Single-Sized CdSe Nanocrystals with Bandgap Photoemission via Non-Injection One-Pot Approach

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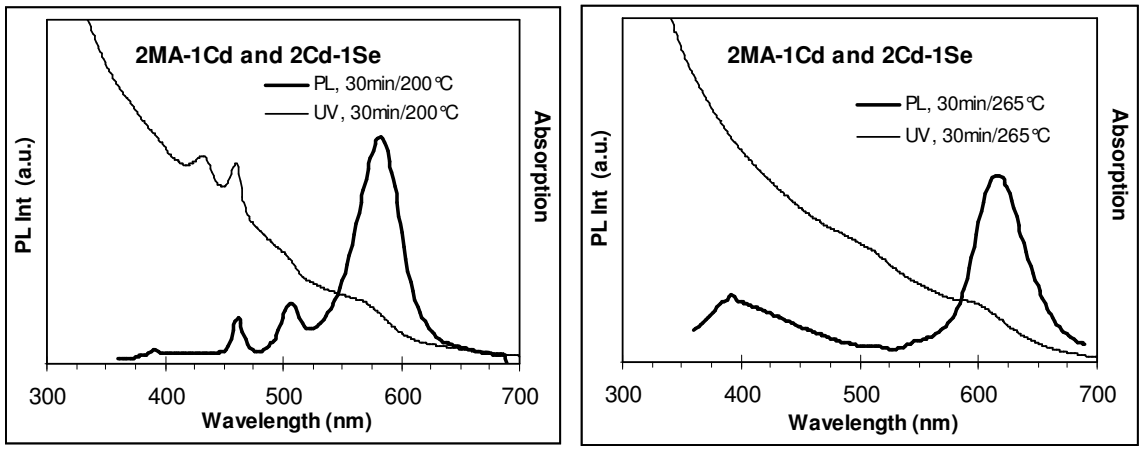


Figure S1. The Absorption (thin line) and photoemission (thick line, excited at 350 nm) spectra of the CdSe nanocrystals from Batch 1a, sampled at 30-minute growth at 200 ^{o}C (left) and at 30-minute growth at 265 ^{o}C (right). The synthesis started with the 2MA-to-1Cd and 2Cd-to-1Se feed molar ratios.

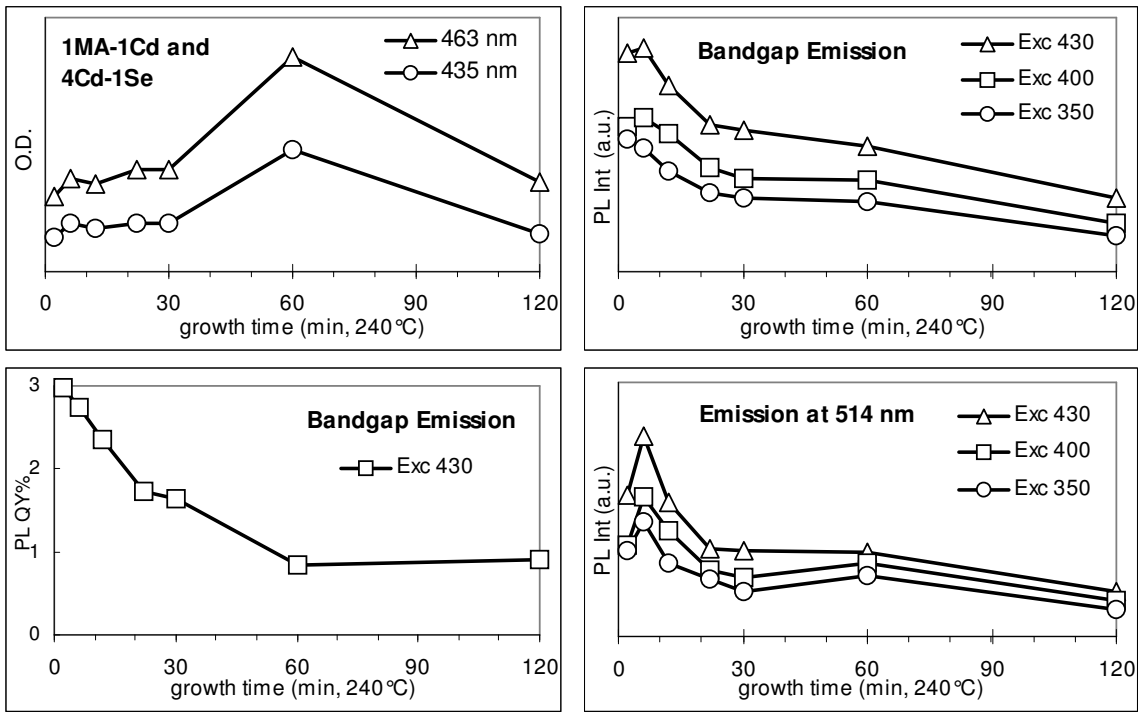


Figure S2. The summary of the optical properties of CdSe MSQD Family 463 at 240 ^{o}C with different growth periods; Batch 2b started with the 1MA-to-1Cd and 4Cd-to-1Se feed molar ratios and nonstop heating from 120 ^{o}C to 240 ^{o}C at a rate of 20 ^{o}C/min. The temporal evolution of the absorption spectra was shown in Figure 2b. The optical density (O.D.) of the absorption doublet, peaking at 463 and 435 nm, corresponding two electronic transitions of 1S(e)-1$S_{3/2}$(h) and 1S(e)-2$S_{3/2}$(h). Figure top-left shows that the two transitions developed in a parallel fashion during the reaction; the optical density of the two peaks increased until 60 min at 240 ^{o}C and then dropped. Figure top-right shows the bandgap PL emission intensity enhanced with the excitation wavelength increased from 350 nm to 400 nm and 430 nm. Figure bottom-left shows the bandgap PL QY with the excitation wavelength of 430 nm. Figure bottom-right shows the intensity of the emission at 514 nm with the excitation wavelength of 350 nm, 400 nm, and 430 nm. The intensity change of the emission at bandgap (465 nm) and at 514 nm follows a similar trend along the reaction at 240 ^{o}C

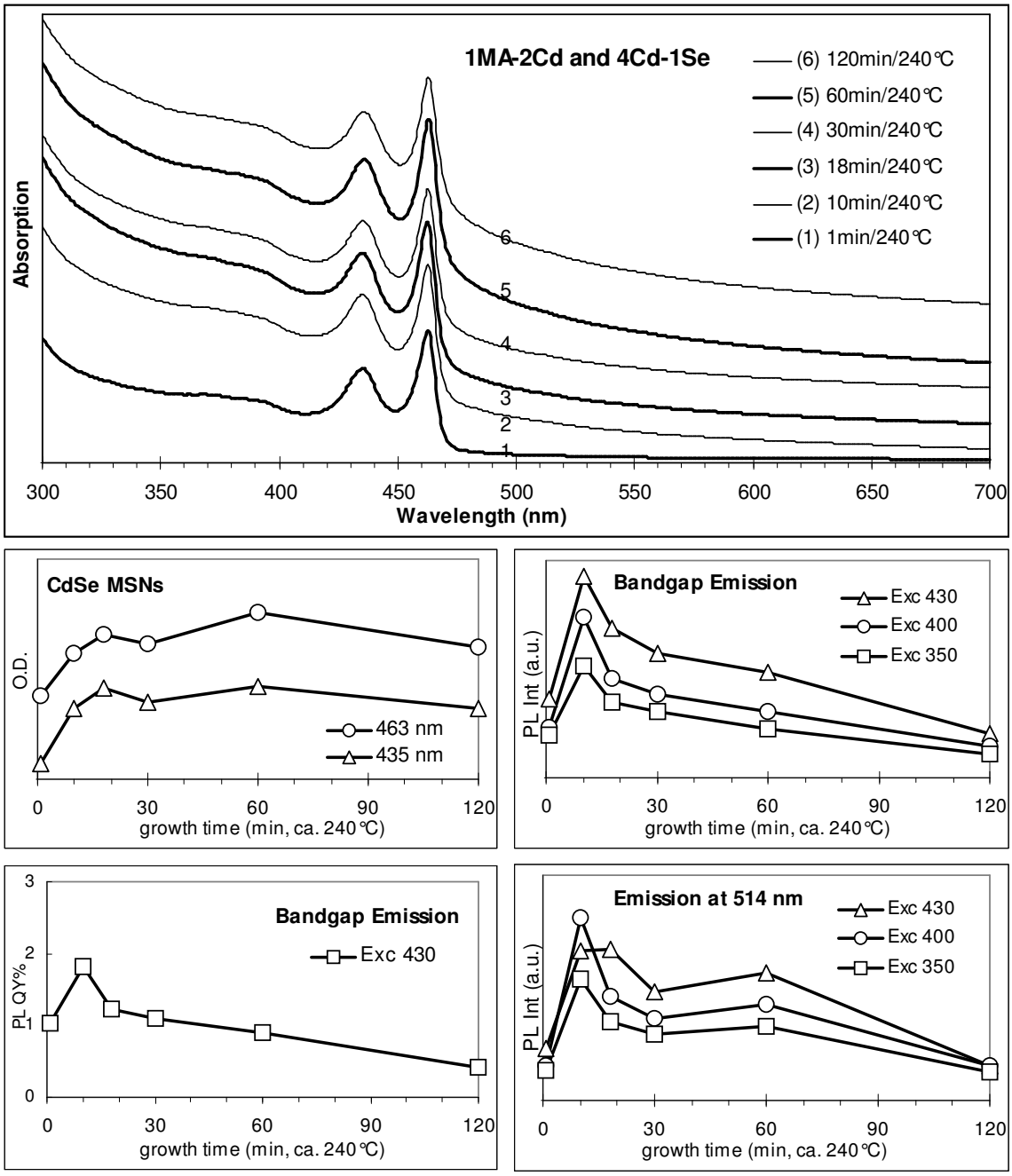
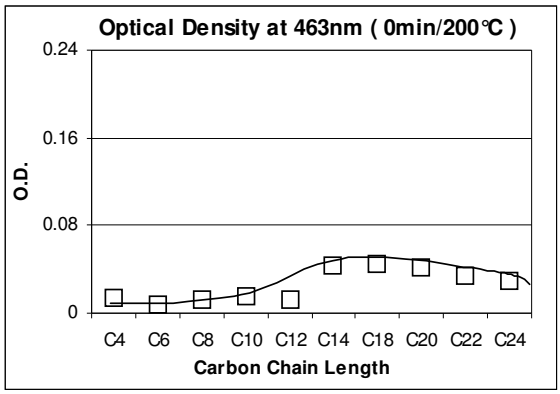
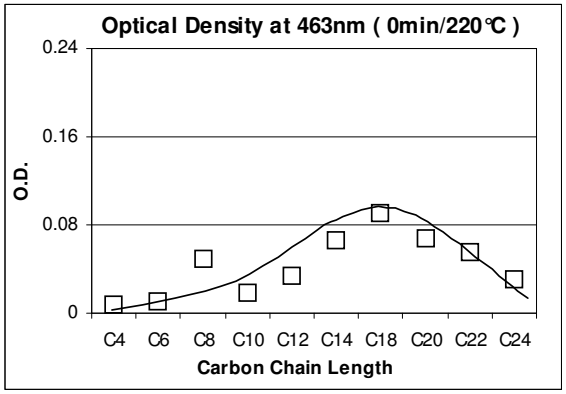
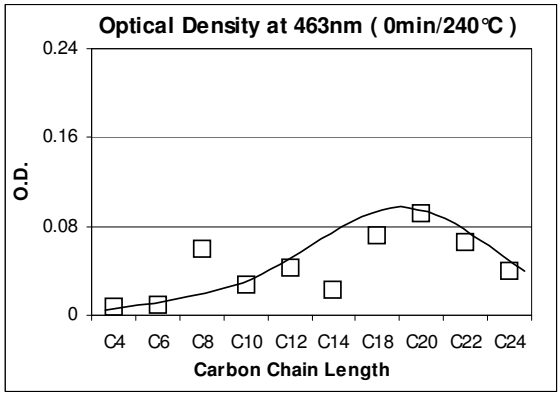


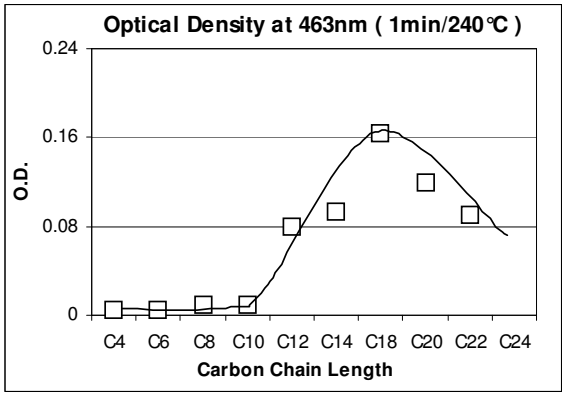
Figure S3. Temporal evolution of the UV-vis absorption spectra (offset, top) of the growing CdSe nanocrystals from the synthetic batch with the feed molar ratios of 1MA-to-2Cd and 4Cd-to-1Se and the nonstop temperature increase pattern from 120 ^{o}C to 240 ^{o}C at a rate of 20 ^{o}C/min. The UV-vis absorption spectra are presented with 20 μL crude product in 3 mL toluene (the y axis maximum of 0.9). The growth similarity of the nanocrystals from Batch 2b

(with the feed molar ratios of 1MA-to-1Cd and 4Cd-to-1Se and the nonstop temperature increase pattern from 120 ^{o}C to 240 ^{o}C at a rate of 20 ^{o}C/min) and Batch S3 is worthy of notice. Figure middle-left shows that the two absorption peaks at 463 and 435 nm, representing the two electronic transitions of 1S(e)-1$S_{3/2}$(h) and 1S(e)-2$S_{3/2}$(h). Figure middle-right shows the bandgap PL emission intensity enhanced with the excitation wavelength increased from 350 nm to 400 nm and 430 nm. Figure bottom-left shows the bandgap PL QY with the excitation wavelength of 430 nm; it is noteworthy that CdSe MSQD Family 463 from Batch 2b exhibited relatively high PL QY, as compared to those from Batch S3. Figure bottom-right shows the intensity of the emission at 514 nm with the excitation wavelength of 350 nm, 400 nm, and 430 nm. The intensity change of the emission at bandgap (465 nm) and at 514 nm follows a similar trend along the reaction at 240 ^{o}C


Optical Density at 463nm (0min/200℃)
0.24
0.16
0.08
0
O.D.
C4 C6 C8 C10 C12 C14 C18 C20 C22 C24
Carbon Chain Length


Optical Density at 463nm (0min/220℃)
0.24
0.16
0.08
0
O.D.
C4 C6 C8 C10 C12 C14 C18 C20 C22 C24
Carbon Chain Length


Optical Density at 463nm (0min/240℃)
0.24
0.16
0.08
0
O.D.
C4 C6 C8 C10 C12 C14 C18 C20 C22 C24
Carbon Chain Length


Optical Density at 463nm (1min/240℃)
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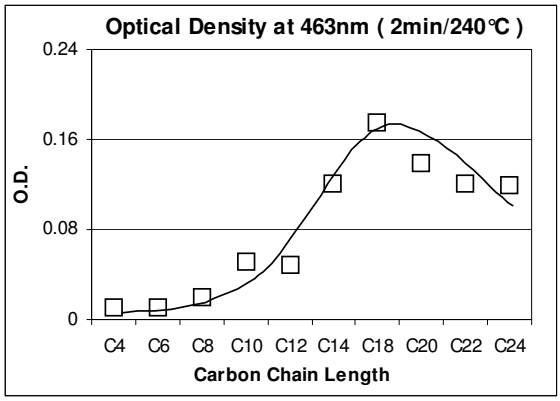
0.16
0.08
0
O.D.
C4 C6 C8 C10 C12 C14 C18 C20 C22 C24
Carbon Chain Length


Optical Density at 463nm (2min/240℃)
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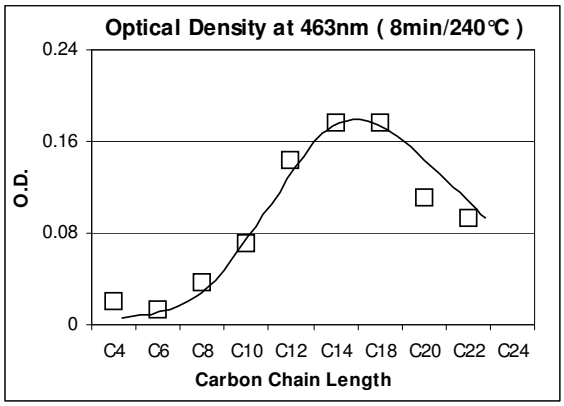
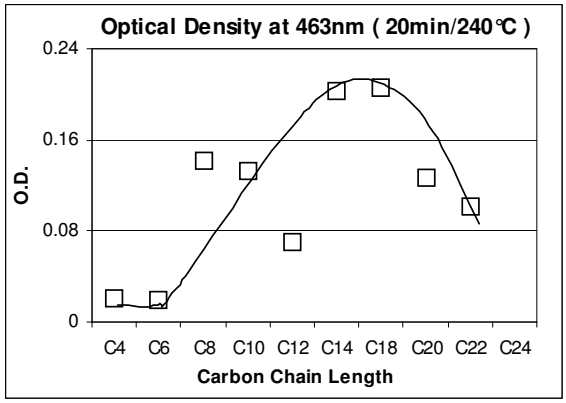
0.16
0.08
0
O.D.
C4 C6 C8 C10 C12 C14 C18 C20 C22 C24
Carbon Chain Length


Optical Density at 463nm (8min/240℃)
0.24
0.16
0.08
0
O.D.
C4 C6 C8 C10 C12 C14 C18 C20 C22 C24
Carbon Chain Length


Optical Density at 463nm (20min/240℃)
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0.16
0.08
0
O.D.
C4 C6 C8 C10 C12 C14 C18 C20 C22 C24
Carbon Chain Length

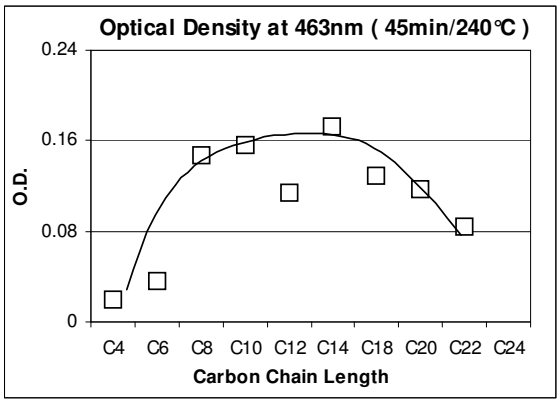
Optical Density at 463nm (45min/240℃)
0.24
0.16
0.08
0
O.D.
C4 C6 C8 C10 C12 C14 C18 C20 C22 C24
Carbon Chain Length

Figure S4. The summary of the optical density at 463 nm of the nanocrystals from the ten batches (shown in Figure 4) and sampled at different growth temperature and periods. It is clear that the overall O.D. of Family 463 increases with reaction temperature and prolonged reaction time. The 90 min/240^{o}C nanocrystal data are similar to those of 45min/240^{o}C nanocrystals, and thus are shown here. The medium-length acids, such as C12-C10, always give high O.D.; for example, for the nanocrystals sampled at 8-20min/240^{o}C, C14 and C18 acids gave the highest O.D.

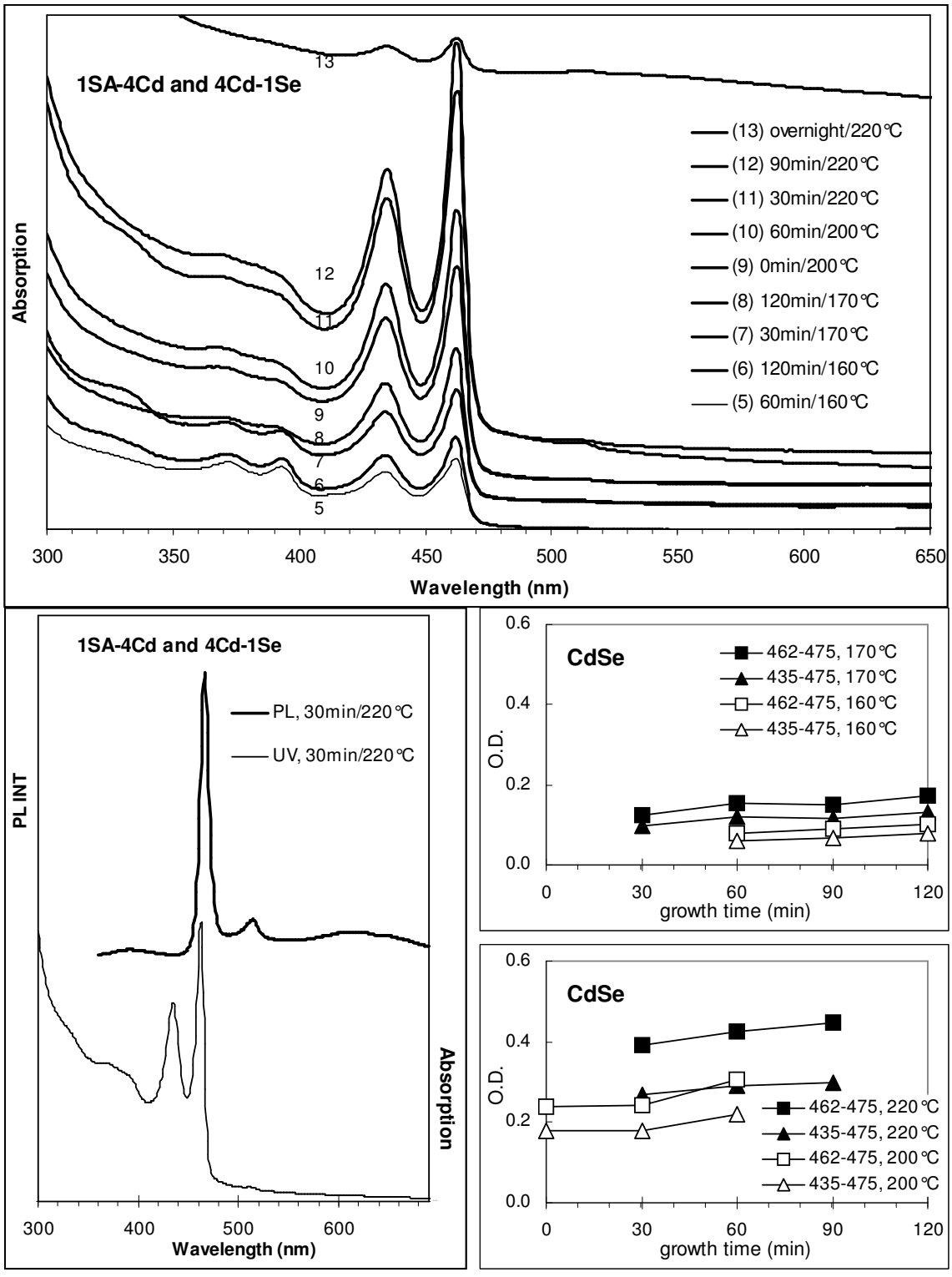

Figure S5. (Top) Temporal evolution of the UV-vis absorption spectra (offset) of the growing CdSe nanocrystals from Batch 5 with the 1SA-to-4Cd and 4Cd-to-1Se feed molar ratios.

The nanocrystal ensembles (5 to 13) sampled with the different growth periods and temperature were indicated (from 60min/140 ^{o}C (Sample 5) to 90min/220 ^{o}C (Sample 12) and overnight/ 220 ^{o}C (Sample 13). The UV-vis absorption spectra are presented with 30 μL crude product in 3 mL toluene (top, the y axis maximum of 0.6). The optical properties of the first five samples are presented in Figure 5. It is clear that the yield of CdSe MSQD Family 463 kept increasing until 90min/220 ^{o}C under our experimental setup and monitoring process; there was a great dissolution/decomposition of Family 463 with overnight heating at 220 ^{o}C. Also, Figure S5 bottom-left shows the absorption (thin line) and photoemission (thick line, excited at 350 nm) spectra of the CdSe MSQDs, Family 463 from Batch 5 with 30-minute growth at 220 ^{o}C. Figure S5 bottom-right summarizes the change of optical density at 462 nm and 435 nm of the nanocrystals with different growth periods (x axis) at the reaction temperature indicated, namely 160 ^{o}C, 170 ^{o}C, 200 ^{o}C, 220 ^{o}C. 475 nm was considered as the bandedge. Again, the absorption doublet (peaking at 435 nm and 462 nm) developed with a synchronized manner; 220 ^{o}C is a good reaction temperature for Family 463.

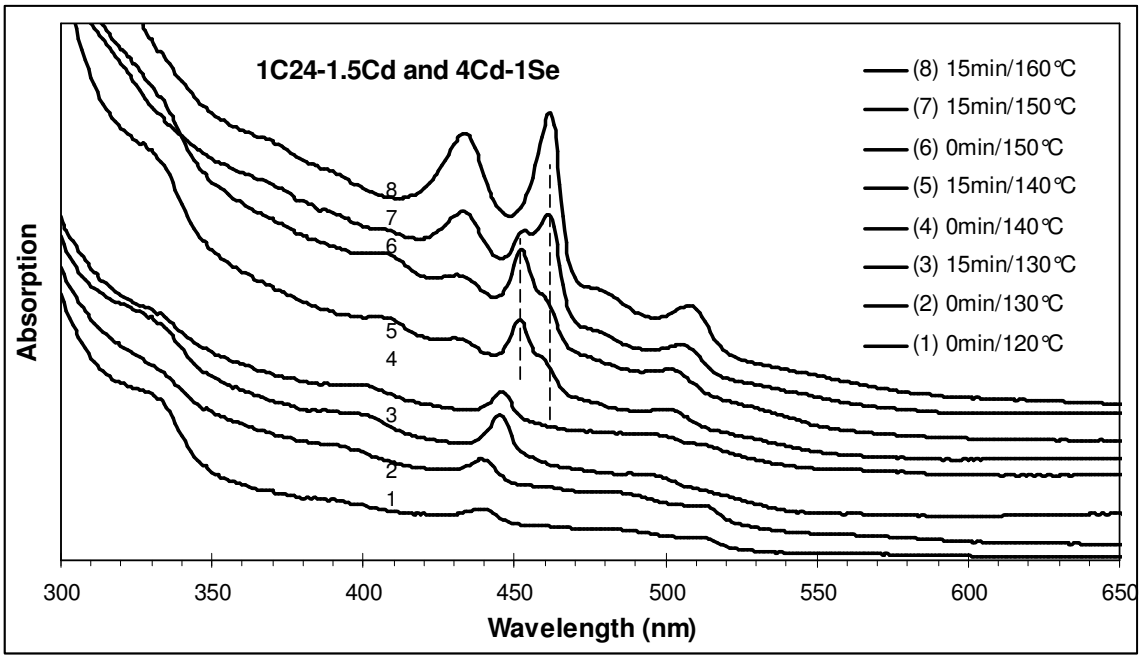

Figure S6. Temporal evolution of the UV-vis absorption spectra (offset) of the growing CdSe nanocrystals from a synthetic batch with the 1C24-to-4Cd and 4Cd-to-1Se feed molar ratios. The UV-vis absorption spectra are presented with 40 μL crude product in 3 mL toluene (the y axis maximum of 0.18). The possible "isomer competing" is worthy of notice; another example is shown in Figure 5.

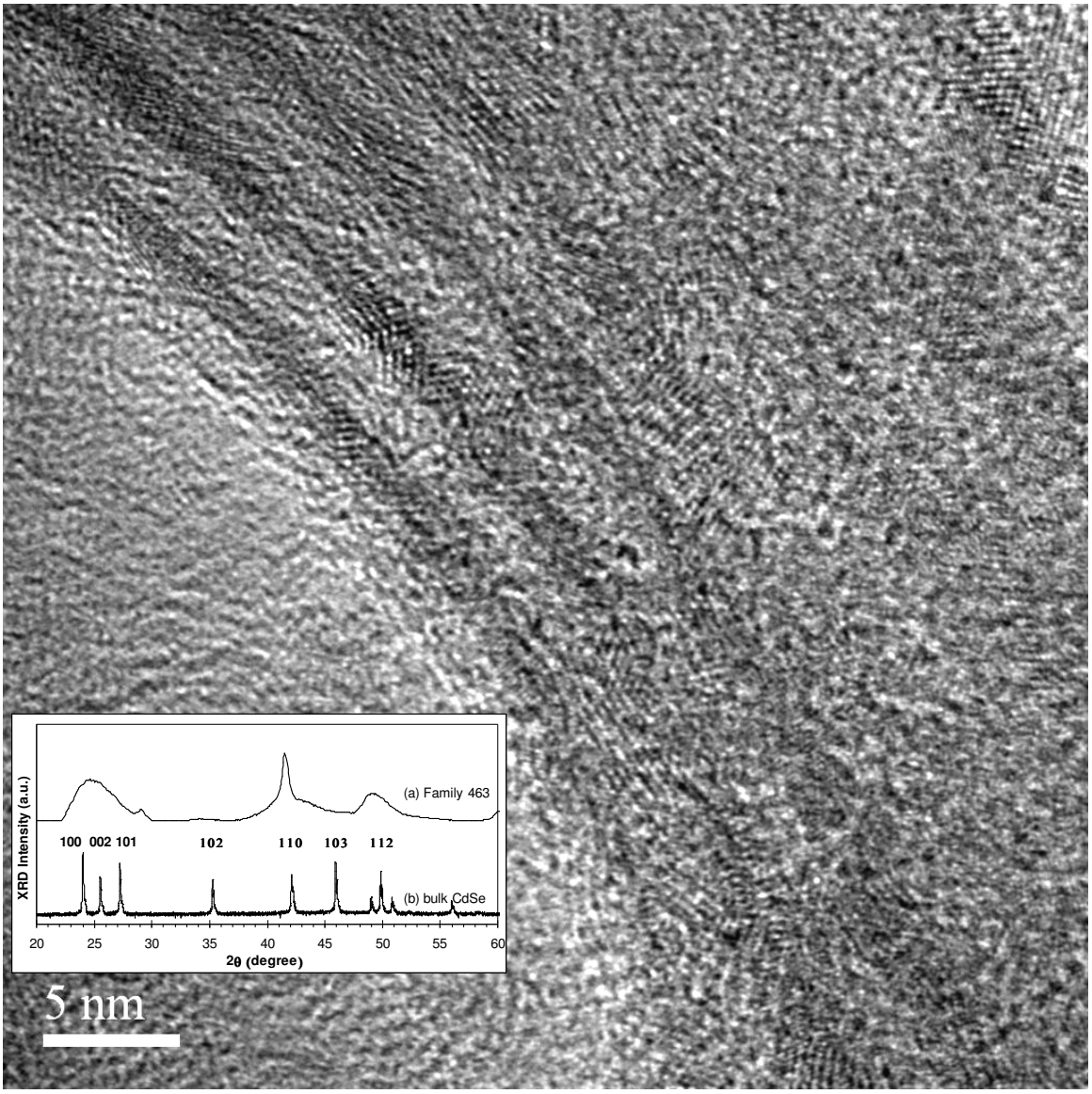

Figure S7. One typical TEM image of our purified Family 463; the TEM grid was prepared from air-dying purified nanocrystal dispersion in toluene. The scale bar is 5 nm. The presence of wire-like aggregates with the width of 2 - 4 nm is interesting. Obviously, TEM is challenged in the size characterization of single-sized nanocrystals, such as CdSe Family 463, due to the ready aggregation/self-assembly during the TEM sample preparation. Another example of the wire-like aggregates is shown in Figure 7. The inset presents two XRD patterns from Family

463 and the bulk CdSe with peaks indexed. The Family 463 was from a batch with the 1MA-to-4Cd and 4Cd-to-1Se feed molar ratios and at the growth of 60min/220^{o}C.

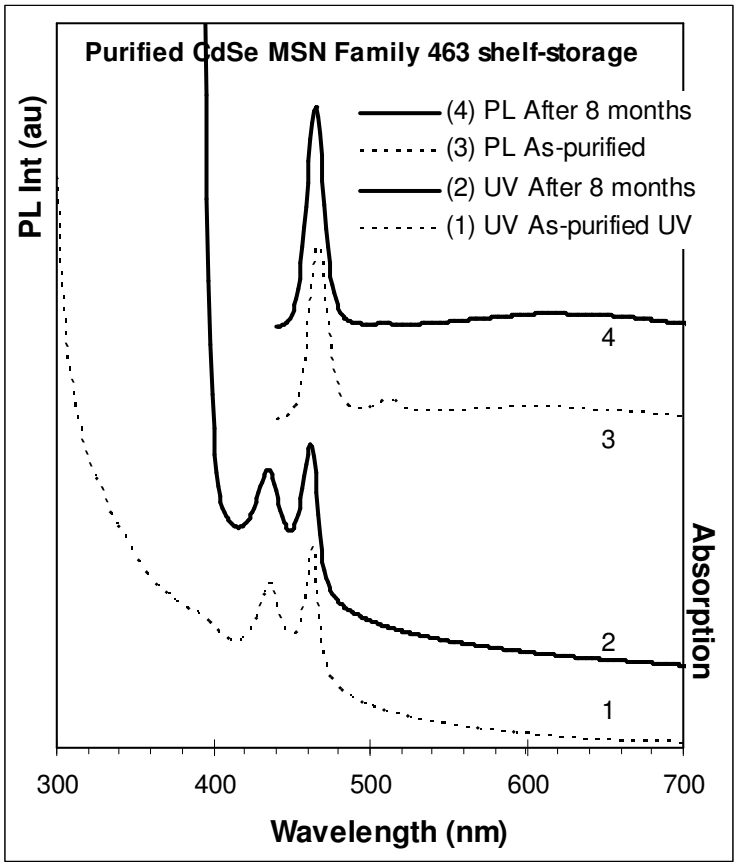

Figure S8. The absorption (Curve 1) and photoemission (Curve 3, excited at 430 nm) spectra of the as-synthesized CdSe MSQDs, Family 463 from a synthetic batch with the 1MA-to-1Cd and 4Cd-to-1Se feed molar ratios and 30-minute growth at 210 ^{o}C. Purification was performed, and the purified CdSe MSQDs were stored for 8 months at room temperature in the dark and then dispersed in toluene for the optical measurement, namely absorption (Curve 2) and emission (Curve 4 with excitation at 430 nm).