

# Direct Synthesis of Six-Monolayer (1.9 nm) Thick Zinc-Blende CdSe Nanoplatelets Emitting at 585 nm

Wooje Cho,<sup>†</sup> Siyoung Kim,<sup>‡</sup> Igor Coropceanu,<sup>†</sup> Vishwas Srivastava,<sup>†</sup> Benjamin T. Diroll,<sup>§</sup> Abhijit Hazarika,<sup>†</sup> Igor Fedin,<sup>†</sup> Giulia Galli,<sup>†,‡,⊥</sup> Richard D. Schaller,<sup>§,||</sup> and Dmitri V. Talapin<sup>\*,†,∇</sup>

<sup>†</sup>Department of Chemistry, University of Chicago, Chicago, Illinois 60637, United States

<sup>‡</sup>Institute for Molecular Engineering, University of Chicago, Chicago, Illinois 60637, United States

<sup>§</sup>Center for Nanoscale Materials, Argonne National Laboratory, Lemont, Illinois 60439, United States

<sup>⊥</sup>Materials Science Division, Argonne National Laboratory, Lemont, Illinois 60439, United States

<sup>||</sup>Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

<sup>∇</sup>James Franck Institute, University of Chicago, Chicago, Illinois 60637, United States

## Supporting Information

Quasi-two-dimensional semiconductor nanoplatelets (NPLs) have garnered widespread interest because of their uniquely narrow emission spectra and favorable characteristics for optical gain and lasing.<sup>1–5</sup> Strongly quantum confined along thickness, NPLs exhibit the electronic structure of quantum wells determined by their thickness, which can be controlled with atomic precision.<sup>6–10</sup> Among all semiconductor NPLs, CdSe NPLs are probably the most studied. So far, four kinds of CdSe NPLs, emitting at around 396 nm, 463 nm, 513 nm, and 553 nm, have been intensely investigated for almost a decade.<sup>11–18</sup> Despite some early confusions in identifying actual thicknesses of those NPLs, they have been successfully assigned to be 2-monolayer (2 ML) to 5-monolayer (5 ML) thickness by high-resolution TEM.<sup>19</sup> Here, *n*ML thickness corresponds to *n* chalcogen layers sandwiched between *n* + 1 metal layers. Another kind of NPLs with 6MLs of CdSe, once briefly mentioned in 2013,<sup>20</sup> however, was not explored, likely because its synthesis proved hard to reproduce. The 6 ML CdSe NPLs can be prepared by the colloidal atomic layer deposition (c-ALD) method,<sup>21</sup> but there have been no reports on direct synthesis of 6 ML CdSe NPLs, and their direct synthesis has been in doubt as being difficult by traditional approaches.<sup>22,23</sup>

Here, we report a reproducible method to obtain 6 ML CdSe NPLs through a direct colloidal synthesis route. In short, the synthesis is based on the conventional method of synthesizing CdSe NPLs<sup>24,25</sup> with a modification of adding small anions such as hydroxides and chlorides. Formation of 6 ML CdSe NPLs does not refute the belief of the absence of 6 ML CdSe NPLs in traditional syntheses,<sup>22,23</sup> yet it shows that an additional control can be enabled over CdSe NPL synthesis, with a small change in chemical conditions. Basic characterizations were performed with transmission electron microscopy (TEM), powder X-ray diffraction (powder XRD), absorption spectroscopy, photoluminescence (PL), and amplified spontaneous emission (ASE). Having a sharp PL emission, 6 ML CdSe NPLs can be used to generate an orange-colored (~610 nm) amplified spontaneous emission (ASE) or a pure red PL (~630 nm) emission by growing CdZnS shells.

The 6 ML CdSe NPL synthesis is based on known methods of producing CdSe NPLs of other thicknesses.<sup>24,25</sup> In a typical

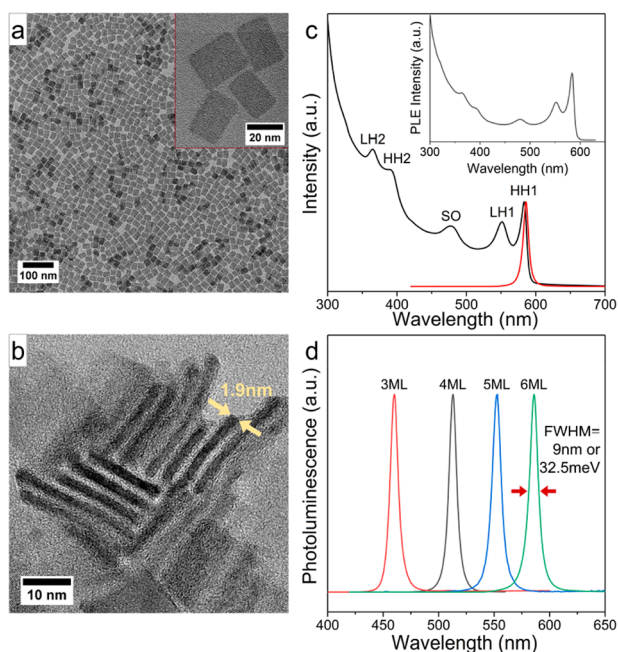
synthesis, 170 mg of cadmium myristate and 14 mL of 1-octadecene (ODE) were mixed in a 100 mL three-neck round-bottom flask and degassed under vacuum at 85 °C for 30 min. Then, the mixture was heated to 250 °C under nitrogen flow. At 250 °C, 12 mg of Se powder well dispersed in 1 mL of ODE with 5 min of sonication was quickly injected (<1 s) to the reaction mixture under vigorous stirring. After 20 s, 60 mg of cadmium acetate hydrate was added to the reaction flask, and the reaction mixture was stirred for another 60 s. Then, 0.15 mL of 0.5 M cadmium chloride aqueous solution was slowly introduced into the reaction flask dropwise in a span of 2 min. After another 3 min, the flask was rapidly cooled to room temperature using compressed air. While the reaction mixture was being cooled down, a solution containing 2 mL of oleic acid in 15 mL of methylcyclohexane (MCH) was injected into the reaction flask at around 150 °C. NPLs were first separated from the reaction batch by centrifugation and dispersed in a minimal amount of MCH. Due to the water added during the synthesis (a bad solvent for oleate-capped nanocrystals), most of the particles were precipitated by centrifugation, including smaller quantum dots. By adding an excess amount of hexanes, smaller quantum dot byproducts could be washed out after centrifugation. The remaining precipitate was dispersed in MCH, and impurities including irregularly shaped particles and 5 ML CdSe NPLs were removed by size-selective precipitation.

TEM images revealed rectangular-shaped 6 ML CdSe NPLs with lateral sizes of 21.0 ± 3.4 nm by 15.7 ± 1.8 nm (Figures 1a and S1). The thickness of the NPLs was 1.85 ± 0.16 nm as estimated from TEM images of stacked NPLs (Figure 1b). This value matches with the dimension of 3 unit cells of zinc-blende CdSe or 6 Se layers sandwiched between 7 Cd layers. The powder XRD pattern and fast Fourier transforms (FFT) of the TEM images confirmed that the NPLs crystallize in the cubic zinc-blende structure as CdSe NPLs of other thicknesses<sup>14,25</sup> (Figure S2). Well-resolved excitonic transitions could be seen in the absorption and PL spectra of the

Received: June 12, 2018

Revised: September 25, 2018

Published: September 26, 2018

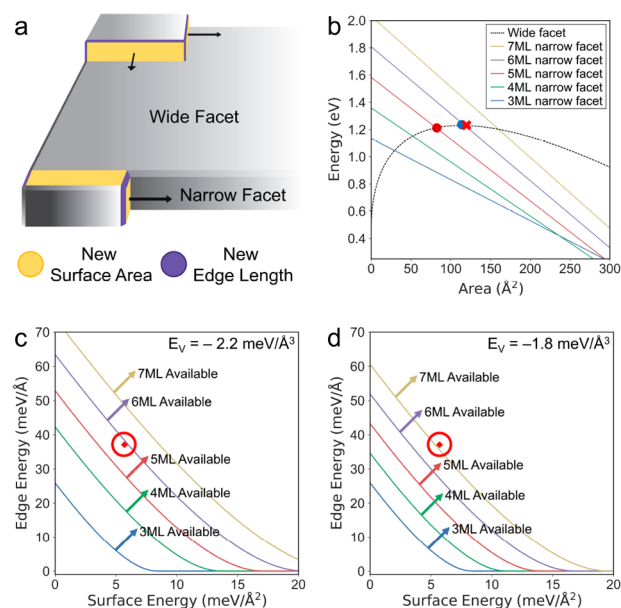


**Figure 1.** (a) TEM image of face-up 6 ML CdSe NPLs. Inset: High resolution TEM image of 6 ML CdSe NPLs. See [Supporting Information](#) for the larger images. (b) High resolution TEM image of stacked 6 ML CdSe NPLs. (c) Absorption (black) and PL emission (red) spectra of 6 ML CdSe NPLs. Inset: Photoluminescence excitation spectrum collected at 585 nm emission wavelength. (d) PL emission spectra of CdSe NPLs of different thicknesses from 3 to 6 ML.

ensemble ([Figure 1c](#)). The absorption had its first heavy-hole (HH1) and light-hole (LH1) excitonic peaks at 583 and 551 nm, respectively, and the split-off hole (SO) transition at 477 nm. Two additional features were visible in the UV range at 392 and 364 nm, which can be attributed to transitions involving states from the second quantum well sub-band heavy-hole (HH2) and light-hole (LH2), respectively. The transition assignment is supported by the calculated electronic structure of 6 ML CdSe NPL ([Figure S3](#)). PL emission peaked at 586 nm with the full width at half-maximum (fwhm) under 9 nm or 32.5 meV ([Figure 1d](#)). A small Stokes shift between the HH1 and the emission band ( $\sim 7$  meV) also represented a common characteristic of CdSe NPLs. Photoluminescence excitation (PLE) spectra taken at various emission wavelengths were almost identical, suggesting that there was no inhomogeneous broadening of the emission band ([Figure S4](#)). The 6 ML CdSe NPLs could achieve 45% quantum yield, and time-resolved PL of the NPLs showed fast radiative decay with  $t_{1/2} = 4.3$  ns, similar to CdSe NPL of other thicknesses<sup>25</sup> ([Figure S5](#)).

We found that water and chloride ions play an essential role in forming 6 ML CdSe NPLs. The only difference in our system and traditional CdSe NPL synthesis was the addition of water or chloride ions. In the presence of different cations, water and chlorides repeatedly produced 6 ML CdSe NPLs ([Figure S6](#)). According to the recently proposed NPL nucleation and growth model by the Norris group,<sup>22</sup> the formation of CdSe NPLs is controlled by the nucleation kinetics. This model follows the general 2D nucleation and growth theory;<sup>26</sup> nanocrystal growth occurs through the nucleation of an island on the nanocrystal facet. The growth conditions are controlled by the reaction kinetics rather than

diffusion, so the growth of a nucleated island is fast, and the rate-limiting step for the growth process is controlled by island nucleation barrier ( $\Delta E$ ). Energy change for a whole nanocrystal can be expressed as  $\Delta E = \Delta V \cdot E_V + \Delta A \cdot E_A + \Delta L \cdot E_L$ , accounting for the changes in volume ( $\Delta V$ ), surface area ( $\Delta A$ ), and edge length ( $\Delta L$ ), with specific energies for unit volume ( $E_V$ ), surface area ( $E_A$ ), and edge length ( $E_L$ ). NPLs can be synthesized only under the condition where the nucleation on a narrow facet is thermodynamically favored over that on a wide facet. Otherwise, nanostructures grow in 3D, forming quantum dots. According to the model ([Figure 2b](#)), a

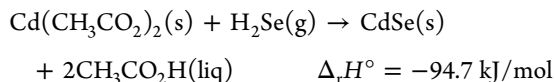


**Figure 2.** (a) Scheme for the growth model of CdSe NPLs reported in [ref 21](#), showing nucleated islands on a wide facet and a narrow facet. (b) Energy change of NPLs caused by an island formation on wide and narrow facets by area of the island. Following [ref 21](#),  $E_V$  of  $-2.2$  meV/ $\text{\AA}^3$ ,  $E_A$  of  $5.7$  meV/ $\text{\AA}^2$ , and  $E_L$  of  $37.1$  meV/ $\text{\AA}$  were used. Blue dot represents the highest point of the wide facet energy curve. Red dot and red X represent the intersections of wide facet and narrow facet energy curves of 5 and 6 ML, respectively. (c) A map showing synthesizability of NPLs by edge energy ( $E_L$ ) and surface energy ( $E_A$ ) at the volume energy ( $E_V$ ) of  $-2.2$  meV/ $\text{\AA}^3$ . Red circle represents the point with  $E_A$  of  $5.7$  meV/ $\text{\AA}^2$  and  $E_L$  of  $37.1$  meV/ $\text{\AA}$ . Up to 5 ML NPLs can form. (d) A map showing synthesizability of NPLs by  $E_L$  and  $E_A$  at the  $E_V$  of  $-1.8$  meV/ $\text{\AA}^3$ . Red circle represents the point with  $E_A$  of  $5.7$  meV/ $\text{\AA}^2$  and  $E_L$  of  $37.1$  meV/ $\text{\AA}$ . Up to 7 ML NPLs can be synthesized.

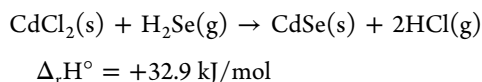
nucleated island on a 5 ML narrow facet can be formed before that on a wide facet, while that on a 6 ML narrow facet cannot. This explains the existence of 5 ML NPLs and the absence of 6 ML NPLs in conventional NPL syntheses.

Following Norris's approach, availabilities of 3 ML to 7 ML NPLs are mapped for different values of  $E_L$  and  $E_A$  ([Figure 2c,d](#)). It is noticeable that 6 ML are only possible with an increased  $E_L$  or  $E_A$ . Considering steric crowding of carboxylate ligands on nanocrystal surfaces,<sup>27,28</sup> an addition of small anionic ligands such as chlorides and possible hydroxides from water is expected to decrease rather than to increase  $E_L$  and  $E_A$ . X-ray fluorescence (XRF) measurements performed on purified 6 ML CdSe NPLs estimated  $\sim 1.6$  mol % of chlorine in the sample, which is equal to 10.4 mol % of total cadmium atoms on the surface of the NPLs ([Figure S7](#)). A possible

explanation can come from an increased  $E_V$ . A small increase in  $E_V$  can avail 6 ML formation (Figure 2d).  $E_V$  can be interpreted as a formation energy of a nucleated island, which is in a crude sense the enthalpy of reaction:



By adding cadmium chlorides to the reaction mixture,  $E_V$  can be increased on average because the reaction from cadmium chloride is endothermic:



According to the model shown in the Figure 2c,d, only a 0.4 meV/Å<sup>3</sup> change, which equals to 2 kJ/mol for zinc-blende CdSe, is more than sufficient to enable the formation of 6 ML CdSe NPLs. Therefore, a small increase in  $E_V$  by incorporating a tiny amount of CdCl<sub>2</sub> (1.9 kJ/mol corresponding to 1.57 mol % of Cl) might be sufficient to change the nucleation barrier ( $\Delta E$ ) and enable formation of 6 ML CdSe NPLs.<sup>29</sup>

Moreover, it was hinted that the direct synthesis of 7 ML CdSe NPLs is also be possible. In some 6 ML CdSe NPL syntheses, absorption and emission features at around 600 nm kept appearing (Figure S8). By fitting the two PL peaks, a sharp peak at 602 nm was revealed to be comparable in line width to the PL peaks of other populations of CdSe NPLs. If the absorption and emission peaks at around 600 nm originate from the same species, it represents a very small Stokes shift, which is a unique characteristic of CdSe NPLs.

In addition to bringing important understanding of NPL formation, 6 ML CdSe NPLs can be useful in a number of practical applications. Excitation of a thin film of 6 ML CdSe NPLs with 400 nm femtosecond laser pulses was used to study optical gain. The 6 ML CdSe NPLs showed sharp ASE emission, red-shifted to 616 nm, which can be due to the emission from the biexciton state (Figure 3a). The ASE threshold was 21 μJ/cm<sup>2</sup>, which is comparable to other reported thresholds for CdSe NPLs.<sup>30,31</sup> The color-pure emission from NPLs is also appealing for lighting and display applications. For displays, PL emission at around 630 nm with narrow line width is desirable for red emitters. CdZnS shells could be successfully grown on 6 ML CdSe NPL cores using

colloidal atomic deposition (c-ALD)<sup>32</sup> (Figure 3b). With the 1 ML shell, 1CdZnS/6CdSe/1CdZnS core-shell nanoplatelets achieved red PL emissions centered at 632 nm with a narrow fwhm of 20 nm or 62 meV. Also, no inhomogeneous broadening was found in 2D contour PL emission-excitation maps (Figure S9). This example shows that 6 ML CdSe NPL can be a good candidate for red emitters.

In conclusion, a synthetic method for 6 ML CdSe NPLs was demonstrated. It was confirmed that 6 ML CdSe NPLs have characteristics similar to already known CdSe NPLs of other thicknesses. The reason for emergence of 6 ML CdSe NPLs upon addition of water and chlorides is not yet fully understood, but we tentatively suggest that change in the nucleation barrier for island formation caused by chlorides may affect the ability to nucleate and grow 6 ML CdSe NPLs. We hope this work can help us better understand II-VI NPLs, their growth, and their applications toward multicolored lasing and next generation displays.

## ■ ASSOCIATED CONTENT

### Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.8b02489.

Experimental procedures and spectral and structural data (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*(D.V.T.) E-mail: [dvtalapin@uchicago.edu](mailto:dvtalapin@uchicago.edu).

### ORCID

Benjamin T. Diroll: 0000-0003-3488-0213

Abhijit Hazarika: 0000-0003-0391-2163

Richard D. Schaller: 0000-0001-9696-8830

Dmitri V. Talapin: 0000-0002-6414-8587

### Notes

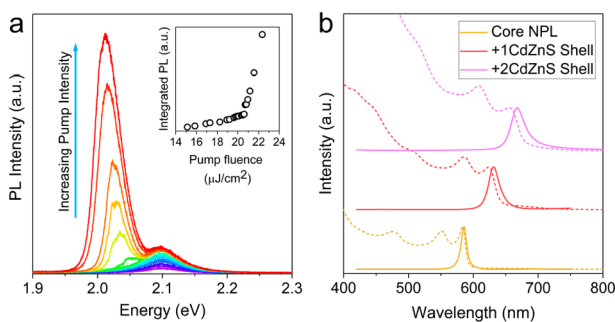
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank Márton Vörös for useful discussions and Ellie Lee for helping with artwork. This work was supported by NSF DMREF Program under Award Nos. DMR-1629601 and DMR-1629383, by NSF under Award No. CHE-1611331, and by the Department of Defense (DOD) Air Force Office of Scientific Research under Grant No. FA9550-15-1-0099. V.S. was supported by the University of Chicago Materials Research Science and Engineering Center funded by NSF under Award No. DMR-1420709, G.G. and S.K. acknowledge support from the Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering, under Contract DE-FG02-06ER46262. This work was performed, in part, at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, and supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.

## ■ REFERENCES

(1) Nasilowski, M.; Mahler, B.; Lhuillier, E.; Ithurria, S.; Dubertret, B. Two-Dimensional Colloidal Nanocrystals. *Chem. Rev.* **2016**, *116*, 10934–10982.



**Figure 3.** (a) ASE of 6ML CdSe NPLs. Inset: Integrated PL area vs pump fluence showing ASE threshold at 21 μJ/cm<sup>2</sup>. (b) Absorption and PL emission spectra of 6 ML CdSe NPL core and *n*CdZnS/6CdSe/*n*CdZnS (*n* = 1, 2) core-shell nanohetero-structure. Dotted lines represent absorption spectra, and solid lines illustrate emission spectra.

- (2) Lembke, D.; Bertolazzi, S.; Kis, A. Single-Layer MoS<sub>2</sub> Electronics. *Acc. Chem. Res.* **2015**, *48*, 100–110.
- (3) Lhuillier, E.; Pedetti, S.; Ithurria, S.; Nadal, B.; Heuclin, H.; Dubertret, B. Two-Dimensional Colloidal Metal Chalcogenides Semiconductors: Synthesis, Spectroscopy, and Applications. *Acc. Chem. Res.* **2015**, *48*, 22–30.
- (4) Lv, R.; Robinson, J. A.; Schaak, R. E.; Sun, D.; Sun, Y.; Mallouk, T. E.; Terrones, M. Transition Metal Dichalcogenides and Beyond: Synthesis, Properties, and Applications of Single- and Few-Layer Nanosheets. *Acc. Chem. Res.* **2015**, *48*, 56–64.
- (5) Bekenstein, Y.; Koscher, B. A.; Eaton, S. W.; Yang, P.; Alivisatos, A. P. Highly Luminescent Colloidal Nanoplates of Perovskite Cesium Lead Halide and Their Oriented Assemblies. *J. Am. Chem. Soc.* **2015**, *137*, 16008–16011.
- (6) Akkerman, Q. A.; Motti, S. G.; Srimath Kandada, A. R.; Mosconi, E.; D'Innocenzo, V.; Bertoni, G.; Marras, S.; Kamino, B. A.; Miranda, L.; De Angelis, F.; Petrozza, A.; Prato, M.; Manna, L. Solution Synthesis Approach to Colloidal Cesium Lead Halide Perovskite Nanoplatelets with Monolayer-Level Thickness Control. *J. Am. Chem. Soc.* **2016**, *138*, 1010–1016.
- (7) Li, Z.; Qin, H.; Guzun, D.; Benamara, M.; Salamo, G.; Peng, X. Uniform thickness and colloidal-stable CdS quantum disks with tunable thickness: Synthesis and properties. *Nano Res.* **2012**, *5*, 337–351.
- (8) Pedetti, S.; Nadal, B.; Lhuillier, E.; Mahler, B.; Bouet, C.; Abécassis, B.; Xu, X.; Dubertret, B. Optimized Synthesis of CdTe Nanoplatelets and Photoresponse of CdTe Nanoplatelets Films. *Chem. Mater.* **2013**, *25*, 2455–2462.
- (9) Scott, R.; Kickhofel, S.; Schoeps, O.; Antanovich, A.; Prudnikau, A.; Chuvilin, A.; Woggon, U.; Artemyev, M.; Achtstein, A. W. Temperature dependent radiative and non-radiative recombination dynamics in CdSe-CdTe and CdTe-CdSe type II hetero-nanoplatelets. *Phys. Chem. Chem. Phys.* **2016**, *18*, 3197–3203.
- (10) Wang, F.; Wang, Y.; Liu, Y.-H.; Morrison, P. J.; Loomis, R. A.; Buhro, W. E. Two-Dimensional Semiconductor Nanocrystals: Properties, Templated Formation, and Magic-Size Nanocluster Intermediates. *Acc. Chem. Res.* **2015**, *48*, 13–21.
- (11) Lhuillier, E.; Pedetti, S.; Ithurria, S.; Heuclin, H.; Nadal, B.; Robin, A.; Patriarche, G.; Lequeux, N.; Dubertret, B. Electrolyte-Gated Field Effect Transistor to Probe the Surface Defects and Morphology in Films of Thick CdSe Colloidal Nanoplatelets. *ACS Nano* **2014**, *8*, 3813–3820.
- (12) Bouet, C.; Mahler, B.; Nadal, B.; Abécassis, B.; Tessier, M. D.; Ithurria, S.; Xu, X.; Dubertret, B. Two-Dimensional Growth of CdSe Nanocrystals, from Nanoplatelets to Nanosheets. *Chem. Mater.* **2013**, *25*, 639–645.
- (13) Chen, Y.; Chen, D.; Li, Z.; Peng, X. Symmetry-Breaking for Formation of Rectangular CdSe Two-Dimensional Nanocrystals in Zinc-Blende Structure. *J. Am. Chem. Soc.* **2017**, *139*, 10009–10019.
- (14) Ithurria, S.; Dubertret, B. Quasi 2D Colloidal CdSe Platelets with Thicknesses Controlled at the Atomic Level. *J. Am. Chem. Soc.* **2008**, *130*, 16504–16505.
- (15) Jana, S.; Phan, T. N. T.; Bouet, C.; Tessier, M. D.; Davidson, P.; Dubertret, B.; Abécassis, B. Stacking and Colloidal Stability of CdSe Nanoplatelets. *Langmuir* **2015**, *31*, 10532–10539.
- (16) Achtstein, A. W.; Schliwa, A.; Prudnikau, A.; Hardzei, M.; Artemyev, M. V.; Thomsen, C.; Woggon, U. Electronic Structure and Exciton-Phonon Interaction in Two-Dimensional Colloidal CdSe Nanosheets. *Nano Lett.* **2012**, *12*, 3151–3157.
- (17) Rowland, C. E.; Fedin, I.; Zhang, H.; Gray, S. K.; Govorov, A. O.; Talapin, D. V.; Schaller, R. D. Picosecond energy transfer and multiexciton transfer outpaces Auger recombination in binary CdSe nanoplatelet solids. *Nat. Mater.* **2015**, *14*, 484–489.
- (18) Rossinelli, A. A.; Riedinger, A.; Marques-Gallego, P.; Knusel, P. N.; Antolinez, F. V.; Norris, D. J. High-temperature growth of thick-shell CdSe/CdS core/shell nanoplatelets. *Chem. Commun.* **2017**, *53*, 9938–9941.
- (19) Mahler, B.; Nadal, B.; Bouet, C.; Patriarche, G.; Dubertret, B. Core/Shell Colloidal Semiconductor Nanoplatelets. *J. Am. Chem. Soc.* **2012**, *134*, 18591–18598.
- (20) Tessier, M. D.; Biadala, L.; Bouet, C.; Ithurria, S.; Abécassis, B.; Dubertret, B. Phonon Line Emission Revealed by Self-Assembly of Colloidal Nanoplatelets. *ACS Nano* **2013**, *7*, 3332–3340.
- (21) Chu, A.; Livache, C.; Ithurria, S.; Lhuillier, E. Electronic structure robustness and design rules for 2D colloidal heterostructures. *J. Appl. Phys.* **2018**, *123*, 035701.
- (22) Riedinger, A.; Ott, F. D.; Mule, A.; Mazzotti, S.; Knüsel, P. N.; Kress, S. J. P.; Prins, F.; Erwin, S. C.; Norris, D. J. An intrinsic growth instability in isotropic materials leads to quasi-two-dimensional nanoplatelets. *Nat. Mater.* **2017**, *16*, 743–748.
- (23) Ott, F. D.; Riedinger, A.; Ochsenein, D. R.; Knüsel, P. N.; Erwin, S. C.; Mazzotti, M.; Norris, D. J. Ripening of Semiconductor Nanoplatelets. *Nano Lett.* **2017**, *17*, 6870–6877.
- (24) Pelton, M.; Ithurria, S.; Schaller, R. D.; Dolzhenkov, D. S.; Talapin, D. V. Carrier Cooling in Colloidal Quantum Wells. *Nano Lett.* **2012**, *12*, 6158–6163.
- (25) Ithurria, S.; Tessier, M. D.; Mahler, B.; Lobo, R. P. S. M.; Dubertret, B.; Efros, A. L. Colloidal nanoplatelets with two-dimensional electronic structure. *Nat. Mater.* **2011**, *10*, 936–941.
- (26) Lovette, M. A.; Browning, A. R.; Griffin, D. W.; Sizemore, J. P.; Snyder, R. C.; Doherty, M. F. Crystal Shape Engineering. *Ind. Eng. Chem. Res.* **2008**, *47*, 9812–9833.
- (27) Boles, M. A.; Ling, D.; Hyeon, T.; Talapin, D. V. The surface science of nanocrystals. *Nat. Mater.* **2016**, *15*, 141–153.
- (28) Zherebetsky, D.; Scheele, M.; Zhang, Y.; Bronstein, N.; Thompson, C.; Britt, D.; Salmeron, M.; Alivisatos, P.; Wang, L.-W. Hydroxylation of the surface of PbS nanocrystals passivated with oleic acid. *Science* **2014**, *344*, 1380–1384.
- (29) See [Supplementary Information](#) for additional details.
- (30) She, C.; Fedin, I.; Dolzhenkov, D. S.; Dahlberg, P. D.; Engel, G. S.; Schaller, R. D.; Talapin, D. V. Red, Yellow, Green, and Blue Amplified Spontaneous Emission and Lasing Using Colloidal CdSe Nanoplatelets. *ACS Nano* **2015**, *9*, 9475–9485.
- (31) She, C.; Fedin, I.; Dolzhenkov, D. S.; Demortière, A.; Schaller, R. D.; Pelton, M.; Talapin, D. V. Low-Threshold Stimulated Emission Using Colloidal Quantum Wells. *Nano Lett.* **2014**, *14*, 2772–2777.
- (32) Ithurria, S.; Talapin, D. V. Colloidal Atomic Layer Deposition (c-ALD) using Self-Limiting Reactions at Nanocrystal Surface Coupled to Phase Transfer between Polar and Nonpolar Media. *J. Am. Chem. Soc.* **2012**, *134*, 18585–18590.
- (33) Christodoulou, S.; Climente, J. I.; Planelles, J.; Brescia, R.; Prato, M.; Martín-García, B.; Khan, A. H.; Moreels, I. Chloride-Induced Thickness Control in CdSe Nanoplatelets. *Nano Lett.* **2018**, DOI: [10.1021/acs.nanolett.8b02361](https://doi.org/10.1021/acs.nanolett.8b02361).

#### NOTE ADDED IN PROOF

After submission of this work, a new study on the transformation of 4 ML CdSe NPLs into thicker NPLs in the presence of CdCl<sub>2</sub> has been reported.<sup>33</sup> Our explanation for direct synthesis of 6 ML CdSe NPLs can be also relevant to the results reported in that study.