agent (see Experimental Section). The Ag shell grew epitaxially on the surface of AuNR cores, which resulted in the formation of AuNR@Ag core–shell nanocuboids. The selected absorption of CTAC on the {100} facets of Ag resulted in the formation of core–shell nanostructures with six {100} facets. The synthesized AuNR@Ag core–shell nanocuboids were found to be monodisperse with a length of 83.9 ± 5.0 nm and width of 56.7 ± 3.1 nm estimated from a particle count > 100 in TEM
images (Figure 2B). TEM images reveal the occupation of the AuNR at the center of each nanocuboids when viewed along the long-axis and from the sides (insets of Figure 2B). The thickness of the Ag shell grown on the sides of AuNR is found to be higher compared to that at the ends, indicating the preferential growth of Ag on the sides compared to the ends. The aspect ratio of AuNR@Ag nanocuboids is smaller than that of the AuNR cores due to the anisotropic Ag shell growth, which is in agreement with a previous report.21

Plasmonic nanorattles were synthesized by adding a Au precursor, i.e., HAuCl₄, to a solution of AuNR@Ag nanocuboids, which galvanically oxidizes the Ag layer to form a porous Ag–Au alloyed layer physically separated from the AuNR core. A TEM image of the Au nanorattles shows the presence of a porous cuboid Au–Ag shell surrounding the intact AuNR core (Figure 2C). From the TEM image, the length and width of the nanorattles were measured to be 89.3 ± 4.9 nm and 60.6 ± 3.0 nm, respectively, and the wall thickness of the shell was measured to be 6.5 ± 0.7 nm (Figure 2C). A higher magnification TEM image reveals a sub-10 nm gap between the edge of the AuNR and the porous plasmonic shell. Such a small gap results in strong plasmon coupling between the solid core and porous shell and the formation of electromagnetic hotspots within the nanostructure.21

The extinction spectrum of AuNRs employed as cores exhibits characteristic bands at 511 and 723 nm, corresponding to the transverse and longitudinal LSPR modes of the nanostructure, respectively (Figure 2D). Following the growth
of a thin Ag layer on the AuNRs, the AuNR core—Ag shell nanostructures exhibited four LSPR bands in the extinction spectrum. The extinction bands at 495 and 570 nm correspond to transverse and longitudinal dipolar LSPR modes, which are clearly blue-shifted relative to those of the AuNRs. The bands at 342 and 420 nm correspond to the transverse octupolar and quadrupolar LSPR modes of the AuNR core—Ag shell nanocuboids. In the galvanic replacement reaction, with the addition of the Au precursor, the LSPR bands associated with the presence of the Ag shell on the AuNR core disappeared. There was a concomitant emergence of LSPR bands at longer wavelengths that red-shifted with an increase in the Au precursor amount. The Au nanorattles dispersed in aqueous solution display an LSPR wavelength maximum at 628 nm and a shoulder at 520 nm. Photographs (shown as insets of the TEM images in Figure 2) of AuNR, AuNR@Ag nanocuboid, and Au nanorattle solutions under ambient light demonstrate the distinct extinction characteristics of the nanostructures.

In addition to the ensemble extinction spectra of nanostructures dispersed in aqueous medium, dark-field scattering spectra of individual nanostructures were also collected. The nanostructures were drop-casted from colloidal solution onto a glass slide, ensuring a low enough area density of coverage such that individual nanostructures could be resolved. The substrate-supported nanostructures were immersed in water and excited by unpolarized white light focused using a dark field condenser. For each sample, an individual emitter was identified from the wide field of emitters, and the scattered light from the emitter was collected using a 100X oil objective, transmitted through a slit, and dispersed onto a grating spectrometer to obtain a scattering spectrum. Figure 2E presents the dark-field scattering spectrum of a representative individual AuNR@Ag nanocuboid. The spectrum shows a band peaked at 564 nm and a shoulder around 500 nm, corresponding respectively to the longitudinal and transverse dipolar LSPR modes of the nanostructure. The scattering spectrum of an individual Au nanorattle is shown in Figure 2F. The stronger band in the spectrum peaked at 677 nm corresponds to the longitudinal dipolar resonance mode, and the weaker one peaked at 612 nm is assigned to the transverse mode. The weak shoulder around 520 nm corresponds to a quadrupolar mode of the Au nanorattle.

Following the synthesis of the nanostructures, we acquired SERS spectra from the nanostructures dispersed in aqueous medium using 514.5 and 785 nm laser excitation. To measure the SERS activity, the nanostructures were exposed to a solution of a model analyte 2-naphthalenethiol which readily chemisorbs on Au and Ag surfaces. The Raman spectrum of bulk 2-NT (powder) is shown in Figure S1 of the Supporting Information. The Au nanorattles exhibited significantly higher SERS enhancement compared to the AuNR@Ag nanocuboids for both 514.5 and 785 nm laser excitation (Figures S2 and S3). The SERS spectra obtained under 514.5 nm laser excitation exhibited significantly higher intensity compared to that obtained using 785 nm excitation, which can be ascribed to the greater proximity of the LSPR bands of the nanostructures in aqueous medium to the 514.5 nm excitation as compared to 785 nm excitation. On the other hand, for isolated nanostructures deposited on silicon substrate, higher SERS intensity was observed for 785 nm laser excitation compared to that under 514.5 nm excitation. In fact, no discernible SERS signal was observed under 514.5 nm laser excitation. This
observation can be attributed to a major shift of the LSPR modes of the nanostructures away from the 514.5 nm excitation. It has been demonstrated that the LSPR wavelength maximum of Ag nanoparticles exhibits a red-shift of around 100 nm when deposited on a glass substrate due to the effective increase in the refractive index of the surrounding medium.2 DDA simulations of the extinction spectra of the AuNR@Ag nanocuboid support such an explanation (Figure S4). The simulated extinction spectrum of AuNR@Ag nanomaterial in water medium shows four LSPR bands around 345, 406, 477, and 582 nm, in close agreement with the experimental extinction spectrum. In addition, the simulations show that a higher RI medium (corresponding to the nanocuboid supported on a Si substrate in air) results in a considerable red-shift of the LSPR bands of the nanomaterial.25 Under these conditions, the extinction contribution at 514.5 nm becomes significantly smaller, whereas the strongest (longitudinal dipolar) LSPR band overlaps considerably with the 785 nm laser, making the latter a significantly better excitation source for obtaining SERS enhancement as compared to the 514.5 nm excitation. These considerations rationalize the choice of the 785 nm laser as the excitation source for subsequent polarization-dependent SERS studies.

Next, we turn our attention to the polarization-dependent SERS activity of anisotropic AuNR@Ag nanocuboids and cuboidal Au nanorattles at the individual nanostructure level. To measure the SERS activity, the nanostructures deposited on a silicon substrate were exposed to 2-NT (10 mM in ethanol). Polarization-dependent SERS spectra were collected from individual nanostructures under 785 nm laser excitation at various orientation angles (Figure 3A,D). The orientation angle was defined as the angle between the long axis of the nanostructure and the direction of the excitation laser polarization. The orientation of the nanostructure relative to the polarization direction of the excitation laser was identified from SEM images spatially correlated to dark-field images (Figures S4 and S5). The SERS spectra obtained from an individual AuNR@Ag nanocuboid at various orientation angles are shown in Figure 3B. The most prominent peaks were observed at 1066 and 1381 cm\(^{-1}\), which correspond to the C–H bending and ring stretching vibrations of 2-NT.53 Each spectrum shown is an average of five spectra collected from the nanostructure under the same orientation. It is worth noting that well-resolved SERS spectra were obtained from individual AuNR@Ag nanocuboids, demonstrating the excellent SERS activity of these nanostructures. The SERS spectra collected from a AuNR@Ag nanocuboid (Figure 3C) at different orientations (–90° to 90°) in 15° intervals show a large variation in the intensity of the Raman bands with a change in the orientation. Maximum SERS activity was observed when the polarization of the laser was at an angle of 30° with respect to long-axis of the nanostructure. The polarization-dependent SERS activity of a cuboid Au nanorattle (Figure 3E) was investigated using a similar method described above. It worth noting that the maximum SERS intensity from the cuboid nanorattle was nearly 3-fold higher than that from the representative AuNR@Ag nanocuboid (Figure 3C,F). The SERS spectra obtained from the cuboid nanorattle at various polarization angles show that the SERS intensity of the most intense Raman band at 1381 cm\(^{-1}\) drops
monotonically from a maximum value at 0° to a minimum at 90° and nearly 90° (Figure 3E,F). This polarization dependence is in stark contrast to that observed in the case of AuNR@Ag nanocuboids. This contrasting behavior can be rationalized by the location of the most intense field hotspots of each of these nanostuctures, as discussed below.

We employed FDTD simulations to understand the electromagnetic field distribution and the SERS enhancement from the plasmonic nanostructures. It is known that the SERS intensity scales as the product of electromagnetic field intensity enhancements at the incident and Stokes-shifted wavelength. Considering that we have employed the most intense Raman band of 2-NT at 1381 cm⁻¹ for probing the polarization-dependent SERS activity, the corresponding Stokes-shifted wavelength is ~880 nm for the 785 nm excitation wavelength. The spatial maps of electromagnetic field intensity around the AuNR@Ag nanocuboid and Au nanorod under 785 nm excitation and at various polarization angles from 0° to 90° are shown in Figure 4AC. The electric field intensity distribution of AuNR@Ag nanocuboids shows that the highest electric field intensity occurs at the corners of the solid nanostructures (termed the nonantenna effect), and maximum enhancement is achieved when the polarization of the laser is along the diagonal of the cuboid (i.e., 30°). On the other hand, in the case of cuboidal Au nanorattles, the highest electric field intensity was found to be at the gap between the AuNR core and the cuboidal shell. The maximum electric field enhancement was observed when the polarization of the laser matched the long-axis of the nanostructures. Figure 4B,D depicts the product of the intensity enhancements at incident and Stokes-shifted wavelengths (|E₀|²|Eₛ|²), which provides a measure of the average SERS enhancement obtained from the AuNR@Ag nanocuboid and the Au nanorod. The magnitude of |E₀|²|Eₛ|² for the cuboidal nanorattle decreased with an increase in the polarization angle with respect to the long axis of the anisotropic nanostructure. On the other hand, the magnitude of |E₀|²|Eₛ|² for the AuNR@Ag nanocuboid exhibited a maximum at a polarization angle of ~30° and 30°. Polarization dependence of the enhancement factor of both nanostructures simulated by FDTD shows excellent agreement with the experimental results.

CONCLUSIONS

In conclusion, we have performed a systematic investigation of the polarization-dependent SERS activity of AuNR@Ag nanocuboids and cuboidal Au nanorattles. Because of the presence of internal electromagnetic hotspots within the nanorattles, they exhibited SERS activity with a significantly different polarization-dependence compared to their solid counterparts, i.e., AuNR@Ag nanocuboids. Similarly to most conventional anisotropic solid nanostructures, the nanocuboids exhibited a polarization-dependent SERS activity that is dominated by their sharp corners and edges. Conversely, for the cuboidal nanorattles, the internal electromagnetic hotspot formed between the AuNR core and the porous Ag--Au shell dominates the SERS activity of the nanorattles. FDTD simulations confirm that the nature of the electric field different polarization-dependence compared to their solid counterparts. The results further our understanding of the SERS activity of this promising class of hollow nanostructures with internal electromagnetic hotspots and provide guidelines for the design of highly efficient SERS substrates based on these nanostructures. More importantly, the results provide detailed insight into the optimal configuration for both solid and hollow anisotropic nanostructures for performing single-nanoparticle-based SERS studies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b00595.

Raman spectrum of bulk 2-NT, SERS spectra collected in aqueous medium, dark-field optical images and SEM images, stability of SERS signal, FDTD simulations, DDA simulations, and calculation of SERS enhancement factor (PDF)

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Notes

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REFERENCES


Supporting Information

Polarization-dependent Surface Enhanced Raman Scattering

Activity of Anisotropic Plasmonic Nanorattles

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**Figure S1.** Raman spectrum of bulk 2-NT.

**Figure S2.** Surface enhanced Raman scattering (SERS) spectra collected from 2-NT adsorbed on Au nanorattles and AuNR@Ag nanocuboids in aqueous media using 785 nm laser excitation.
Figure S3. SERS spectra collected from 2-NT adsorbed on Au nanorattles and AuNR@Ag nanocuboids in aqueous media using 514.5 nm laser excitation.

Figure S4. DDA simulated extinction spectra of AuNR@Ag nanocuboids in water (black) and on a Si substrate in air (red). Inset shows schematic of the nanostructure with dimensions. Data points obtained from calculation are connected by a spline curve.
Figure S5. (A) Dark-field optical image of Au nanorattles adsorbed on a silicon substrate. Labels 1, 2 and 3 each identify a representative Au nanorattle for polarization-dependent SERS measurement. (B) SEM image of Au nanorattles adsorbed on a silicon substrate from the region marked by the white dashed box in (A). (C) Enlarged SEM image clearly identifying the three representative Au nanorattles from (B).
Figure S6. (A) Dark-field optical image of AuNR@Ag nanocuboids adsorbed on a silicon substrate. Labels 1-6 each identify a representative AuNR@Ag nanocuboid for polarization-dependent SERS measurement. (B) SEM image of AuNR@Ag nanocuboids adsorbed on a silicon substrate from the entire region shown in (A). (C) Enlarged SEM image clearly identifying the six representative AuNR@Ag nanocuboids from (B).
Figure S7. Stability of SERS signal at 1066 cm$^{-1}$ and 1381 cm$^{-1}$ peaks obtained from an individual Au nanorattle at a polarization angle of 0°.

Figure S8. Normalized SERS intensity (at the 1381 cm$^{-1}$ peak) of an individual Au nanorattle as a function of polarization angle. The blue line is a fit to the cos$^2$ function. The error bars represent the standard deviation of five identical measurements performed at each polarization angle.
Figure S9. Finite-difference time-domain (FDTD) simulations showing the electric field distribution around a AuNR@Ag nanocuboid under various incident polarization angles using 880 nm excitation wavelength. The incident polarization angle is 0°, 15°, 30°, 45°, 60°, 75° and 90° in (i)-(vii) respectively.

Figure S10. FDTD simulations showing the electric field distribution around an Au nanorattle under various incident polarization angles using 880 nm excitation wavelength. The incident polarization angle is 0°, 15°, 30°, 45°, 60°, 75° and 90° in (i)-(vii) respectively.
The SERS enhancement factor (EF) for each Au nanostructure was calculated by using the equation\(^2\):

\[
EF = \frac{l_{\text{SERS}}}{l_{\text{bulk}}} \frac{N_{\text{SERS}}}{N_{\text{bulk}}} \quad (1)
\]

where \(l_{\text{SERS}}\) and \(l_{\text{bulk}}\) are intensities of the same Raman band in the SERS and bulk spectra, \(N_{\text{SERS}}\) is the number of the 2-naphthalenethiol molecules bound to the surface of the Au nanostructure and \(N_{\text{bulk}}\) is the number of the 2-naphthalenethiol molecules in the excitation volume. For the Au nanorattle, \(l_{\text{SERS}}\) is \(\sim 1545\) counts and \(l_{\text{bulk}}\) is \(\sim 125\) counts. A Raman spectrum of 2-naphthalenethiol in the bulk was collected using a 20x microscopy objective with a numerical aperture (NA) of 0.4. The approximate laser spot size with the 20x objective was obtained using the following expression:

\[
\omega_0 = 4\lambda/\pi NA \quad (2)
\]

where \(\omega_0\) is the minimum waist diameter for a laser beam of a wavelength \(\lambda\) focused by an objective with a numerical aperture NA. So for the 20x objective,

\[
\omega_0 = \frac{(4)(0.785)}{\pi(0.4)} = 2.5 \text{ \mu m}.
\]

\[
z_0 = \frac{2\pi\omega_0^2}{\lambda} = \frac{2\pi(2.5\mu m)^2}{0.785} = 50 \text{ \mu m}
\]

So, the focal volume \((\tau) = \left(\frac{\pi}{2}\right)^{1.5}\omega_0^2z_0 = \left(\frac{\pi}{2}\right)^{1.5} \times 2.5\mu m \times 50 = 614.75 \text{ \mu m}^2\). Density of the 2-naphthalenethiol is \(1.55 g/cm^3\) and the molecular mass of 2-naphthalenethiol is 160.24 (g/mol). Therefore,

\[
N_{\text{bulk}} = \frac{(1.55 g/cm^3)(614.75 \mu m^3)}{160.24 (g/mol)} = 5.95 \times 10^{-12} \text{ mol}
\]

The volume of an individual Au nanorattle with edge dimension of 89.3 x 60.6 x 60.6 nm and a AuNR core with length of 49.9 nm and width of 14.4 nm is estimated to be

\[
(89.3 - 13)(60.6 - 13)^2 - \left[\pi(7.2)^2 \times 35.5 + \frac{4}{3} \times \pi \times (7.2)^3\right] = 165533.3 \text{ nm}^3
\]

\[
N_{\text{SERS}} = \frac{(1.55 g/cm^3) \times 165533.3 \text{ nm}^3}{160.24} = 1.60 \times 10^{-18} \text{ mol}
\]

\[
EF = \frac{l_{\text{SERS}}}{l_{\text{bulk}}} \frac{N_{\text{SERS}}}{N_{\text{bulk}}} = \frac{1545}{125} \times \frac{1.60 \times 10^{-18}}{5.95 \times 10^{-12}} = 4.60 \times 10^7
\]
Supporting Information References:
