

Mesoscale Quantum-Confined Semiconductor Nanoplatelets through Seeded Growth

Stephanie Marie Tenney, Lauren A. Tan, Mikayla L. Sonnleitner, Anthony V. Sica, Ashley Jiwon Shin, Ricky Ronquillo, Tasnim Ahmed, Timothy Luke Atallah, and Justin Ryan Caram*



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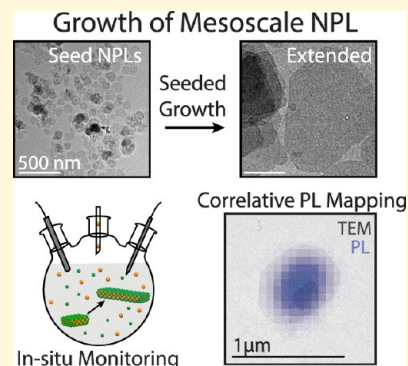


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ABSTRACT: We demonstrate the preparation of mesoscale semiconductor (II–VI) nanoplatelets (NPLs) for the first time using colloidal seeded growth. These nanoplatelets are quantum-confined and atomically precise but grown to a length scale compatible with conventional optical imaging and microscopic manipulation (even reaching $>1 \mu\text{m}^2$) offering an opportunity to bridge the application space between nanocrystals and two-dimensional (2D) materials. Using CdTe as a model system, we develop a seeded growth procedure, show the parameters that control extension, and apply them to a variety of thicknesses and compositions. In situ spectroscopy demonstrates that addition onto the nanoplatelet seeds is not continuous and likely occurs through ripening. Finally, we use correlative optical and electron microscopy to demonstrate that at large sizes, photoluminescence (PL) mapping of the entire structure can be resolved including spatial inhomogeneities. Overall, these results show that nanoplatelets can be compared to 2D semiconductors while maintaining the advantages of scalable colloidal synthesis, thickness tunability, and solution processability.



INTRODUCTION

II–VI semiconductor nanoplatelets (NPLs) are a class of nanocrystals with atomically precise confinement in the thickness dimension. They show exceptional photophysical properties, including narrow linewidths, tunable emission, large absorption cross sections, and high quantum yields.^{1–3} They are also structurally versatile, able to vary in composition from CdX (X = S, Se, Te) to HgX, and are amenable toward lateral and longitudinal heterostructures—all while maintaining their discrete monolayer (ML) thicknesses.^{1,4–8}

Due to their similar anisotropic structure, a comparison can be made between NPLs and van der Waals (vdW) two-dimensional (2D) materials. Both systems display strong exciton binding energy, dielectric screening by external environments, and thickness-dependent band structure.^{9–11} Additionally, NPLs may also show exotic properties characteristic of vdW materials, such as single-photon emission, topological insulation, spin–orbit effects, and fractional quantum hall effects.^{12–14} Unlike conventional exfoliated vdW 2D materials that often display a finite thickness distribution, II–VI semiconductor NPLs may be prepared with monodispersed thickness through colloidal methods, with direct bandgaps for all thicknesses, and chemical tunability through ligand design.¹⁵ Realizing the connections to 2D vdW materials requires NPLs with sufficiently large lateral areas, especially to integrate them into single nanoplatelet devices or high-performance thin-film devices.¹⁶

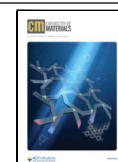
Prior work has shown that CdX and HgX NPLs can be synthesized with lateral dimensions (longest edge) up to ~ 500 nm using a slow injection of precursors, although most procedures utilize fast injection that results in smaller lateral sizes of 100–200 nm or less.¹⁷ Studies of smaller NPLs reveal lateral size dependence of photophysical properties including an enhanced absorption cross section, giant oscillator strength, altered spontaneous and stimulated emission thresholds, modified biexciton quantum yield, and depressed Auger recombination.^{18–22} However, the absence of a standardized procedure to synthesize larger NPLs limits the exploration of such properties of bulk II–VI nanosheets, which may behave more similarly to their 2D vdW semiconducting cousins. Ultrathin nanosheets of other semiconducting materials have been colloiddally synthesized, such as Cu_{2-x}S ,²³ In_2Se_3 ,^{24,24} PbS ,²⁵ perovskite CsPbBr_3 ,^{26,26} and a host of transition metal dichalcogenides (TMDs). Despite this variety, robust control of large-area II–VI nanosheets with optical properties akin to their highly confined small-area analogs has not been shown.

To synthesize mesoscale NPLs, we develop a seeded growth method inspired by previously demonstrated growth of core-

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crown NPLs. In a typical core-crown growth procedure, an amount of presynthesized NPLs are used as seeds and a second reaction introduces a chalcogen precursor of a different composition to yield a heterostructure.^{7,27–32} The extension method of small CdSe NPLs from ~ 300 to 4000 nm^2 is similar, but it uses the same precursor compositions injected into a solution of NPL seeds at slower rates.^{33–35} We build on these procedures in our seeded growth but carefully explore the parameters to yield NPLs that are more than double in size while maintaining their size confinement in the thickness dimension.

We show that careful control of the reaction parameters that affect 2D NPL growth allows us to demonstrate the optimal conditions for mesoscale CdTe NPLs and investigate how the NPL population evolves during the seeded growth process. We then utilize correlative imaging of single NPLs using a combination of fluorescence and electron microscopy to show that large NPLs exhibit lateral heterogeneity in their photoluminescence (PL). Overall, this study demonstrates that mesoscale II–VI NPLs can possess differing electronic structures within a single NPL and represent a new class of colloidal 2D semiconductors rather than confined single emitters. Finally, the advent of mesoscale 2D vdW materials has enabled a generation of novel electronic devices as a result of their microscopic characterization and control, and a similar application space may exist for colloidal NPLs.^{36–38} Their size may make them similarly amenable to direct microscopic manipulation and could pave the way for more advanced, single nanocrystal devices derived from colloidal confined II–VI semiconductors.

EXPERIMENTAL SECTION

Materials. Cadmium acetate dihydrate (Acros, 98%), selenium powder (Acros, 99.5%), tellurium powder (Acros, 99.8%), cadmium oxide (Alfa Aesar, 99.95%), cadmium bromide tetrahydrate (Acros, 98%), oleic acid (Alfa Aesar, 99%), tri-*n*-octylphosphine (TOP) (Alfa Aesar, 90%), 1-octadecene (ODE) (Alfa Aesar, 90%), mercury(II) acetate (Chem-Impax International, 98.0%), ethanol (Fisher, 95.27%), hexanes (Fisher, 98.5%), toluene (Alpha Aesar, 99.8%), propionic acid (Fisher), and oleylamine (Tokyo Chemical, 50.0%) were used.

Synthesis of Precursors. *Cadmium Propionate (Cd(prop))*. CdO powder (1.036 g) was mixed with propionic acid (10 mL) under argon flow for 1 h. The flask was then heated at $140\text{ }^\circ\text{C}$ after opening to the atmosphere to reduce the volume by half. The white solution was precipitated with acetone and centrifuged. The supernatant was discarded, and the solid was dried and stored in a vacuum desiccator.

TOP-Te (1 M). Following Izquierdo et al.,⁴ in a small flask, 0.254 g of Te powder and 2 mL of tri-*n*-octylphosphine (TOP) were degassed under vacuum at room temperature. Then, under argon flow, the solution was stirred at $275\text{ }^\circ\text{C}$ until the dissolution was complete, and the solution turned yellow. The solution was cooled and stored under argon.

TOP-Se (1 M). Following Izquierdo et al.,⁴ 0.144 g of Se powder and 2 mL of tri-*n*-octylphosphine (TOP) were stirred at room temperature under argon flow until dissolved to form a clear solution. The solution was stored under argon.

Two Monolayer CdTe Seed Nanoplatelets. Following Pedetti et al.,²⁷ 170 mg of cadmium propionate, $104\text{ }\mu\text{L}$ of oleic acid, and 10 mL of octadecene (ODE) were degassed for 1 h at $90\text{ }^\circ\text{C}$. Under argon flow, the temperature was increased to $180\text{ }^\circ\text{C}$ and $130\text{ }\mu\text{L}$ of 1 M TOP-Te diluted in $650\text{ }\mu\text{L}$ of ODE was swiftly injected. After 20 min, 1 mL of oleic acid was added and the reaction was cooled to room temperature. The crude mixture was precipitated with ethanol and centrifuged twice and then resuspended in 10 mL of hexanes.

Three Monolayer CdTe Seed Nanoplatelets (Slow Injection). Adapted from Izquierdo et al.,^{4,5} 260 mg of cadmium propionate, $160\text{ }\mu\text{L}$ of oleic acid, and 20 mL of ODE were degassed under vacuum at $90\text{ }^\circ\text{C}$ for 1 h. Under argon flow, the reaction was heated to $210\text{ }^\circ\text{C}$ and 0.200 mL of 1 M TOP-Te mixed with 3.75 mL of octadecene was injected with a syringe pump at a rate of 5 mL/h . Once the injection was complete, 0.500 mL of oleic acid was injected and the solution was cooled to room temperature. The nanoplatelets were precipitated with 15 mL of hexanes and 15 mL of ethanol, centrifuged, and resuspended in 20 mL of hexanes. Assuming that the reaction goes to completion, the 3 mL of NPL solution will contain a total of 0.2 mmol of Te and 0.26 mmol of Cd in the NPLs, giving a concentration of 13 mM total cadmium in the NPL seed solution.⁴

Three Monolayer CdSe Seed Nanoplatelets (Slow Injection). Adapted from Izquierdo et al.,^{4,5} 240 mg of cadmium acetate dihydrate, 0.150 mL of oleic acid, and 15 mL of ODE were degassed under vacuum at $80\text{ }^\circ\text{C}$ for 1 h. Under argon flow, the reaction was heated to $195\text{ }^\circ\text{C}$ and 0.4 mL of 1 M TOP-Se mixed with 3.75 mL of ODE was injected with a syringe pump at a rate of 5 mL/h . Once the injection was complete, the solution was cooled to room temperature and the nanoplatelets were precipitated with 15 mL of hexanes and 15 mL of ethanol, centrifuged, and resuspended in 20 mL of hexanes.

Four Monolayer CdSe Seed Nanoplatelets. Following Pedetti et al.,²⁷ 340 mg of cadmium myristate, 24 mg of Se powder, and 30 mL of ODE were degassed for 20 min at room temperature. The temperature was then increased to $240\text{ }^\circ\text{C}$ under argon flow. When it reached $205\text{ }^\circ\text{C}$, 80 mg of cadmium acetate was added and the solution turned red. Then, when the solution reached $240\text{ }^\circ\text{C}$, it was left to react for 12 min followed by the addition of 2 mL of oleic acid and rapid cooling to room temperature. The crude reaction mixture was added to 30 mL of hexanes and 40 mL of ethanol and centrifuged at 6000 rpm for 10 min, followed by resuspension in 10 mL of hexanes.

Five Monolayer CdSe Seed Nanoplatelets. Following Pedetti et al.,²⁷ 340 mg of cadmium myristate and 28 mL of ODE were degassed for 20 min at room temperature. Under argon flow, the solution was heated to $250\text{ }^\circ\text{C}$ at which point 24 mg of Se powder suspended in 2 mL of ODE was swiftly injected. After 30 s, 300 mg of cadmium acetate was also added. The reaction was held at $250\text{ }^\circ\text{C}$ for an additional 7 min, followed by the addition of 1 mL of oleic acid and rapid cooling to room temperature. The crude reaction mixture was added to 30 mL of hexanes and 40 mL of ethanol and centrifuged at 6000 rpm for 10 min, followed by a resuspension in 10 mL of hexanes. Further purification was done by adding 1:4 ethanol to hexanes and centrifuging at 6000 rpm .

Seeded Growth. In a three-neck round-bottom flask, 65 mg of cadmium propionate (0.25 mmol), 0.040 mL of oleic acid, and 5 mL of octadecene were degassed under vacuum at $80\text{ }^\circ\text{C}$ for 20 min. Under Ar flow, the solution was heated to a target growth temperature between 200 and $260\text{ }^\circ\text{C}$ depending on the thickness (see Table S1) and 0.250 mL of $\sim 13\text{ mM}$ CdX seeds in hexanes were injected when the temperature reached $200\text{ }^\circ\text{C}$. The concentration of the seed solutions varies with each synthesis, so the concentration of each was adjusted by measuring the optical density (OD) of the heavy hole (hh) relative to the 13 mM CdTe heavy hole OD. Once at the final growth temperature (Table S1), a solution of 0.050 mL of 1 M TOP-X ($X = \text{Te}$ for CdTe and Se for CdSe) mixed with 0.500 mL of ODE was injected with a syringe pump at 0.55 mL/h . Immediately after the injection was complete, 0.250 mL of oleic acid was injected, and the solution was cooled. The nanoplatelets were then centrifuged at 9000 rpm for 5 min and resuspended in 10 mL of hexanes.

Cation Exchange. In a round-bottom flask, 0.240 mL of large CdTe NPLs in hexanes (without further dilution from seeded growth, the concentration will have a maximum of 7.3 mM Cd in the NPLs) and 6.0 mL of hexanes were mixed. Then, 0.600 mL of 10 mM $\text{Hg}(\text{OAc})_2$ in oleylamine was added and stirred at room temperature for 3.5 h, monitored by the absorption of the light and heavy holes. The HgTe absorption spectra stopped changing by 3.5 h and the heavy hole optical density was greater than the light hole (lh), upon which point the reaction is considered complete.⁴ Once complete, the

nanoplatelets were then centrifuged at 9000 rpm for 5 min and resuspended in 5 mL of hexanes.

Characterization. Absorption spectra were acquired with an Agilent Cary 60 UV–vis spectrophotometer. Photoluminescence (PL) was collected using an Ocean Optics Flame-S-VIS–NIR-ES spectrometer and a Horiba Scientific PTI QuantaMaster400 spectrometer. Quantum yield measurements were collected using an integrating sphere. Reflectance measurements were collected using an Ocean Insight QR200-12-MIXED reflectance probe and an Avantes DH-2000 UV–VIS–NIR light source. Dynamic light scattering (DLS) was collected using a Coulter Beckman Dynamic Light Scattering Analyzer—N4 Plus at an angle of 62.6°.

Transmission electron microscopy (TEM) images were acquired with a FEI Tecnai T12 120 kV TEM. The nanoplatelets were diluted in hexanes and drop casted on Ted Pella, Inc. carbon/formvar 300 mesh copper grids.

Photoluminescence imaging experiments were conducted on a home-built optical microscope. All NPLs were excited using a 405 nm pulsed diode laser (LDH-P-C-405 PicoQuant) with a power of 0.15 μ W. The NPL sample slide is fixed to a piezo stage (Mad City Labs Nano-View/M 200-3), and the epifluorescence is sent through a 100 $\times$ oil objective (Nikon MRD01905) and filtered using a 425 nm longpass dichroic filter. Wide-field images were collected using an sCMOS camera (Zyla sCMOS, Andor) (Figure S1b). Acquisition time was on average 10 s.

For time-correlated single-photon counting, all NPLs were excited using a 405 nm pulsed diode laser. For NPLs on TEM grids, epifluorescence of the sample was collected through the microscope using a 100 $\times$ objective (Nikon MRD01905). The laser was filtered using a 425 nm longpass filter and the emission was then focused onto an avalanche photodiode (APD, PD050-CTD, Micro Photon Devices). Photon streams were timed by a HydraHarp 400 (Picoquant) in time-tagged time-resolved (TTTR) mode. For NPLs in solution, these measurements were collected using superconducting nanowire single-photon detectors (SNSPDs), due to shorter instrument response functions at 405 nm.

RESULTS AND DISCUSSION

We start by showing two exemplars of the seeded growth process in Figure 1. Following literature procedures, we produce 2 and 3 monolayer (ML) CdTe seeds with an average lateral extent of 90 ± 2 and 370 ± 11 nm, respectively (results of size counting in Table S3).^{4–6} Two ML CdTe seed NPLs are synthesized by a fast injection of trioctylphosphine telluride (TOP-Te) into a cadmium propionate solution at 180 °C. For 3 ML seed NPLs, we follow a slow injection method, where TOP-Te is continuously injected into a solution of cadmium propionate at 210 °C. All NPL products are then centrifuged and resuspended in fresh solvent to be used as seeds for subsequent growth. We then extend these NPL seeds to lateral sizes of 1000–1500 nm by reintroducing them to a second, slower injection of new chalcogen precursor and carefully control the rate of growth (further details in the Experimental Section). Despite the change in size, the larger NPLs retain their absorption and emission profiles after this seeded growth process (Figure 1b), suggesting no change in thickness with an increase in lateral size. The quantum yields for CdTe NPLs remain low with <1% before and 3% after seeded growth for 2 ML and <1% before and after for 3 ML, but this is expected due to their large lateral areas and potential for defects.³⁹ Photoluminescence lifetimes of NPLs in solution show similar results before and after seeded growth of ~ 30 ps (Figure S2).

In Figure 2, we demonstrate the scope of this procedure by applying the conditions of seeded growth to various compositions (specifically CdTe NPLs (2–3 ML) and CdSe NPLs (3–5 ML)) and measure the change in lateral extent

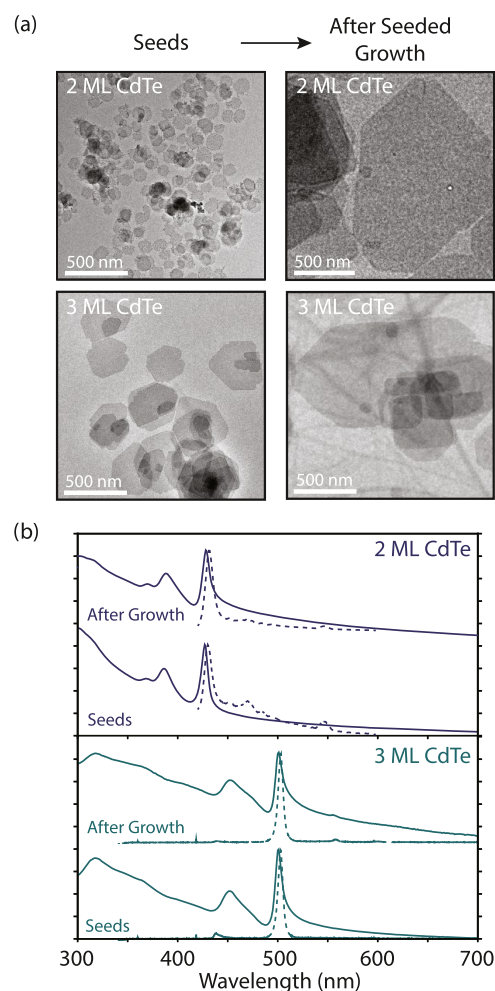


Figure 1. (a) TEM of 2 and 3 ML CdTe NPL seeds before and after seeded growth. (b) Absorption (solid lines) and photoluminescence (PL, dashed lines) spectra before and after seeded growth.

using TEM (Figure 2a). We observe the greatest enhancement in CdTe NPLs, but all materials show a significant change of at least twice the mean size while maintaining their absorption and emission (Figure S3 and Table S3). We note that, in contrast to the large CdTe, CdSe remain smaller, more rectangular, and show emission from defects or other NCs after seeded growth (Figure S3) despite exploring how differing cadmium precursors may affect the growth (Figure S4). We found that short-chain cadmium precursors work best for CdSe extension (similar to CdTe) and hypothesized that slightly differing synthetic procedures, higher nucleation barriers, and/or surface strain properties result in smaller CdSe NPLs.^{40,41} In Figure 2b, we show representative TEM of the CdTe and CdSe NPLs after seeded growth as well as extended HgTe NPLs (additional TEM images used for counting are shown in Figure S5). Extended 2 and 3 ML CdTe can be isolated after seeded growth and introduced to a solution of mercury acetate dissolved in oleylamine at room temperature to yield large HgTe NPLs through a cation exchange process (further details in the Experimental Section). This demonstrates that large CdTe NPLs are robust enough to undergo a complete cation exchange while maintaining their large-area morphology and thickness, giving access to mesoscale NIR-emissive NPLs (Figure S6).

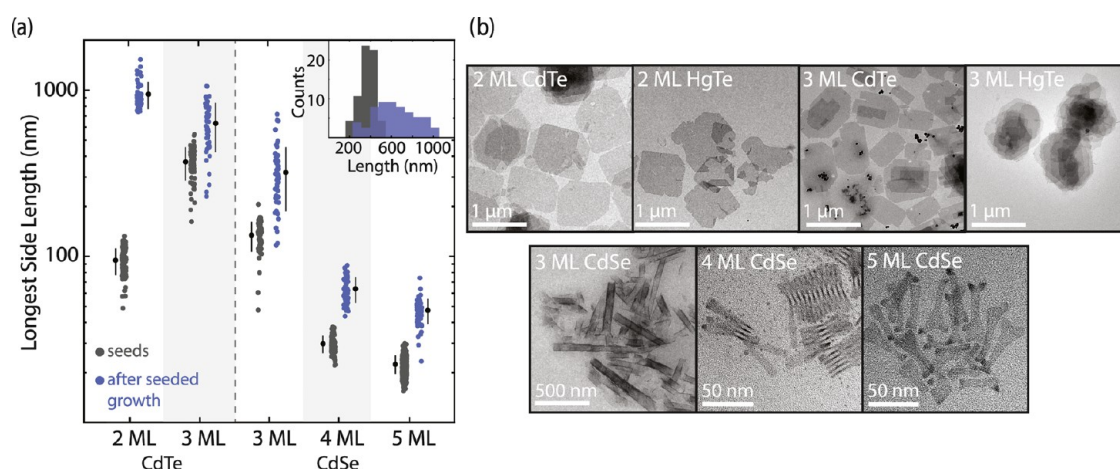


Figure 2. (a) Difference in lateral sizes before (gray) and after (blue) seeded growth for various CdX NPL thicknesses. Solid colored circles represent the counts for each size distribution, while the solid black circles show the mean and standard deviation of each condition explored. Inset shows an example of the full histogram of sizes before (gray) and after (blue) seeded growth for 3 ML CdTe. (b) Representative TEM images of NPLs after seeded growth, including HgTe from cation exchange with large CdTe.

To demonstrate that the seeded growth process is necessary, we performed two control experiments—slow injection without seeds and fast injection with seeds—and both produced NPLs less than ~ 500 nm in size along with many three-dimensional (3D) nanocrystals (Figure S8). We then hypothesized that the same parameters that govern 2D NPL nucleation and growth including temperature, injection rate, and precursor concentration are important for controlling size during seeded growth and can be tuned to optimize the procedure.^{33,40,42} Additionally, these parameters are important for maintaining a regime of growth, which outcompetes the critical supersaturation for nucleation and suppresses secondary nucleation.^{33,43,44} We indeed find that the largest NPLs occur within a narrow range of optimized conditions and show how the experimental parameters of the slow injection seeded growth affect the extension in 3 ML CdTe by isolating each variable individually (Figure 3). First, slightly elevated temperatures relative to the initial seed growth (3 ML CdTe initial seed growth is done at 210 °C) result in large extended NPLs; however, this also results in a broadening of the size distribution. Beyond 230 °C, NPLs smaller than the seed NPLs nucleate during the growth (secondary nucleation). Temperatures below the initial seed temperature also nucleate smaller NPLs and produce a size distribution that has a lower mean size than the seeds (Figure S9). Second, the injection rate must be slowed significantly to favor large NPL growth (0.55 mL or 0.055 mmol/h compared to 5 mL or 0.25 mmol/h in a typical 3 ML CdTe NPL synthesis) but must still be high enough to maintain the kinetic instability driving 2D growth.⁴⁰ Too slow of an injection rate (<0.55 mL/h of 0.1 M TOP-Te) forms many 3D agglomerates alongside the NPLs (Figure S5), while too fast (>1 mL/h) forms primarily secondary NPLs. Finally, the concentration of seeds affects the amount of edge sites for monomers to be added—too low results in few extended NPLs while too high results in clumps of large NPLs, both of which lead to many secondary NPLs. The conditions that we use for further spectroscopic investigation are indicated by the (*) in Figure 3b.

To understand how NPL growth is occurring during this process, we now explore the reaction dynamics as a function of time in Figure 4. We perform *in situ* and *ex situ* spectroscopy and microscopy on our optimized seeded growth reaction

(0.55 mL/h injection rate of 0.1 M TOP-Te at 220 °C). Using a reflectance probe to monitor changes in optical density (OD), we track changes in the light hole (lh) and heavy hole (hh) excitonic features as well as the scatter profile (at 600 nm) over the course of a 2 h growth period (Figure 4a,b, more details in Figure S10). Their evolution is highlighted by taking slices of the spectra over time (Figure 4c). We interpret the increase in OD of the excitonic features to indicate the formation of new platelet area (either small secondary platelets or extension of the seeds), while we hypothesize that the scatter mostly informs about the formation of the larger platelet structures. We motivate our assignments by noting that scatter increases nonlinearly with the size of NPL, while absorption is proportional to the number of unit cells in the semiconductor—allowing us to distinguish between the two despite a lower concentration of large NPLs.⁴⁵ These assignments allow us to qualitatively follow the reaction as a function of time. We observe two major growth periods of the excitonic features—a rapid initial increase from 0 to 20 min and another smaller increase from 30 to 45 min. Beyond this point, the change in OD is slow and continual. The scatter profile at 600 nm shows an oscillatory behavior that appears anticorrelated to the excitonic features during the first hour. We also note the growth of thicker NPL species (indicated by absorption at 550 and 650 nm) after 60 min, but they are not as significant after the reaction is quenched and the nanoplatelets are centrifuged and resuspended. Thicker NPLs appear in relatively low concentration compared to the 3 ML NPLs (Figure S11).

To understand the morphological changes in the NPLs during seeded growth, we utilize TEM and dynamic light scattering (DLS) to track the populations of seeds and secondary NPLs during the reaction. In Figure 4d, we show the TEM of the largest platelets during the stages of growth. Before any TOP-Te has been injected (0 min), there is a slight dissolution around the edges of the NPLs, which can explain the very slight loss of OD during the first few minutes. Once the injection has begun, however, we see the edges fill out and become rectangular. At 30 min, we observe secondary nucleation starting to occur alongside a noticeable extension in the larger NPLs. Interestingly, this extension does not appear to be continuous during the last 30 min—a nucleation

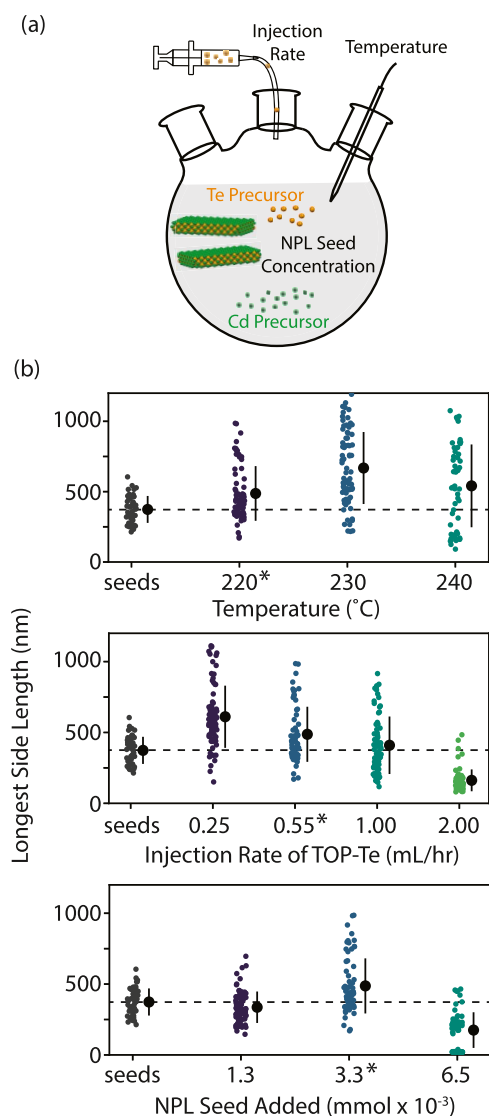


Figure 3. (a) Experimental diagram of explored reaction conditions and (b) size distributions of the longest edge of 3 ML CdTe NPLs after seeded growth (measured from TEM images, Figure S7) compared to the seeds. Solid colored circles represent the counts for each size distribution, while the solid black circles show the mean and standard deviation of each condition explored. The dashed line represents the average size of the initial seeds. The (*) indicates control conditions when changing other variables independently.

burst of many small NPLs is noticeable by 45 min, and only after that burst are the largest NPLs formed (60 min).

The composition of seeds and secondary NPLs is homogenous, and we cannot use the excitonic features to distinguish between the two populations. To get an ensemble measure of NPL behavior, we use DLS (Figure 4e, more details in the Supporting Information) to obtain insight into the change in total population, both small and large. This results in a relative size measurement that avoids counting bias and indicates the presence of multiple size distributions (Figure 4e). We note that the hydrodynamic radius is derived for a spherical particle and does not reflect the absolute size of the NPLs, but DLS has been used with good agreement to TEM sizes for small NPLs (~ 10 – 100 nm lateral sizes).^{46–48} Our CdTe NPLs are laterally much larger, so we do not expect quantitative agreement with TEM size as we do not correct for

their greater anisotropy. We observe that from 0 to 45 min, the overall population distribution is decreasing in size, which is explained by the nucleation of secondary small NPLs. At 60 min, there is some scattering from larger particles, which coincides with the appearance of the ~ 1 μm NPLs. Continuing the growth beyond an hour continues with yet another nucleation burst of smaller NPLs, while it seems that the large NPLs have reached a maximum size between 1000 and 1500 nm and do not continue to extend. The small secondary NPLs appear to become stable and large enough to extend themselves at this point and reach ~ 500 nm by 2 h (Figure S12)—limiting the maximum size of the larger seeded NPLs.

By connecting the results from reflectance, TEM, and DLS to describe what is occurring during the seeded growth process, we see stepwise or oscillatory changes in the spectra and size that correlate to secondary nucleation bursts followed by a slowed growth period, which results in the extension of the seed NPLs. This suggests that the lateral extension is not a continual addition of CdTe unit cells but rather can be explained through the balance of nucleation, growth, and ripening that has been described in the literature.^{42,49–51} As discussed previously, a prerequisite for large lateral sizes appears to be the presence of seeds, slow injection, and slightly elevated temperatures relative to original nanocrystal growth, further supporting that gradual buildup of monomer concentration and the presence of reactive edges allow for growth accompanied with periodic secondary nucleation. Other aspects of our results also support the understanding of lateral ripening—in a traditional fast injection NPL synthesis, the monomer would continue to be used up until the thinner NPLs are no longer stable and dissolve onto the next thicker nuclei.⁴⁹ In our experiments, the constant injection of monomer maintains the high concentration and prevents major shifts toward thicker NPLs. Further supporting the dominant role of concentration and buildup, if we only consider the amount of precursor added, rather than time, we see the stages occurring at certain concentration thresholds (Figures S13 and S14). This suggests that a more dynamic control of concentration may be useful for generating even larger NPL structures.

We turn our efforts to microscopy to further study the photophysical properties of mesoscale NPLs. To confirm the presence of dispersed platelets, we perform correlative light and electron microscopy. Correlative imaging has been used previously on nanocrystals and 2D materials to study photophysical properties such as plasmonic behavior, catalysis, and defect emission in relation to their structure.^{52–56} We adapt these methods here to perform photoluminescence (PL) mappings of our large NPLs. In Figure 5, we demonstrate that single NPL structures can be observed under conventional light and fluorescence microscopy (similar to their TMD counterparts). The lateral extent of our NPLs allows us to resolve PL beyond the point spread function, and the entire NPL can be visualized with standard wide-field microscopy. This is advantageous for studying NPLs because confirming the isolation of single NPLs in the literature relies on resolving fluorescence blinking or single-photon emission (through second-order photon correlations)—properties of which may not be universal across different compositions and sizes.^{3,21} By imaging the PL over the entire NPL structure, we utilize a method that allows for further studies of single-crystal NPL dynamics.

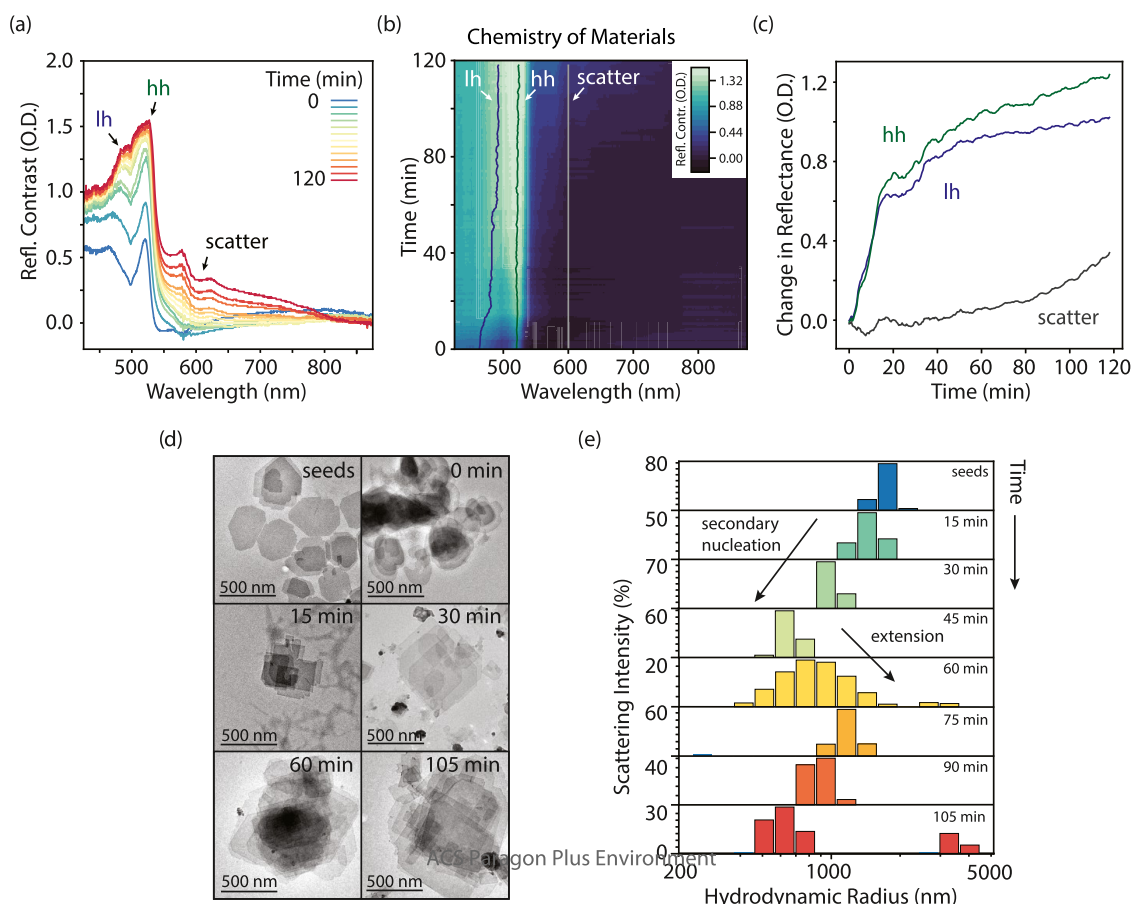


Figure 4. (a) Reflectance contrast collected *in situ* (data shown for every 10 min) for the duration of a seeded growth of 3 ML CdTe. (b) Reflectance contrast change over time, sampled every 30 s with slices taken at the heavy hole (hh), light hole (lh), and 600 nm (scatter). (c) Time slices are shown in more detail, highlighting the evolution of the excitonic transitions during seeded growth. (d) TEM during the early stages of growth starting with seeds before any precursor was added. (e) Dynamic light scattering (DLS) of aliquots taken every 15 min during seeded growth of 3 ML CdTe.

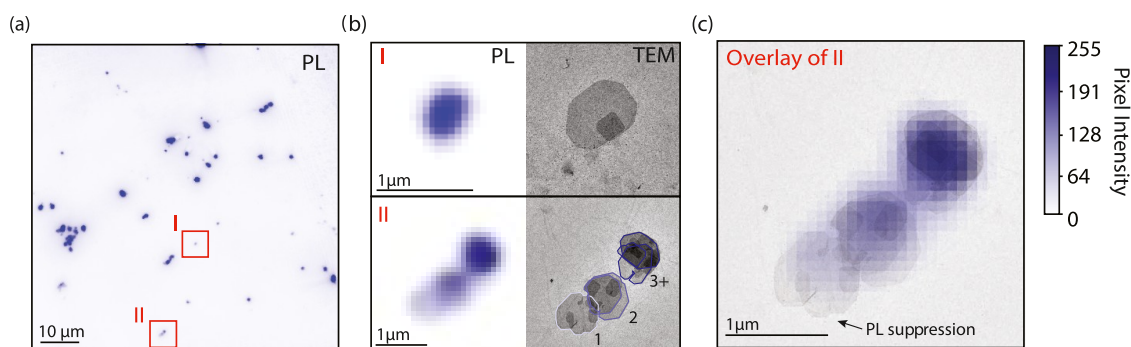


Figure 5. (a) Photoluminescence imaging of large 3 ML CdTe NPLs, showing a single NPL (I) and a group of NPLs (II). (b) TEM for spots (I) and (II) correlated to their PL, with the domains of 1, 2, and 3+ NPLs marked in (II). (c) Overlay of PL and TEM for spot (II), showing spatial heterogeneity of PL in the single NPL, as well as the integer increase in pixel intensity as the size of the stack increases.

To correlate light and electron microscopy, large NPLs obtained through seeded growth are diluted and drop cast onto a TEM grid with an alphanumeric reference pattern. The grid is then sealed between microscope slides, and the PL is imaged using an inverted microscope equipped with an sCMOS camera (more details in Figure S1). Figure 5a shows the PL for a square within the grid, along with closeups (Figure 5b spots (I) and (II)) correlated to TEM images. The image alignment process is described in Figure S15, along with an additional example of correlation with the same methods applied. We can

resolve the entire structure of a single NPL that is bright and does not contain any large tears (Figure 5b(I)), and we also examine a set of NPLs (Figure 5b(II)) to study defects and NPL stacking.

For image (II), when the PL and TEM images are overlaid (Figure 5c), we observe spatial heterogeneity within the lower, single NPL. The lower half of the NPL is nonemissive and may be defective from the large tear. A closer examination (Figure S16) shows that PL is suppressed around the edges and what we hypothesize is a screw dislocation. The PL suppression

could also be due to quenching from energy transfer that arises from the proximity of the multiple large NPL stack.⁵⁷ As additional demonstrations of our NPL imaging technique, the number of NPLs within a stack can be resolved using the intensity of the imaged PL (Figure 5b,c), as shown by the near integer increase in the intensity that correlates to 1, 2, and 3+ NPLs—confirmed by TEM. We collect PL lifetimes and observe variability depending on the number of NPLs within isolated stacks (Figure S17). With increasing number of NPLs, the average lifetime decreases, which is consistent with a change in nonradiative pathways due to energy transfer amongst the stack and the increased likelihood of exciton trapping by a nonemissive NPL.^{57,58}

Overall, the observation of lateral heterogeneity in PL draws comparison to 2D semiconductors where this can be demonstrated from many effects including defects, strain, chemical heterogeneity, and manipulation by 0D–2D heterostructures.^{59–66} These vdW materials exhibit localized electronic structure changes that do not quench the entire nanostructure and can be spatially resolved through PL mapping. The heterogeneity of PL in our large NPLs contrasts them with smaller NPLs, which have not demonstrated this behavior. Direct application into single crystal devices will allow for further studies of mesoscale NPL properties.

CONCLUSIONS

We demonstrate the controlled growth of mesoscale II–VI semiconductor NPLs, which reach areas up to 2.25×10^6 nm² for the first time. We confirm our understanding of NPL growth by applying the parameters that drive 2D extension toward the development of a seeded growth process for CdTe NPLs. *In situ* methods allow us to study the competing growth between secondary nucleation and lateral extension during this process. We also show that this seeded growth procedure can be applied to NPLs of different thicknesses and compositions, with large extensions in 2–3 ML CdTe (as well as HgTe after cation exchange) and limited extension in 3–5 ML CdSe. These mesoscale NPLs have large areas while maintaining thickness confinement that allow them to uniquely contain properties of both quantum dots and 2D materials, showing promise in single nanocrystal devices. In contrast to more traditional 2D materials, these NPLs are amenable to the wide variety of colloidal synthetic techniques (cation exchange and crown/shell growth, ligand exchanges, etc.) to develop new and interesting interfaces and may benefit from improved electronic properties through surface ligand protection. Finally, their lateral sizes allow us to apply a method of PL imaging across the entire NPL and correlate it to structure *via* TEM. Through this method, we isolate single NPLs and show that mesoscale NPLs have properties similar to 2D semiconductors—demonstrating a new class of material to bridge the gap between quantum-confined nanocrystals and 2D materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.2c01144>.

Additional experimental details and additional characterization including absorption and photoluminescence, TEM, reflectance, and photoluminescence lifetimes (PDF)

AUTHOR INFORMATION

Corresponding Author

Justin Ryan Caram – Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569, United States; orcid.org/0000-0001-5126-3829; Email: jcaram@chem.ucla.edu

Authors

Stephanie Marie Tenney – Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569, United States; orcid.org/0000-0001-7749-9944

Lauren A. Tan – Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569, United States

Mikayla L. Sonleitner – Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569, United States

Anthony V. Sica – Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569, United States

Ashley Jiwon Shin – Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569, United States; orcid.org/0000-0001-8871-5753

Ricky Ronquillo – Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569, United States

Tasnim Ahmed – Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569, United States; orcid.org/0000-0002-5990-3891

Timothy Luke Atallah – Department of Chemistry and Biochemistry, Denison University, Granville, Ohio 43023, United States; orcid.org/0000-0003-2863-6601

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.chemmater.2c01144>

Author Contributions

S.M.T. and L.A.T. synthesized and characterized all materials along with help from M.L.S. The photoluminescence imaging was done by A.V.S. and T.L.A., lifetimes were collected by A.V.S., and T.A. and R.R. assisted with size counting, and image alignment and processing was done by A.J.S.

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Notes

The authors declare no competing financial interest.

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