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Supporting Information

**ABSTRACT:** Thick-shell CdSe/nCdS ( $n \ge 10$ ) nanocrystals were recently reported that show remarkably suppressed fluorescence intermittency or "blinking" at the single-particle level as well as slow rates of Auger decay. Unfortunately, whereas CdSe/ nCdS nanocrystal synthesis is well-developed up to  $n \le 6$  CdS monolayers (MLs), reproducible syntheses for  $n \ge 10$  MLs are less understood. Known procedures sometimes result in homogeneous CdS nucleation instead of heterogeneous, epitaxial CdS nucleation on CdSe, leading to broad and multimodal particle size distributions. Critically, obtained core/shell sizes are often



below those desired. This article describes synthetic conditions specific to thick-shell growth ( $n \ge 10$  and  $n \ge 20$  MLs) on both small (sub2 nm) and large (>4.5 nm) CdSe cores. We find added secondary amine and low concentration of CdSe cores and molecular precursors give desired core/shell sizes. Amine-induced, partial etching of CdSe cores results in apparent shell-thicknesses slightly beyond those desired, especially for very-thick shells ( $n \ge 20$  MLs). Thermal ripening and fast precursor injection lead to undesired homogeneous CdS nucleation and incomplete shell growth. Core/shells derived from small CdSe (1.9 nm) have longer PL lifetimes and more pronounced blinking at single-particle level compared with those derived from large CdSe (4.7 nm). We expect our new synthetic approach will lead to a larger throughput of these materials, increasing their availability for fundamental studies and applications.

# INTRODUCTION

Core/shell colloidal semiconductor nanocrystals are one of the most active areas of nanotechnology research.<sup>1,2</sup> Semiconductor nanocrystals are ideal chromophores and fluorophores because of their broad intense absorption ( $\varepsilon \approx 10^5$  to  $10^6$  M<sup>-1</sup> · cm<sup>-1</sup>),<sup>3-5</sup> size- and composition-tunable band gap (250-4000 nm), narrow ( $\leq$ 25 nm) and long-lived emission (20 ns CdSe,<sup>6</sup> 1  $\mu$ s PbSe<sup>7</sup>), and photostability and chemical stability.<sup>8-15</sup> Colloidal semiconductors have a coating surface-ligand layer, which makes them amenable to surface modification and readily dispersible in organic and aqueous solvents. In core/shell architecture, two or more semiconductors can be manipulated to obtain unique optoelectronic properties. Relative band alignment can be used to confine the electron and hole wave functions together to the core in a "type-I" configuration or independently from each other to core and shell in a "type-II" configuration.<sup>16,17</sup> The pressure, or "strain", exerted by the shell can also be used to tune the core's conduction band energy level.<sup>18</sup> The resulting degree of electronhole overlap determines the photoluminescence (PL) and Auger exciton decay rates.  $^{19-21}\,$ 

For cadmium chalcogenides, early core/shell preparations relied on reaction between cores and organometallic shell precursors,  $^{22-29}$  single-source precursors (SSPs),  $^{30,31}$  or photodegradation of surface ligands.<sup>32</sup> Successive ion layer adsorption and reaction (SILAR), originally developed for thin films, has become the method of choice to prepare core/shell and multishell nanocrystals.<sup>33-39</sup> Thermal cycling-single precursor (TC-SP) has led to core/shells with narrower size dispersions and better color purity.40,41 Other approaches that facilitate core/shell formation include minimizing the core-shell lattice mismatch, reducing stress-induced defects through grading,<sup>42,43</sup> and using chemical compatibility to build core/shells around structurally disparate materials.44

Very recently, thick-shell CdSe/nCdS ( $n \ge 10$ ) core/shell nanocrystals were reported that showed remarkably suppressed fluorescence intermittency or "blinking" at the single-particle level.<sup>45,46</sup> This has spurred intense study into the blinking suppression mechanism and photophysics of these materials.<sup>6,47</sup> Among questions that remain unanswered is whether CdSe core size<sup>52</sup> as well as core—shell interface nature (abrupt vs graded)<sup>53</sup> play a role in determining the unique optical properties of these materials. These questions are of particular relevance

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and timeliness because radially graded alloy CdZnSe/ZnSe nanocrystals have been reported to display nonblinking behavior.<sup>54</sup>

To address these questions, reproducible syntheses are needed. Crystalline CdSe and CdS both exist in cubic (zinc blende) or hexagonal (wurtzite) form, and their lattice mismatch is only 3.7% (zinc blende–zinc blende) or 3.9% (wurtzite–wurtzite). The synthesis of CdSe/nCdS nanocrystals is well-developed up to a shell-thickness of about six ( $n \le 6$ ) monolayers (MLs),<sup>55</sup> but only recently have there been reports on the growth of 10 ( $n \le 10$ )<sup>54</sup> or more ( $n \ge 10$ ) MLs.<sup>57</sup> Synthesizing such thick-shell materials involves unique technical challenges. We have observed large amounts of unreacted precursors after several SILAR injections lead to CdS homonucleation instead of epitaxial heterogeneous nucleation on CdSe, resulting in poor, broad, and multimodal size distributions. Core/shell sizes obtained using available procedures are less than desired.

Appearance of CdS homonuclei during CdSe/CdS nanocrystal growth is difficult to detect by absorption and PL spectroscopies. Free CdS homonuclei and CdS shells share similar absorption features. If clustering occurs, then energy transfer from larger band gap CdS homonuclei to smaller band gap CdSe/CdS materials can render the former "silent" by PL. Even more difficult to detect is unreacted Cd and S precursors because they are spectroscopically silent except at bluer wavelengths (higher energies) than those where nanocrystals absorb. In this Article, we present a thorough investigation of CdSe/nCdS synthetic conditions using SILAR, emphasizing growth of very thick CdS shells ( $n \ge 10$  and even  $n \ge 20$  MLs). We start by growing thick CdS shells on small, sub-2 nm CdSe cores, selected as a test bed on the basis of their relative instability and propensity to dissolve at high-temperature, then extend the method to large, ca. 4.7 nm, CdSe cores. We present several control experiments to probe and document specific challenges associated with synthesizing these materials including effects of added primary and secondary amines and core and precursor concentration on CdS homogeneous versus heterogeneous nucleation, ripening, and CdSe core etching.

## EXPERIMENTAL SECTION

**Materials.** Cadmium oxide (CdO, 99.998%), sulfur (S<sub>8</sub>, 99.999%), trioctylphosphine (TOP, 90%), and oleic acid (90%) were purchased from Alfa Aesar; selenium (Se, pellets,  $\geq$  99.999%), octadecyl amine (octadecyl-NH<sub>2</sub>) (90%), and dioctylamine (98%) ((octyl)<sub>2</sub>NH) were purchased from Sigma-Aldrich; and 1-octadecene (ODE) (90%) and oleylamine (oleyl-NH<sub>2</sub>) (80–90%) were purchased from Acros. Bis(2,2,4-trimethylpentyl)phosphinic acid (TMPPA) (CYANEX 272) was obtained from Cytec Industries. Procedures were performed under a dry inert gas atmosphere (N<sub>2</sub> or Ar) in a glovebox or a Schlenk line.

**CdSe Cores.** *Small Cores*. Sub-2 nm CdSe was synthesized by a slightly modified literature procedure.<sup>58</sup>

0.16 M TOPSe/ODE. Se (71.4 mg, 904  $\mu$ mol), TOP (577 mg, 1.56 mmol), and ODE (4.00 g, 15.84 mmol) were stirred and heated until optically clear.

Synthesis. CdO (15.0 mg, 117  $\mu$ mol), TMPPA (304 mg, 1.05 mmol), and ODE (4.00 g, 15.84 mmol) were degassed under vacuum at 80 °C for 30 min, refilled with Ar, and heated to 300 °C for 6 h until optically clear. Solution was heated to 325 °C and 0.16 M TOPSe/ODE (5.7 mL, 904  $\mu$ mol) was swiftly injected. After ~5 s, mixture was allowed to cool to room

temperature (RT). This reliably produced CdSe with first absorption peak (1S) between 480 and 496 nm (six runs: 480, 480, 496, 490, 485, and 488 nm).

*Large Cores.* Ca. 4.7 nm CdSe was synthesized by a slightly modified literature procedure.<sup>59</sup>

2.1 *M TOPSe*. Se (144 mg, 1.82 mmol) and TOP (797 mg, 2.15 mmol) were stirred and heated until optically clear.

0.2 M Cd(oleate)<sub>2</sub>. CdO (318 mg, 2.48 mmol), oleic acid (3.09 g, 10.94 mmol), and ODE (7.11 g, 28.16 mmol) were degassed under vacuum at 80 °C for 60 min, refilled with Ar, and heated to 240 °C until optically clear.

Synthesis. Oleyl-NH<sub>2</sub> (5 mL, 15.14 mmol) or  $(octyl)_2$ NH (5 mL, 16.55 mmol) was degassed under vacuum at 80 °C for 30 min, then refilled with Ar. We added 2.1 M TOPSe (0.15 mL, 315  $\mu$ mol), and the temperature increased to 300 °C. After 5 min, 0.2 M Cd(oleate)<sub>2</sub> (1.5 mL, 300  $\mu$ mol) was quickly injected, and the temperature adjusted to 280 °C. Aliquots (<0.05 mL) were taken at different times analyzed by absorption and PL. After 10 min, the mixture was allowed to cool to RT.

*Core Purification.* CdSe cores were washed twice just prior to shell-growth by precipitation with 4:1 v/v acetone—methanol mix. and centrifugation at 4200 rpm for 10 min.

CdSe/nCdS Core/Shells. Precursors. We prepared 0.2 M Cd(oleate)<sub>2</sub> as described above for large CdSe cores. For 0.2 M Cd(oleate)<sub>2</sub>-oleyl-NH<sub>2</sub>, CdO (640 mg, 4.98 mmol), oleic acid (6.18 g, 21.88 mmol), and ODE (4.39 g, 17.41 mmol) were degassed under vacuum at 80 °C for 60 min, refilled with Ar, and heated to 240 °C until optically clear. Freshly degassed oleyl- $NH_2$  (12.5 mL, 37.85 mmol) was injected, and the mixture stirred at 60 °C for 20 min. For 0.1 M Cd(oleate)<sub>2</sub>-amine, oleyl-NH<sub>2</sub> (12.5 mL, 37.85 mmol) or (octyl)<sub>2</sub>NH (12.5 mL, 41.36 mmol) was degassed under vacuum at 80 °C for 30 min, refilled with Ar, and transferred to another flask containing 0.2 M  $Cd(oleate)_2$ (12.5 mL). The mixture was stirred at 60 °C for 20 min. For 0.2 M S<sub>8</sub>, S<sub>8</sub> (159 mg, 4.97 mmol) and ODE (19.73 g, 78.13 mmol) were degassed under vacuum at 80 °C for 30 min, refilled with Ar, and heated to 180 °C for 20 min until optically clear. For 0.1 M S<sub>8</sub>, S<sub>8</sub> (79.0 mg, 2.47 mmol) and ODE (19.73 g, 78.13 mmol) were degassed under vacuum at 80 °C for 30 min, refilled with Ar, heated to 180 °C for 20 min until optically clear, and allowed to cool to RT.

*Core Solutions.* Freshly made and washed CdSe ( $\leq 12$  h) was dissolved in hexane (5 mL) (sub-2 nm) or toluene (5 mL) (ca. 4.5 nm). CdSe concentrations were determined from 1S peak using extinction coefficients.<sup>3-5,60</sup>

Shell Growth. An aliquot containing  $1.5 \times 10^{-7}$  mol or  $7.5 \times 10^{-8}$  mol CdSe, respectively, for 19 or 10  $\mu$ M initial concentration was dried under vacuum at RT. ODE (4 mL, 12.5 mmol) and amine (3.001 g octadecyl-NH<sub>2</sub>, 11.13 mmol; or 3.7 mL oleyl-NH<sub>2</sub>, 11.20 mmol; or 3.8 mL (octyl)<sub>2</sub>NH, 12.57 mmol) were added. Mixture was degassed under vacuum at 80 °C for 30 min, refilled with Ar, and heated to the initial shell-growth temperature (sub-2 nm: 200 °C 1–2 MLs, 230 °C 3–6 MLs, 240 °C >6 MLs; ca. 4.5 nm: 235 °C 1 to 2 MLs, 245 °C >2 MLs).<sup>55</sup> Cd and S precursors were introduced alternatingly using programmable syringe pumps, each followed by 15 min wait.<sup>33</sup> Cd precursor was injected first. Shell growth was monitored by absorption or transmission electron microscopy (TEM) of aliquots (≤0.05 mL) every other theoretical ML. Mixture was allowed to cool to RT 15 min after last S injection.

Core/Shell Purification. Core/shells were washed three times by precipitation with a 1:1 v/v acetone—methanol mixture and centrifugation at 4200 rpm for 10 min.

**Structural Characterization.** *X-ray Diffraction.* Powder X-ray diffraction (XRD) was measured using Cu K $\alpha$  radiation on Scintag XDS-2000 diffractometer.

Transmission Electron Microscopy. TEM was conducted on carbon-coated copper grids using FEI Technai G2 F20 fieldemission scanning transmission electron microscope (STEM) at 200 kV (point-to-point resolution <0.25 nm, line-to-line resolution <0.10 nm). Elemental composition was characterized by energy-dispersive spectroscopy (EDS)

Particle Analysis. Dimensions were measured manually or with ImageJ for >50–100 particles. Averages are reported  $\pm$  standard deviations.

**Optical Characterization.** *Ensembles.* Absorption spectra were measured with photodiode array Agilent 8453 UV-vis spectrophotometer. Steady-state PL spectra were measured with a Horiba-Jobin Yvon Nanolog scanning spectrofluorometer with photomultiplier detector. PL quantum yields (QYs) were measured by known procedures.<sup>46,61,62</sup> Absorption and PL emission spectra were measured twice, and average QY was recorded.

Single Particles. PL Lifetimes. Nanocrystals were dispersed onto quartz substrates from dilute hexane to surface densities  $\sim 0.01/\mu m^2$  mounted on an optical microscope translation stage and excited at 405 nm with 50 ps pulses through 60×, 1.2 NA water immersion objective (Olympus, used to collect PL). Pulseto-pulse separation (100–200 ns) was set much longer than PL decay to ensure exciton relaxation between pulses. PL was sent to Perkin-Elmer avalanche photodiode (SPCM AQR-14) through long-pass excitation/emission filter that rejected scattered light. Single photon counting was performed using PicoQuant Time Harp200 correlation hardware. Overall system's time resolution was 400 ps.

Blinking Statistics . Blinking statistics were collected on prism-based total internal reflection fluorescence microscope (TIRFM).<sup>63</sup> Samples were excited with 10 mW 488 nm argon cw laser (Uniphase, San Jose, CA) and PL -filtered with long-pass 488 RazorEdge filter (Rochester, NY) and collected on Andor iXon^{EM}+ 897 camera (Belfast; 512  $\times$  512 imaging array, 16  $\mu m$   $\times$ 16  $\mu$ m). Exposure time was 50 ms with 100 gain, frame transfer mode. Nanocrystals were diluted in toluene, 6 µL deposited on 22 mm<sup>2</sup> coverslip (Corning, NY) and immediately covered by 18 mm<sup>2</sup> coverslip. After toluene evaporated, sample was placed into TIRFM and data collected after 30 min to minimize sample drift. We collected 6000 total frames (5 min) per view. ImageJ was used for background subtraction and recording individual traces. Regions of interest around optically resolved nanocrystals were defined with time series analyzer. PL intermittency frequency and duration were derived for individual dots.

### RESULTS AND DISCUSSION

In a typical CdSe/CdS core/shell growth experiment, enough Cd and S precursors are added to grow a CdS shell of a desired thickness, expressed as the theoretical or "calculated" number of CdS MLs. Assuming complete (100%) precursor conversions, the calculated core/shell particle size (diameter) is then compared with the experimentally "observed" particle size (diameter), commonly measured by TEM. The method of choice for CdSe/CdS core/shell growth uses SILAR conditions with cadmium-oleate (Cd(oleate)<sub>2</sub>) and elemental sulfur (S<sub>8</sub>) precursors and 1-octadecene (ODE) solvent.<sup>45,46,55–57</sup> Some reports use 60–180 min (3 h Cd, 1 h S, 4 h/ML),<sup>46,57</sup> and others use 10–15 min<sup>45,55,56</sup> annealing or "wait" times between injections.



Long times may help ripen undesired CdS homonuclei, dissolving them in favor of heterogeneous epitaxial nucleation atop existing CdSe/CdS core/shells (Scheme 1a-c). However, long wait times result in 40 (1.7 days) and 80 h (3.3 days) to grow 10 and 20 CdS MLs, respectively. These long reaction times increase the odds that impurities (air, moisture) could affect shell growth. Short annealing times are more appealing to synthetic chemists, provided new synthetic conditions are found to increase the speed of ripening.

In our investigation, freshly washed CdSe cores were dissolved in ODE and amine (see below) and subjected to different SILAR<sup>33</sup> CdS shell-growth conditions using short 15 min annealing times and Cd(oleate)<sub>2</sub> and S<sub>8</sub> precursors (each in ODE or ODE-amine; see the Experimental Section and Table 1). Our experiments started with 19  $\mu$ M solution of "small" CdSe cores  $(1.9 \pm 0.2 \text{ nm}, 1\text{S} = 480 - 494 \text{ nm})^{58}$  and high 1.5 M concentration of primary octadecyl amine. ODE solutions of Cd and S precursors did not contain amine (#1 Table 1 and Figure 1). Problems that plague thick-shell core/shell syntheses were immediately clear: Shell-growth (Scheme 1a) was accompanied by many small ca. 2 nm CdS homonuclei (Scheme 1b), and size distributions were large. Critically, core/shells never grew to desired CdS shell thicknesses. Small final particle sizes were observed by TEM. Attempts to grow 13.1 CdS MLs and 23.5 CdS MLs lead instead to 3.7 and 5.3 CdS MLs, respectively (#1 Table 1 and Figure 1). Instead of an ideal one-to-one correlation between desired and observed shell thicknesses, plotting calculated versus TEM-measured shell thicknesses (#CdS MLs) invariably gave a very small slope, m = 0.15 to 0.20.

Adding Primary Amine. Initial failure to achieve desired shell-thicknesses and ubiquitous presence of small CdS homonuclei leads us to think a ripening additive could benefit shellgrowth. Ripening could dissolve CdS homonuclei in favor of epitaxial growth atop existing CdSe/CdS core/shells, leading to effective shell growth (Scheme 1c). Primary amines are known ripening agents.<sup>55,58,59</sup> Octadecyl-NH<sub>2</sub> was present in the starting CdSe core solution, but it was severely diluted during shellgrowth because neither precursor contained amine: Octadecyl-NH<sub>2</sub> concentration decreased by one order of magnitude during shell growth from 1.5 M to ca. 0.15 M, minimizing its ripening effect. We thus repeated the reaction while maintaining a recurrent

*		CdSe core solution	μ		$\operatorname{Cd}\operatorname{sltn.}^{b}$	S sltn.	Cd:S	calculated <sup>c</sup>	experimental <sup>d</sup>
	conc. <sup>b</sup>	1S (size)	amine $(type)^b$	conc.	amine (type)	conc. <sup>b</sup>		#MLs(c/s size)	#MLs(c/s size) <sup>d</sup>
1	$19 \ \mu M$	$480~\mathrm{nm}~(1.9\pm0.2~\mathrm{nm})$	octadecyl-NH <sub>2</sub> (1°) 1.5 M	0.2 M	none	0.2 M	1:1	$13.1(9.6 \text{ nm})^c$	$3.7 \ (4.1 \pm 1.3 \ { m nm})^d$
2	$M\mu$	480 nm $(1.9 \pm 0.2 \text{ nm})$	oley $INH_2$ (1°) 1.5 M	0.2 M	oleylNH $_2$ (1 $^\circ$ ) 1.SM	0.2 M	1:1	$23.5(15.6 \text{ nm})^c$ 11.9(8.9 nm) <sup>c</sup>	$5.3~(5.1\pm2.2~{ m nm})^{d}$ $3.0~(3.8\pm0.7~{ m nm})^{d}$
ŝ	19 µМ	494 nm $(1.9 \pm 0.2 \text{ nm})$	oleyINH $_2$ (1°) 1.5 M	0.2 M	oleyINH $_2$ (1 $^\circ$ ) 1.5M	0.2 M	1.3:1	$23.5(15.6 \text{ nm})^c$ 11.9(8.9 nm) <sup>c</sup>	5.2 $(5.0 \pm 1.1 \text{ mm})^d$ 2.4 $(3.4 \pm 0.6 \text{ mm})^d$
4	$10 \ \mu M$	488 nm $(1.9 \pm 0.2 \text{ nm})$	oleyINH <sub>2</sub> (1°) 1.5 M	0.1 M	oleyl $\mathrm{NH}_2$ $(1^\circ)$ 1.5M	0.1 M	1:1	$23.5(15.6 \text{ nm})^c$ 11.9(8.9 nm) <sup>c</sup>	$3.1 (3.8 \pm 0.7 \text{ nm})^d$ $4.2 (4.4 \pm 0.8 \text{ nm})^d$
								$23.5(15.6 \text{ nm})^c$ $35.1(22.4 \text{ nm})^c$	$7.4~(6.3\pm1.0~{ m nm})^d$ 8.3 $(6.8\pm1.0~{ m nm})^d$
S	$10 \ \mu M$	484 nm (1.9 $\pm$ 0.2 nm)	$(octyl)_2NH (2^\circ) 1.6 M$	0.1 M	$(octyl)_2NH (2^\circ) 1.7M$	0.1 M	1:1	$7.2(6.2 \text{ nm})^c$ $9.6(7.6 \text{ nm})^c$	5.2 $(5.2 \pm 0.6 \text{ nm})^d$ 11.2 $(8.7 \pm 1.0 \text{ nm})^d$
								$11.9(8.9 \text{ nm})^c$	$14.4 \ (10.6 \pm 1.0 \text{ nm})^d$
6	$10 \ \mu M$	$625 \text{ nm} (4.7 \pm 0.6 \text{ nm})$	$(octyl)_2NH (2^\circ) 1.6 M$	0.1 M	$(octyl)_2NH (2^\circ) 1.7M$	0.1 M	1:1	$14.2(10.2 \text{ nm})^c$ $6.0(8.2 \text{ nm})^c$	$17.9~(12.6\pm1.2~{ m nm})^d$ $5.1~(7.7\pm0.8~{ m nm})^d$
								$8.0(9.3 \text{ nm})^c$	8.1 (9.4 $\pm$ 1.1 nm) <sup>d</sup> 11.0 (11.1 $\pm$ 2.2 nm) <sup>d</sup>
								$12.0(11.7 \text{ nm})^c$	$13.4 (12.4 \pm 2.2 \text{ nm})^d$
<sup>a</sup> CdSe col <sup>c</sup> Theoretic	re solution: 4 $r$ :al/calculated $v$	nL of ODE, 3.7 to 3.8 mL o value. <sup>d</sup> Nanocrystallite sizes	of amine. <sup>b</sup> Error estimates: C :: given individually for each r	dSe core con neasurement	centrations: $\pm 2\%$ . Amine, as $\pm$ standard deviations.	cadmium, and s	ulfur precursor	· concentrations: $\leq 1\%$	(maximum uncertainty)

Table 1. Synthesis of Thick-Shelled CdSe/nCdS Nanocrystals

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**Figure 1.** Experimentally observed versus calculated (desired) CdSe/ nCdS particle size (a) and shell thickness (b): From small CdSe (1.9 nm): 19  $\mu$ M, 0.2 M Cd,S (1:1), no added amine (black circles, Table 1#1); 19  $\mu$ M, 0.2 M Cd,S (1:1), 1.5 M 1°(oleyl)amine (violet diamonds, Table 1#2); 19  $\mu$ M, 0.2 M Cd,S (1.3:1), 1.5 M 1°(oleyl)amine (green triangles, Table 1#3); 10  $\mu$ M, 0.1 M Cd and S (1:1), 1.5 M 1°(oleyl)amine (orange squares, Table 1#4);10  $\mu$ M, 0.1 M Cd,S (1:1), 1.6 to 1.7 M 2°(dioctyl)amine (blue circles, Table 1#5). From large CdSe (4.7 nm): 10  $\mu$ M, 0.1 M Cd,S (1:1), 1.6 to 1.7 M 2°(dioctyl)amine (red circles, Table 1#6).

stream of primary amine. We specifically added 1.5 M oleyl-NH<sub>2</sub> to Cd precursor. (See the Experimental Section and Table 1.) Particle size dispersions obtained this way were narrower; however, overall results were unsatisfactory as follows: Attempts to grow 11.9 and 23.5 CdS MLs lead instead to 3.0 and 5.2 CdS MLs, respectively (#2 Table 1 and Figure 1). For this set of conditions, the slope of desired versus observed CdS MLs plot remained 0.15 to 0.20.

Adding Excess Cadmium. Recent studies used 30% excess Cd (1.3:1 Cd to S ratio) to make CdSe/nCdS core/shell nanocrystals with thin-to-medium shell thicknesses  $(n \le 6)$ .<sup>55</sup> Unfortunately, adding 30% excess Cd precursor did not produce very thick CdS shells ( $n \ge 10$ ). Attempts to grow 11.9 and 23.5 CdS MLs lead instead to 2.4 and 3.1 CdS MLs, respectively (#3 Table 1 and Figures 1 and 2a). A plot of observed versus desired CdS MLs had slope = 0.13, lower than the two methods above. Incomplete shell growth must be accompanied by large buildup of unreacted Cd and S precursors, saturating the solution and resulting in CdS homogeneous nucleation. CdS homonuclei may act as seeds for isocrystalline CdS shell growth, resulting in wide size distributions. This explains why when using 30% excess Cd apparent shell thicknesses measured by TEM for  $\geq 10$  MLs are less than the  $\leq 6$  MLs documented in the literature (see above and Table 1 #3).55

**Lowering CdSe-Core and Cd,S-Precursor Concentrations.** We reasoned that decreasing Cd and S precursor concentrations as well as initial CdSe (core) concentration could suppress homogeneous nucleation. Lower CdSe concentration would keep nanocrystals soluble for longer. Large nanocrystals tend to precipitate out of solution (e.g., shell-thicknesses  $n \ge 14$  MLs for CdSe  $(1.9 \text{ nm}), n \ge 10$  MLs for CdSe  $(4.7 \text{ nm}); \ge 10$  nm particle sizes at 19 mM CdSe). We attempted shell growth halving CdSe





**Figure 2.** Selected particle size histograms: From small CdSe (1.9 nm): (a) 19 µM, 0.2 M Cd,S (1.3:1), 1.5 M 1°(oleyl)amine (Table 1#3). (b) 10 µM, 0.1 M Cd,S (1:1), 1.5 M 1°(oleyl)amine (Table 1#4). (c) 10 µM, 0.1 M Cd,S (1:1), 1.6 to 1.7 M 2°(dioctyl)amine (Table 1#5). From large CdSe (4.7 nm): (d) 10 µM, 0.1 M Cd,S (1:1), 1.6 to 1.7 M 2°(dioctyl)amine (Table 1#6) (≥ 50–100 particles counted each case).

(10  $\mu$ M) and Cd and S (0.1 M each) concentrations while supplying a recurrent stream of 1° oleyl-NH<sub>2</sub> (#4 Table 1 and Figures 1 and 2b). This resulted in  $n \ge 6$  CdS MLs: Attempts to grow 11.9, 23.5, and 35.1 CdS MLs resulted in 4.2, 7.4, and 8.3 CdS MLs, respectively (#4 Table 1 and Figures 1 and 2b). A plot of observed versus desired CdS MLs had slope = 0.24, slightly higher than the other three methods above.

**Primary versus Secondary Amines.** While primary amines aid ripening, they could simultaneously coordinate to Cd and lower precursor reactivity;<sup>46</sup> the Crystal Structure Database contains several six-coordinate cadmium—carboxylate complexes with monodentate nitrogen ligands (Scheme 1d).<sup>64–68</sup> To probe this issue, we injected Cd(oleate)<sub>2</sub> to TOPSe/TOP/ODE in 1° oleyl-NH<sub>2</sub> or 2° (octyl)<sub>2</sub>NH<sup>46,69,70</sup> at 300 °C and observed CdSe growth at 280 °C. After 1 min, CdSe nanocrystals showed 1S = 606 nm (2.05 eV) in 1° oleyl-NH<sub>2</sub>, and 1S = 631 nm (1.97 eV) in 2° (octyl)<sub>2</sub>NH (Figure 3). Clearly, CdSe made in 1° oleyl-NH<sub>2</sub> was smaller (ca. 4.7 nm) than in 2° (octyl)<sub>2</sub>NH (ca. 6.1 nm). It took 5 min for CdSe growth-rate to stabilize (to become constant) in 1° oleyl-NH<sub>2</sub> but under 1 min in 2° (octyl)<sub>2</sub>NH (growth may occur via ripening) (Figure 3). This indicates that Cd(oleate)<sub>2</sub> reacts much faster in secondary than primary amines.<sup>46,69,70</sup> Therefore, replacing 1° amine with bulkier 2° amine would suppress Cd(oleate)<sub>2</sub> coordination while maintaining ripening.<sup>58</sup>



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**Figure 3.** Synthesis CdSe nanocrystals in 1° (oleyl-) versus 2° (dioctyl-) amine: Time evolution of absorption and PL spectra (a), 1S peak (b,c), calculated size (d), and  $PL_{max} (\pm^{1}/_{2} fwhm)$  (e).

Growing Thick ( $n \ge 10$ ) CdS Shells on Small CdSe (1.9 nm). We reattempted CdS shell-growth on small CdSe cores (10  $\mu$ M) using 0.1 M Cd and S while supplying recurrent stream of 2° (octyl)<sub>2</sub>NH (introduced in CdSe and Cd solutions) (#5 Table 1 and Figures 1, 2c, and 3). This method is superior to all prior conditions: Preparations aimed at growing 7.2, 9.6, 11.9, and 14.2 CdS MLs resulted in 5.2, 11.2, 14.4, and 17.9 CdS MLs, respectively (#5 Table 1 and Figures 1, 2c, and 3). A plot of observed versus desired CdS MLs had slope = 1.28, much higher than other methods (and higher than unity, m > 1; see below).

**Growing Thick (** $n \ge 10$ **) CdS Shells on Large CdSe (4.7 nm).** Using superior conditions above, we attempted CdS shell growth on large CdSe (4.7 nm) (10 $\mu$ M) using 0.1 M Cd and S while supplying recurrent stream of 2° (dioctyl)amine (introduced in CdSe and Cd solutions) (#6 Table 1 and Figures 1, 2d, and 3).<sup>46,69,70</sup> These conditions were successful: Preparations aimed at growing 6, 8, 10, and 12 CdS MLs resulted in 5.1, 8.1, 11.0, and 13.4 CdS MLs, respectively (#6 Table 1 and Figures 1, 2d, and 3). A plot of observed versus desired number of CdS MLs had slope = 1.12 (also m > 1; see below).

Observed versus Desired Shell Thickness: Significance of Slope >1. We were puzzled after plotting observed versus desired CdS MLs yielded slopes >1. This occurred when growing thick ( $\geq$ 10 MLs) CdS shells on both small and large CdSe cores using optimum conditions. It is physically impossible for CdS shells to grow thicker than initially estimated given a CdSe core



**Figure 4.** Thick-shell CdSe/nCdS nanocrystals: Top (Table 1#5): From small CdSe ( $1.9 \pm 0.2 \text{ nm}$ ) (a), CdSe/5.2CdS ( $5.2 \pm 0.6 \text{ nm}$ ) (b), CdSe/11.2CdS ( $8.7 \pm 1.0 \text{ nm}$ ) (c), CdSe/14.4CdS ( $10.6 \pm 1.0 \text{ nm}$ ) (d), and CdSe/17.9CdS ( $12.6 \pm 1.2 \text{ nm}$ ) (e). Bottom (Table 1#6): From large CdSe ( $4.7 \pm 0.6 \text{ nm}$ ) (f), CdSe/5.1CdS ( $7.7 \pm 0.8 \text{ nm}$ ) (g), CdSe/8.1CdS ( $9.4 \pm 1.1 \text{ nm}$ ) (h), CdSe/11CdS ( $11.1 \pm 2.2 \text{ nm}$ ) (i), and CdSe/13.4CdS ( $12.4 \pm 2.2 \text{ nm}$ ) (j).



Figure 5. Absorption spectra (arbitrarily normalized) (a,c) and PL spectra (normalized by O.D. at  $\lambda$ exc = 510 nm) (b,d) of thick-shell CdSe/nCdS nanocrystals based on small CdSe (1.9 nm) (a,b) and large CdSe (4.7 nm) (c,d).

size assuming complete precursor conversion. We could have overestimated CdSe size or concentration (available extinction coefficient data vary somewhat);<sup>3-5,60,71,72</sup> however, more likely is CdSe could get etched in amine-rich medium before shell growth. CdSe etching was observed for different conditions<sup>73,74</sup> and reagents,<sup>75-80</sup> including amines.<sup>81</sup> Etching before shell growth decreases CdSe core size, rendering precursor amounts larger than needed and resulting in shell thicknesses larger than estimated; this assumes that the CdSe material that is removed during the etching process exists in a yet unidentified inactive, unrecoverable form. Assuming that etching removes a constant number of MLs on small and large CdSe cores, that is, assuming that etching occurs to constant depth on any CdSe surface, this will be more significant for small CdSe (1.9 nm) than for large CdSe (4.7 nm) cores. In agreement with this idea, plotting observed versus desired shell thicknesses resulted in slope not only above unity (>1) but also higher for small (m = 1.28) than for large cores (m = 1.12) (Figure 1a).

**Core-Etching before Shell-Growth.** To probe etching, we monitored "apparent" core size right before shell growth by UV– vis and PL starting with CdSe (1.9 nm) having first absorption peak 1S = 480 nm (2.58 eV) and PL<sub>max</sub> = 493 nm (full width at half-maximum, fwhm = 19 nm) (Figure 6A). Upon washing, CdSe size decreased very slightly to "1.88" nm, calculated from 1S = 478 nm (2.59 eV) (redder PL<sub>max</sub> = 505 nm and fwhm = 27 nm are attributable to wider size distribution) (Figure 6B).



Figure 6. Amine-induced CdSe etching: 1st (1S) absorption (a,b), apparent size (c) and  $PL_{max}(\pm^{1}/_{2}fwhm)$  (d). CdSe cores: freshly made (crude) (A), washed (B), heated to 75 (C), 190 (D), and 200 °C for 10 min (E), and 20 min (F).

Washed cores were introduced into ODE/(octyl)<sub>2</sub>NH and heated to 75 °C. This caused CdSe size to decrease to "1.79" nm, with 1S = 467 nm (2.66 eV) and PL<sub>max</sub> = 484 nm (fwhm = 31 nm) (Figure 6C). Increased heating to 190 °C resulted in smaller CdSe size of "1.62" nm, with 1S = 450 nm (2.76 eV) and PL<sub>max</sub> = 465 nm (fwhm = 41 nm) (Figure 6D). After heating for 10 min at initial shell-growth temperature of 200 °C, CdSe size was "1.70" nm, with 1S = 457 nm (2.71 eV) and PL<sub>max</sub> = 475 nm (fwhm = 41 nm) (Figure 6E). After 20 min, CdSe size was "1.74" nm with 1S = 461 nm (2.69 eV) and PL<sub>max</sub> = 476 nm (fwhm = 33 nm) (Figure 6F).

This demonstrates CdSe core etching occurs prior to CdS shell-growth.<sup>81</sup> Fast etching in hot  $(octyl)_2$ NH removes CdSe surface material. Going from RT to 200 °C causes 0.28 nm deep CdSe surface etching or ~0.5 MLs (cubic-lattice-parameter = 0.605 nm). Assuming that amine etching proceeds to equal depths on small (1.9 nm) and large (4.7 nm) cores, we calculate that etching decreases nanocrystal volumes by 38 and 16.8%, respectively. Amine-induced etching may arise from quick equilibration between free amine, CdSe, and unidentifiable complexes similar to those in Scheme 1d. Equilibration appears fast and temperature-dependent and is more prominent with increasing temperature (Figure 6C,D). At constant temperature, slow ripening occurs as evidenced by steady regrowth of CdSe over time at 200 °C (Figure 6E,F).

Growing Very Thick ( $n \ge 20$ ) CdS Shells on CdSe. Amineinduced CdSe-etching is most dramatic when growing very thick ( $n \ge 20$  MLs) CdS shells. Figure 7 shows TEM of CdSe (1.9 nm)/27CdS and CdSe (4.7 nm)/27CdS obtained by attempting to grow CdSe (1.9 nm)/('18')CdS and CdSe (4.7 nm)/('18')CdS, respectively. The disparity between observed and desired CdS MLs becomes much more prominent as CdS MLs increase (discussion above).

Annealing Time and Injection Rate. Having optimum shellgrowth conditions, we explored annealing and precursor injection rate effects during thick CdSe/nCdS core/shell growth. Annealing could thicken CdS shells from unreacted precursors or cause CdSe/CdS interfacial allowing via Se–S exchange and diffusion. We explored annealing using large CdSe (4.7 nm)/ 18CdS nanocrystals, picked for easier characterization. Upon



**Figure 7.** Growth of very thick  $(n \ge 20)$  CdSe/nCdS nanocrystals: TEM of (a) CdSe (1.9 nm)/27CdS (17.7  $\pm$  1.3 nm) and (b) CdSe (4.7 nm)/27CdS (20.3  $\pm$  1.4 nm). (c) Corresponding size histograms.

annealing at 245 °C for 180 min, TEM showed multiple small ca. 2 nm CdS homonuclei, severely decreasing the avergae particle size and widening the size distribution from  $13.6 \pm 3.0$  to  $7.4 \pm 5.6$  nm. Without considering CdS homonuclei, size distribution remained  $13.9 \pm 3.2$  nm, and thus annealing did not increase core/shell particle size. Similar effects may occur when using longer wait times (1-3 h) between SILAR injections,<sup>46,57</sup> strengthening the case for short wait times (15 min).<sup>45,55,56</sup> Seldom mentioned in SILAR literature are injection rate effects. We attempted growing CdSe/('12')CdS core/shells using precursor injection rates of 0.2 and 0.4 mL/min and obtained CdSe/ 9.9CdS( $10.2 \pm 1.4 \text{ nm}$ ) and CdSe/5.5CdS ( $7.7 \pm 0.9 \text{ nm}$ ; plus many CdS homonuclei), respectively. Therefore, faster injection rates fail in yielding thick shells. (See the Supporting Information.)

Structure and Composition Analysis. Small  $(1.9 \pm 0.2 \text{ nm})$ CdSe used here has cubic, zinc blende structure evidenced by energy difference between second (1P) and first (1S) excitonic (absorption) peaks (1P–1S = 303 ± 14 meV, 1S = 2.56 ± 0.03 eV).<sup>56,82–84</sup> Large (4.7 ± 0.6 nm) CdSe has hexagonal, wurtzite structure evidenced by energy difference between second (1P) and first (1S) excitonic (absorption) peaks (1P–1S = 32.5 ± 0.4 meV, 1S = 2.02 ± 0.01 eV).<sup>56,82</sup> The presence of hexagonal, wurtzite phase in large CdSe cores is evidenced by hexagonal packing seen by TEM (Figure 4f) and 002 peak in XRD (Figure 8a). This agrees with reports on large CdSe made in 1° amines. (See the Experimental Section.)<sup>59</sup> After shell growth, TEM shows cubic and tetrahedral morphologies, suggesting that core/shells derived from small CdSe (1.9 nm) remain mostly cubic, whereas those from large CdSe (4.7 nm) structurally transform from hexagonal to cubic. Ligand-induced structural transformations are known,<sup>87</sup> including cases with 1° amines.<sup>56</sup>



**Figure 8.** (a) CdSe and CdSe/nCdS ( $n \ge 10$ ) XRD (bulk hexagonal-W and cubic-ZB patterns shown for comparison). Comparison of calculated and experimental (EDX) % weight (b) and % atom (c) as a function of shell thickness (*n*) for CdSe (4.7)/nCdS.

However, XRD shows that significant hexagonal domains are still present, as evidenced by 002(hexagonal)-to-100 and 101(cubic) peak ratios (Figure 8a). Unlike CdSe, which prefers hexagonal structure, CdS prefers cubic structure. CdSe/nCdS core/shells contain much more S than Se: At n > 6 MLs, <10 wt % and <15 at % is Se (Figure 8b,c). Energy-dispersive X-ray spectros-copy (EDS) on core/shells with different thickness shows strong correlation between theoretical and experimental compositions (Figure 8b,c).

**Optical Characterization.** Ensemble. CdSe/nCdS 1S peak and PL<sub>max</sub> red shift with shell thickness (*n*) (Figure 5b). This red shift is more pronounced for small CdSe (1.9 nm) than for large CdSe (4.7 nm) (~100 versus ~15 nm for 15CdS MLs, respectively).<sup>55</sup> PL peaks at 30–40% QY for low-to-moderate shellthicknesses of ca. 4 to 5 MLs, then decreases with shell thickness. (Some batches reached ~100% QYs, but typical peaks were ~30–40%; there is no consensus as to whether this is an inherent property or signals thicker-shell surface defects.)<sup>6,47–49</sup>

Single Particle. To learn more about thick-shell CdSe/CdS structure—property relationships, we recorded single-particle PL exciton lifetime and fluorescence intermittency (blinking) via fluorescence microscopy. CdSe (1.9 nm)/15CdS and CdSe (4.7 nm)/15CdS PL exciton-lifetimes were 55 and 10 ns, respectively (Table 2 and Supporting Information). Significantly shorter PL lifetimes for large CdSe/CdS indicate stronger electron—hole overlap and agree well with recent calculations.<sup>6,52</sup> In CdSe (4.7 nm)/15CdS, electron and hole wave functions are both strongly confined to CdSe core (type-I configuration), resulting in strong electron—hole overlap and short PL exciton lifetime.<sup>52</sup> In contrast, in CdSe (1.9 nm)/CdS, electron wave function

Table 2.	Single-Particle (	Optical	Behavior	of Thic	k-Shelled
CdSe/nC	CdS Nanocrystals	5			

		>99%	>80%
	exciton lifetime	non-blinking	non-blinking
sample	$(\tau/ns)$	fraction	fraction
CdSe (1.9 nm)/15CdS	55	2	63
CdSe (4.7 nm)/15CdS	10	54	93

delocalizes out of CdSe core into CdS shell (quasi-type-II configuration), resulting in poor electron—hole overlap and longer PL exciton lifetime.<sup>52</sup> Under the microscope with continuous 488 nm laser excitation, >99 and >80% nonblinking (constantly on) nanocrystal fractions for CdSe (1.9 nm)/15CdS are 2 and 63%, respectively; >99 and >80% nonblinking fractions for CdSe (4.7 nm)/15CdS are 54 and 93%, respectively. (See the Supporting Information.) This suggests that type-I CdSe/nCdS nanocrystals based on larger CdSe (4.7 nm) cores show moresuppressed (less) blinking than quasi-type-II CdSe/nCdS nanocrystals based on smaller CdSe (1.9 nm) cores. Additional theoretical and experimental spectroscopic studies will be needed to explain this behavior.

### CONCLUSIONS

We carried out a thorough investigation of thick-shelled  $CdSe/nCdS(n \ge 10)$  nanocrystal synthesis using short and accessible 15 min wait times between SILAR injections. We explored added amine, amine type (1° vs 2°), CdSe core, and precursor concentration, Cd:S ratio, annealing time, and injection-rate effects on the synthesis of these materials. Successful thick-shell growth presents unique challenges compared with core/shells with thin shells. Main obstacles include suppressing CdS-homogeneous nucleation, which occurs at high precursor concentration and in the absence of ripening agent. Additionally, coordination of primary amines to Cd precursor decreases its reactivity and leads to incomplete shell growth. On the basis of structural and optical characterization, we found that added secondary amine and low-core and precursor concentrations introduced at slow injection rates result in core/shells with desired shell thickness and particle size. Amine-induced CdSesurface etching decreases the core-size prior to shell growth and significantly affects growth of very thick shells ( $n \ge 20$  MLs). The presented method works well for small CdSe (1.9 nm) and large CdSe (4.7 nm) cores. Core/shells derived from small CdSe (1.9 nm) cores have longer PL lifetimes and more pronounced blinking at single-particle level compared with those derived from large CdSe (4.7 nm) cores. We expect that these results will lead to larger throughput of these materials, increasing their availability for fundamental studies and applications.

## ASSOCIATED CONTENT

**Supporting Information.** Synthesis, annealing, injection rate, blinking, and lifetime data. This material is available free of charge via the Internet at http://pubs.acs.org.

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