Supporting Information

Non-Injection One-Pot Synthesis of Photoluminescent Colloidal Homogeneously-Alloyed CdSeS Quantum Dots

Jianying Ouyang,[1] Maxime Vincent,[1] David Kingston,[2] Pierre Descours,[1] Thibault Boivineau,[1] Md. Badruz Zaman,[1] Xiaohua Wu,[3] and Kui Yu[1]*

[1]Steacie Institute for Molecular Sciences,
National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

[2]Institute for Chemical Process and Environmental Technology,
National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

[3]Institute for Microstructural Sciences,
National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

*to whom correspondence should be addressed.

Table S1. Systematic study of our non-injection one-pot approach to colloidal photoluminescent (PL) CdSeS QDs, with the actual amount of the chemicals used for our regular-scale syntheses of the batches presented in the manuscript Figures 1 and 2, with a fixed 16S-to-1MBTS feed molar ratio, except for Batch 6 with 9.3S-to-1MBTS. For the synthesis of CdSe, * represents that cadmium myristate was made ex-situ by a reaction of CdO and myristic acid in ODE and was purified by recrystallization with toluene. The temporal evolution of the optical properties of the growing nanocrystals from Batch 2, 3, 4, 5, and 6 are also shown in Figure S1-a to S1-e, respectively.

Batch	Feed molar ratio	Cd(OAc)2•2H2O (mg)	Myristic Acid (mg)	Se (mg)	S (mg)	MBTS (mg)	ODE (g)
1	1Cd-1S	14.34	23.61	0	1.70	1.22	5
2:Fig S1-a	2Cd-0.6Se-1.4S	26.84	45.85	2.38	2.46	1.49	5
3:Fig S1-b	3.5Cd-0.6Se-1.4S	46.64	91.83	2.37	2.26	1.46	5
4:Fig S1-c	2Cd-1Se-1S	26.83	45.84	3.96	1.61	1.05	5
5:Fig S1-d	3.5Cd-1Se-1S	46.31	91.40	4.04	1.61	1.04	5
6:Fig S1-e	3.5Cd-1.4Se-0.6S	46.40	90.80	5.50	0.96	1.07	5
7	2Cd-1Se	57.83*	*	4.14	0	0	5

Table S2. The summary of the QY% and PL FWHM (nm) of the 30min/240°C CdSeS QDs from Batch 2-6 as shown in Figures 1 and 2 and Table S1, together with the 60min/240°C CdSeS QDs. Batch Fig S3 with ***** had the feed molar ratio of 9.2acid-to-1Cd with the growth at 300 °C, and temporal evolution of the optical properties of the growing nanocrystals from this batch is shown in Figure S3.

Batch	Feed molar ratio	30min/240 °C QDs		60min/240 °C QDs	
		QY%	, FWHM (nm)	QY%	, FWHM (nm)
2:Fig S1-a	2Cd-0.6Se-1.4S	7.5,	36.5	4.2,	34.1
3:Fig S1-b	3.5Cd-0.6Se-1.4S	7.8,	42.4	6.5,	41.0
4:Fig S1-c	2Cd-1Se-1S	5.7,	33.6	4.8,	34.9
5:Fig S1-d	3.5Cd-1Se-1S	6.5,	41.1	7.2,	44.2
6:Fig S1-e	3.5Cd-1.4Se-0.6S	4.0,	43.9	4.3,	44.7
Fig S3	2Cd-1Se-1S*	13.2,	38.6	11.6,	39.4

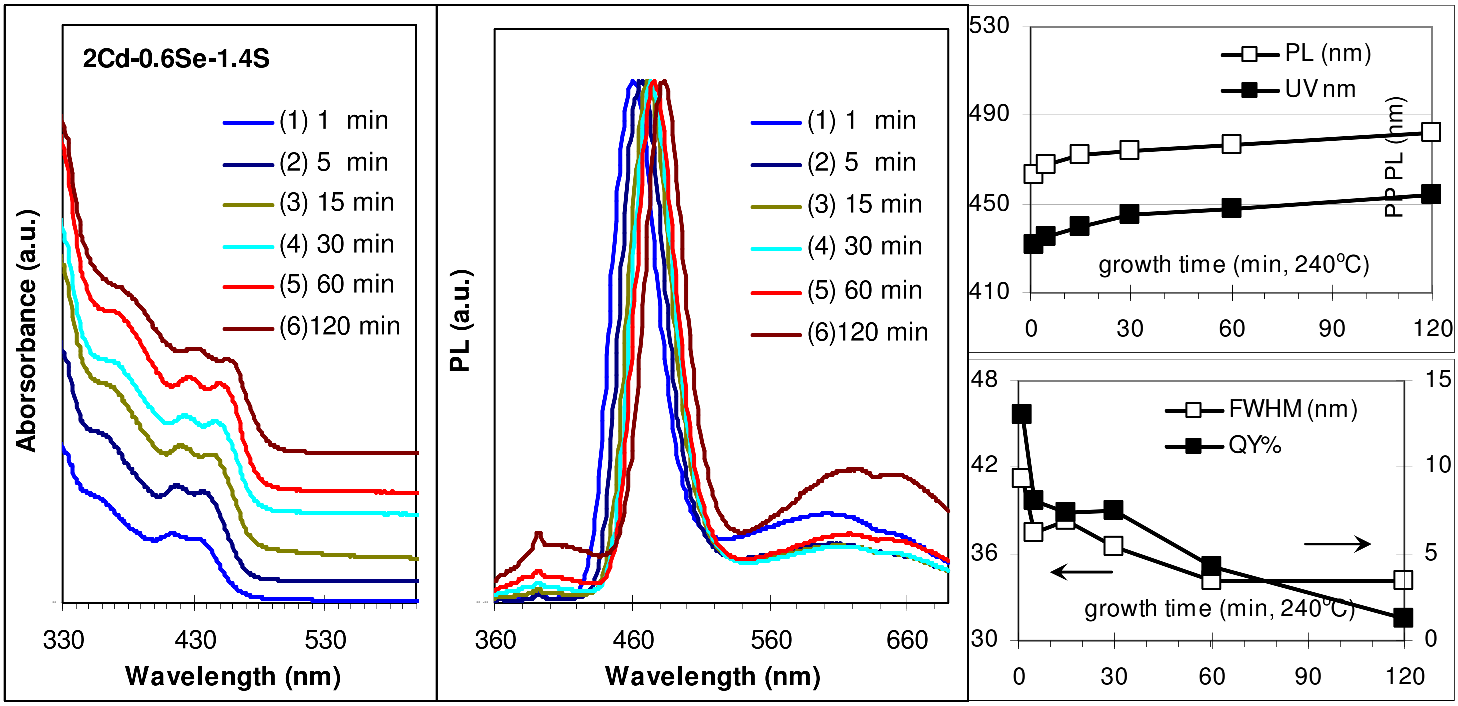

Figure S1-a: Temporal evolution of the UV-Vis absorption spectra (left, offset) and emission spectra (middle, normalized, the excitation wavelength 350 nm.) of the growing CdSeS nanocrystals from the synthetic batch with the feed molar ratio of 2Cd-to-0.6Se-to-1.4S and 16S-to-1MBTS, the batch of which is discussed in the manuscript Figures 1 and 2. The nanocrystals with the different growth periods (in minutes as indicated, at 240 °C) are represented by different colours. At the early growth stage (not shown), no obvious absorption was detected until 200 °C, suggesting that during the temperature increasing from 120 to 240 °C at 10 min/°C, the nanocrystal formation was trivial below 200 °C; a distinctive 1st excitonic absorption peak started to appear at 220 °C, indicating that relatively descent nanocrystals started to form at this temperature; this peak quickly red shifted with the temperature increased to 240 °C. Similar early growth trends were also found in other synthetic batches with the various feed molar ratios. The summary of the temporal evolution of the bandgap peak positions (PP, nm) of the absorption (■) and emission (□) is shown in right-top part, while the right-bottom part for the temporal evolution of the photoluminescent quantum yield (PL QY) (■, in toluene with 400 nm excitation, right y) and PL FWHM (□, left y). The growing QDs are narrow in size distribution, as suggested by their rich absorption fine substructures and relatively small PL FWHM.

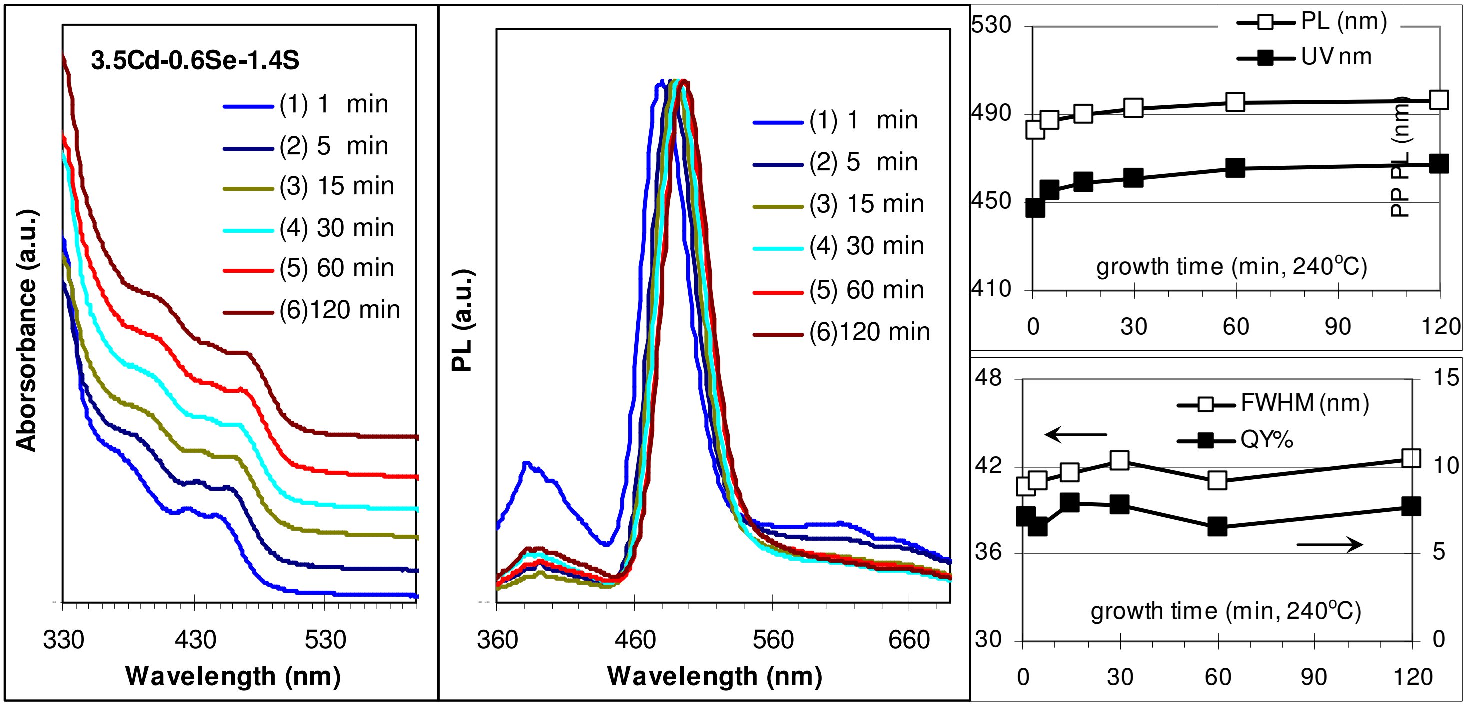

Figure S1-b: Temporal evolution of the UV-Vis absorption spectra (left, offset) and emission spectra (middle, normalized) of the growing CdSeS nanocrystals from the synthetic batch with the feed molar ratio of 3.5Cd-to-0.6Se-to-1.4S and 16S-to-1MBTS, the batch of which is discussed in the manuscript Figures 1 and 2. The nanocrystals with the different growth periods (in minutes as indicated, at 240 ^{o}C) are represented by different colours. The excitation wavelength was 350 nm. The summary of the temporal evolution of the bandgap peak positions (PP, nm) of the absorption (■) and emission (□) is shown in right-top part, while the right-bottom part for the temporal evolution of the photoluminescent quantum yield (PL QY) (■, in toluene with 400 nm excitation, right y) and PL FWHM (□, left y).

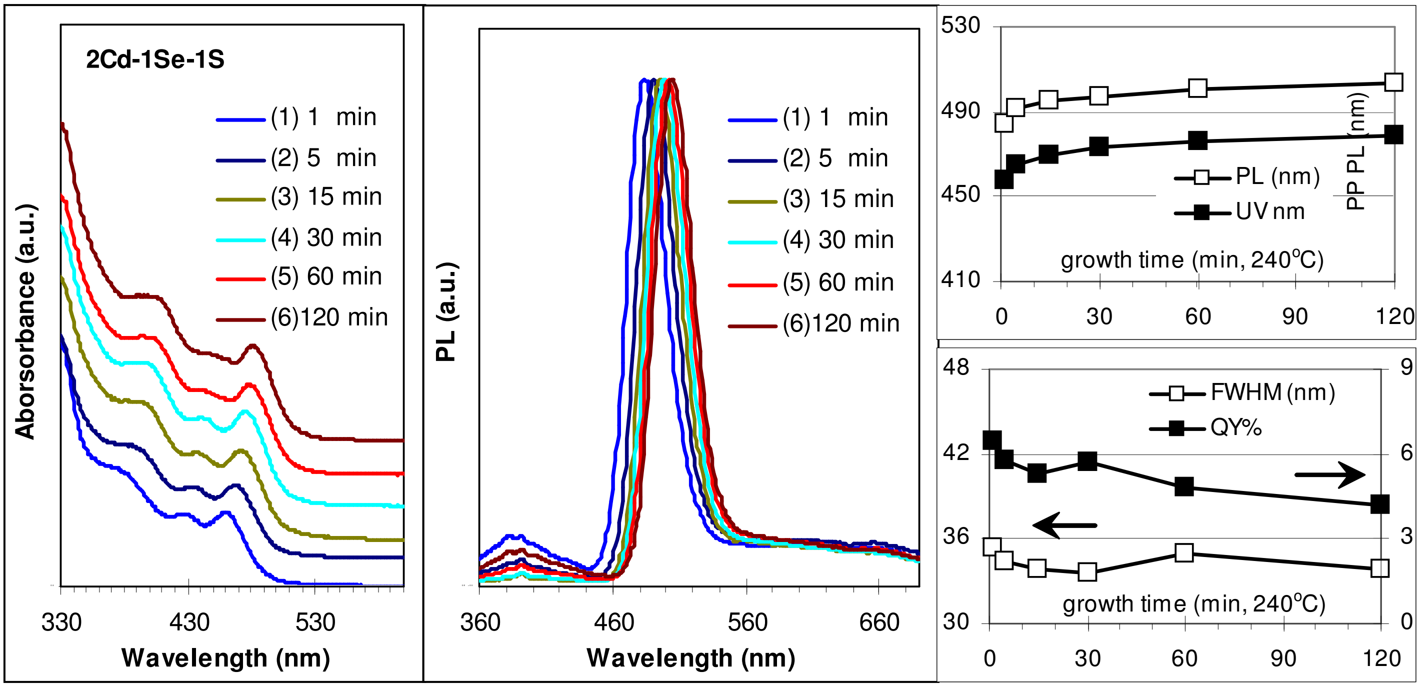

Figure S1-c: Temporal evolution of the UV-Vis absorption spectra (left, offset) and emission spectra (middle, normalized) of the growing CdSeS nanocrystals from the synthetic batch with the feed molar ratio of 2Cd-to-1Se-to-1S and 16S-to-1MBTS, the batch of which is discussed in the manuscript Figures 1 and 2. The nanocrystals with the different growth periods (in minutes as indicated, at 240 °C) are represented by different colours. The excitation wavelength was 350 nm. The summary of the temporal evolution of the bandgap peak positions (PP, nm) of the absorption (■) and emission (□) is shown in right-top part, while the right-bottom part for the temporal evolution of the photoluminescent quantum yield (PL QY) (■, in toluene with 400 nm excitation, right y) and PL FWHM (□, left y).

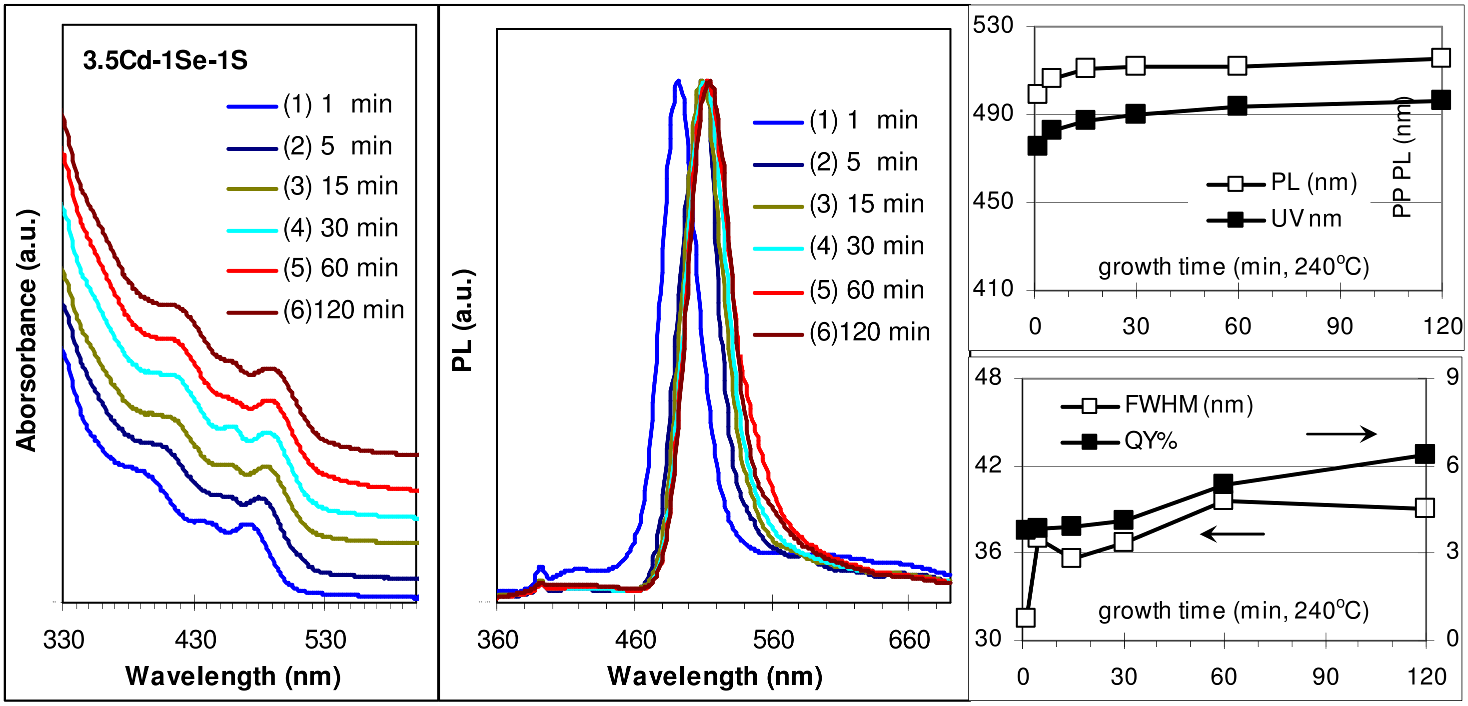

Figure S1-d: Temporal evolution of the UV-Vis absorption spectra (left, offset) and emission spectra (middle, normalized) of the growing CdSeS nanocrystals from the synthetic batch with the feed molar ratio of 3.5Cd-to-1Se-to-1S and 16S-to-1MBTS, the batch of which is discussed in the manuscript Figures 1 and 2. The nanocrystals with the different growth periods (in minutes as indicated, at 240 °C) are represented by different colours. The excitation wavelength was 350 nm. The summary of the temporal evolution of the bandgap peak positions (PP, nm) of the absorption (■) and emission (□) is shown in right-top part, while the right-bottom part for the temporal evolution of the photoluminescent quantum yield (PL QY) (■ in toluene with 400 nm excitation, right y) and PL FWHM (□, left y).

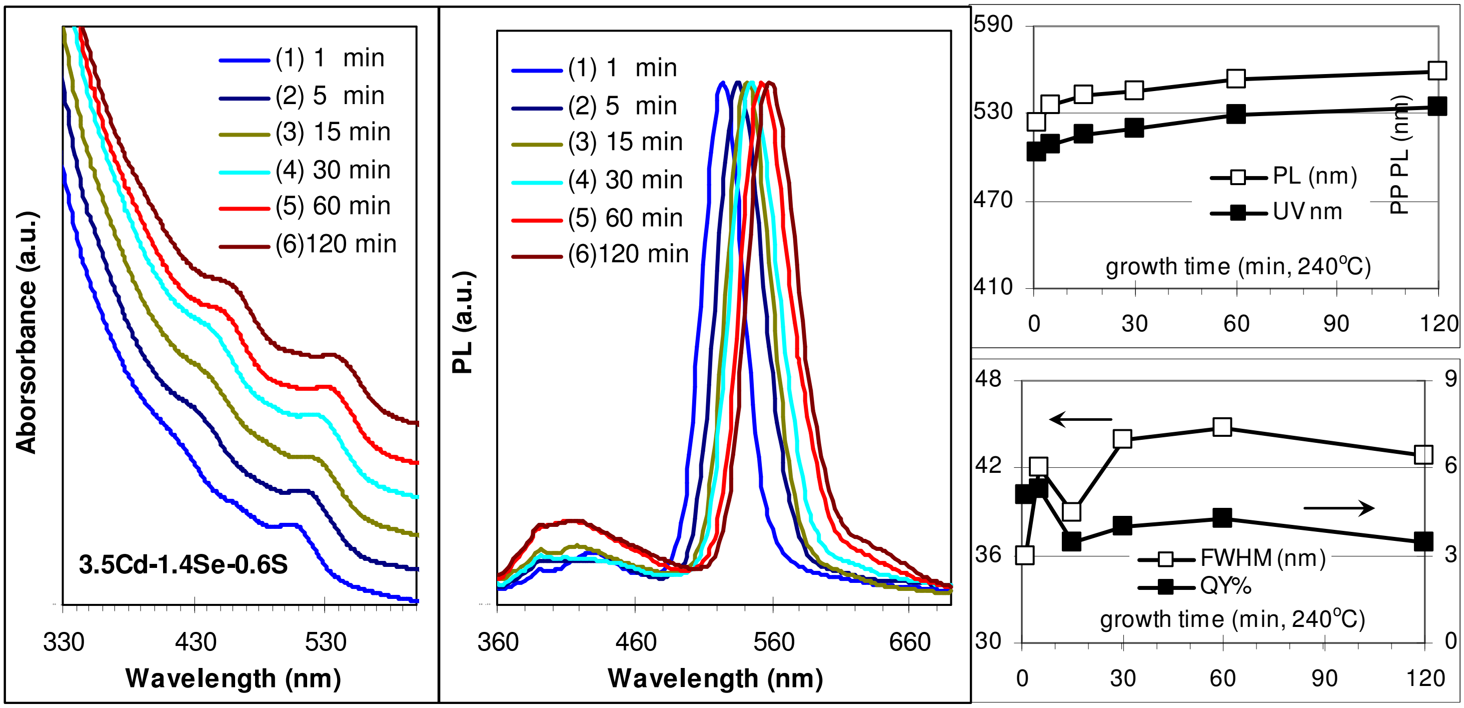

Figure S1-e: Temporal evolution of the UV-Vis absorption spectra (left, offset) and emission spectra (middle, normalized) of the growing CdSeS nanocrystals from the synthetic batch with the feed molar ratio of 3.5Cd-to-1.4Se-to-0.6S and 9.3S-to-1MBTS, the batch of which is discussed in the manuscript Figures 1 and 2. The nanocrystals with the different growth periods (in minutes as indicated, at 240 ^{o}C) are represented by different colours. The excitation wavelength was 350 nm. The summary of the temporal evolution of the bandgap peak positions (PP, nm) of the absorption (■) and emission (□) is shown in right-top part, while the right-bottom part for the temporal evolution of the photoluminescent quantum yield (PL QY) (■, in toluene with 400 nm excitation, right y) and PL FWHM (□, left y).

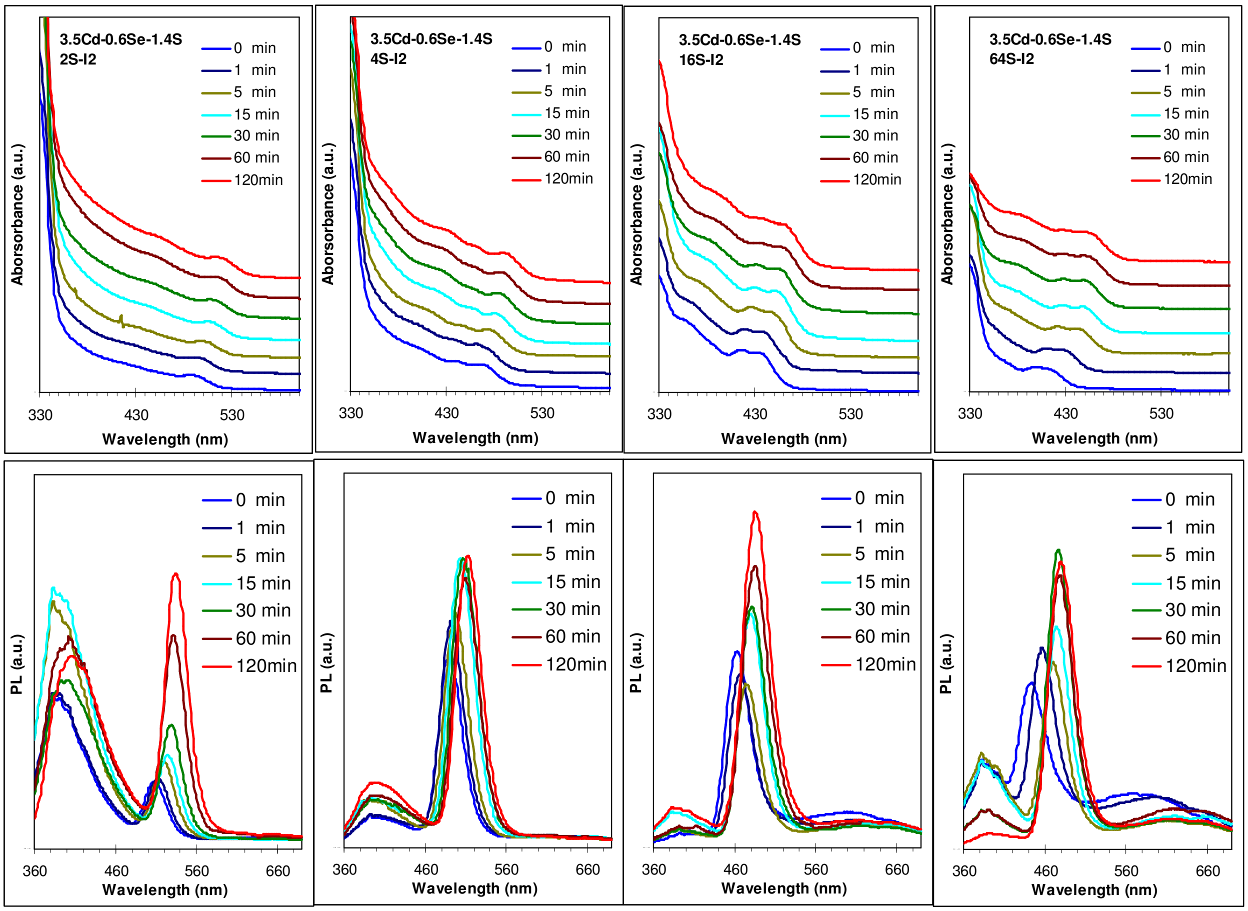

Figure S2-a: Temporal evolution of the UV-Vis absorption spectra (top, offset) and emission spectra (bottom) of the growing CdSeS nanocrystals from the synthetic batches with the fixed feed molar ratio of 3.5Cd-to-0.6Se-to-1.4S but different S-to-MBTS feed molar ratios, the batches of which are discussed in the manuscript Figure 3. The nanocrystals with the different growth periods (in minutes as indicated, at 240 °C) are represented by different colours. The excitation wavelength was 350 nm. From top to bottom, the batches are corresponding to those shown in Figure 3 Curves 4, 3, 2, and 1 with the 2S-to-1MBTS, 4S-to-1MBTS, 16S-to-1MBTS, and 64S-to-1MBTS feed molar ratios, respectively. Note that I2 in Figure S2 represents MBTS.

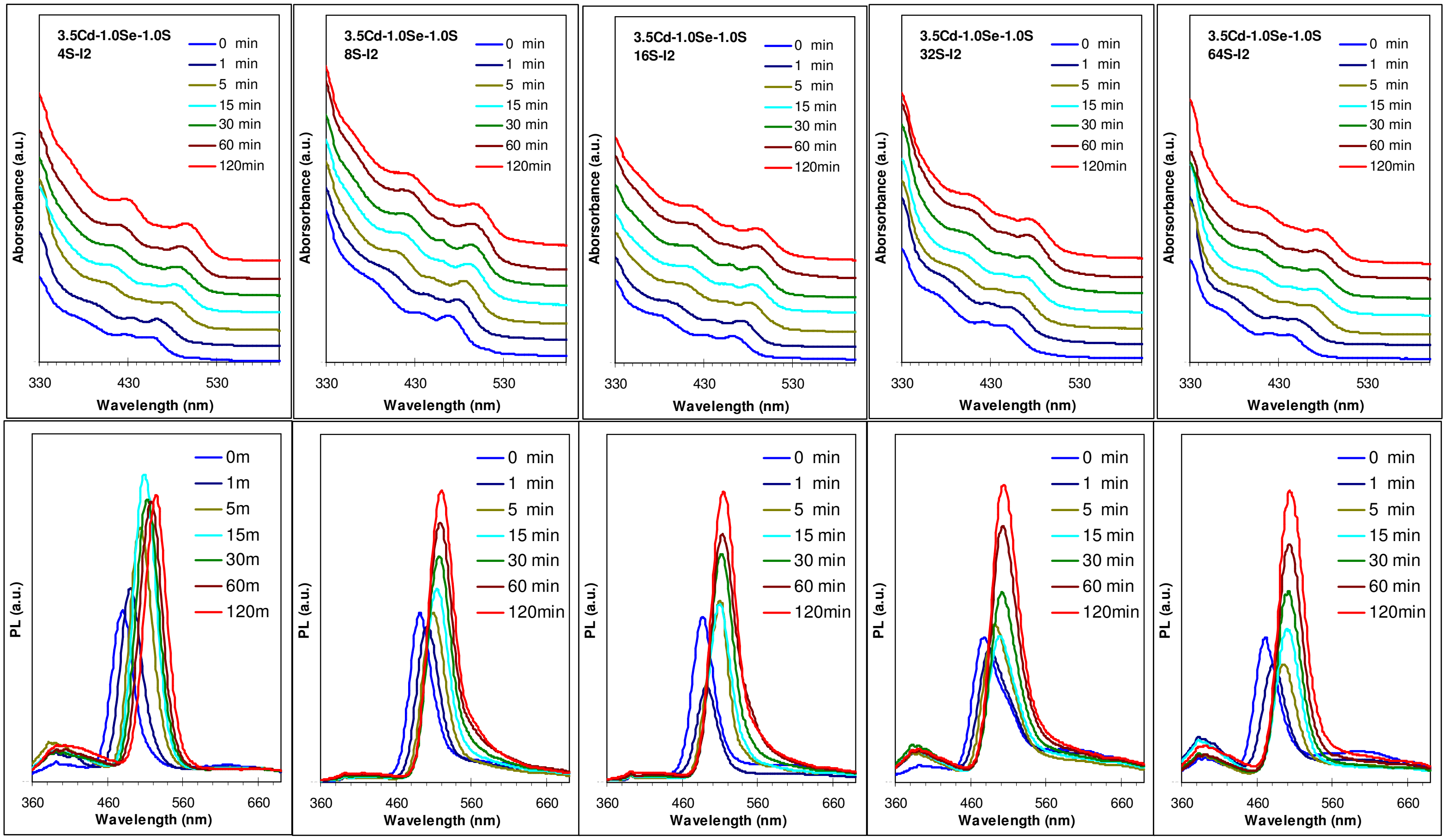

Figure S2-b: Temporal evolution of the UV-Vis absorption spectra (top, offset) and emission spectra (bottom) of the growing CdSeS nanocrystals from the synthetic batches with the fixed feed molar ratio of 3.5Cd-to-1Se-to-1S but different S-to-MBTS feed molar ratios. Similar batches but with 3.5Cd-to-0.6Se-to-1.4S are discussed in the manuscript Figure 3. The nanocrystals with the different growth periods (in minutes as indicated, at 240 ^{o}C) are represented by different colours. The excitation wavelength was 350 nm. From left to right, the batches have 4S-to-1MBTS, 8S-to-1MBTS, 16S-to-1MBTS, 32S-to-1MBTS, and 64S-to-1MBTS feed molar ratios, respectively. Note that I2 in Figure S2 represents MBTS.

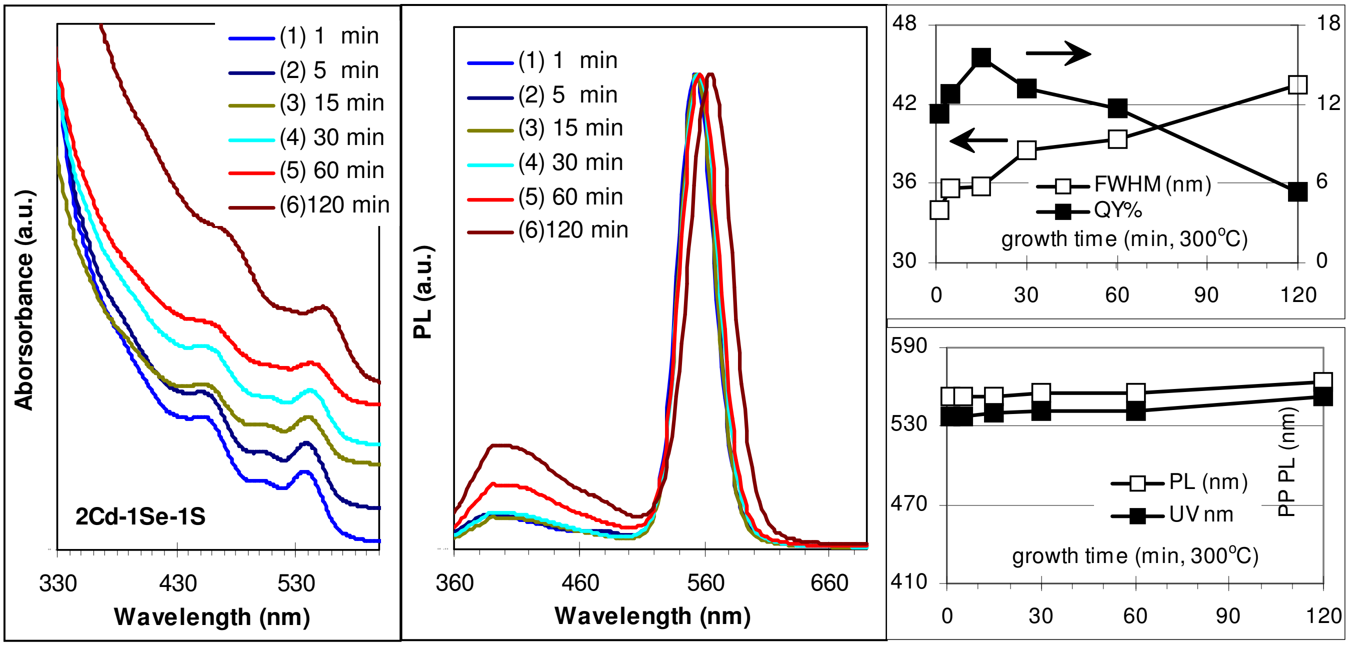

Figure S3: Temporal evolution of the UV-Vis absorption spectra (left, offset) and emission spectra (middle, normalized) of the growing CdSeS nanocrystals from the synthetic batch with the feed molar ratio of 2Cd-to-1Se-to-1S, 16S-to-1MBTS, and 9.2acid-to-1Cd. The nanocrystals with the different growth periods (in minutes as indicated, at 300 ^{o}C) are represented by different colours. The excitation wavelength was 350 nm. The summary of the temporal evolution of the band-gap peak positions (PP, nm) of the absorption (■) and emission (□) is shown in right-top part, while the right-bottom part for the temporal evolution of the photoluminescent quantum yield (PL QY) (■, in toluene with 400 nm excitation, right y) and PL FWHM (□, left y). It is evident that the nanocrystals, from this batch with the relatively high acid-to-Cd feed molar ratio and the relatively high growth temperature, namely 300 ^{o}C, exhibit relatively small trap emission and relatively high QY as compared to those from the batch (shown in Figure S1-c) with 240 ^{o}C growth; also, the current batch results in large nanocrystals.

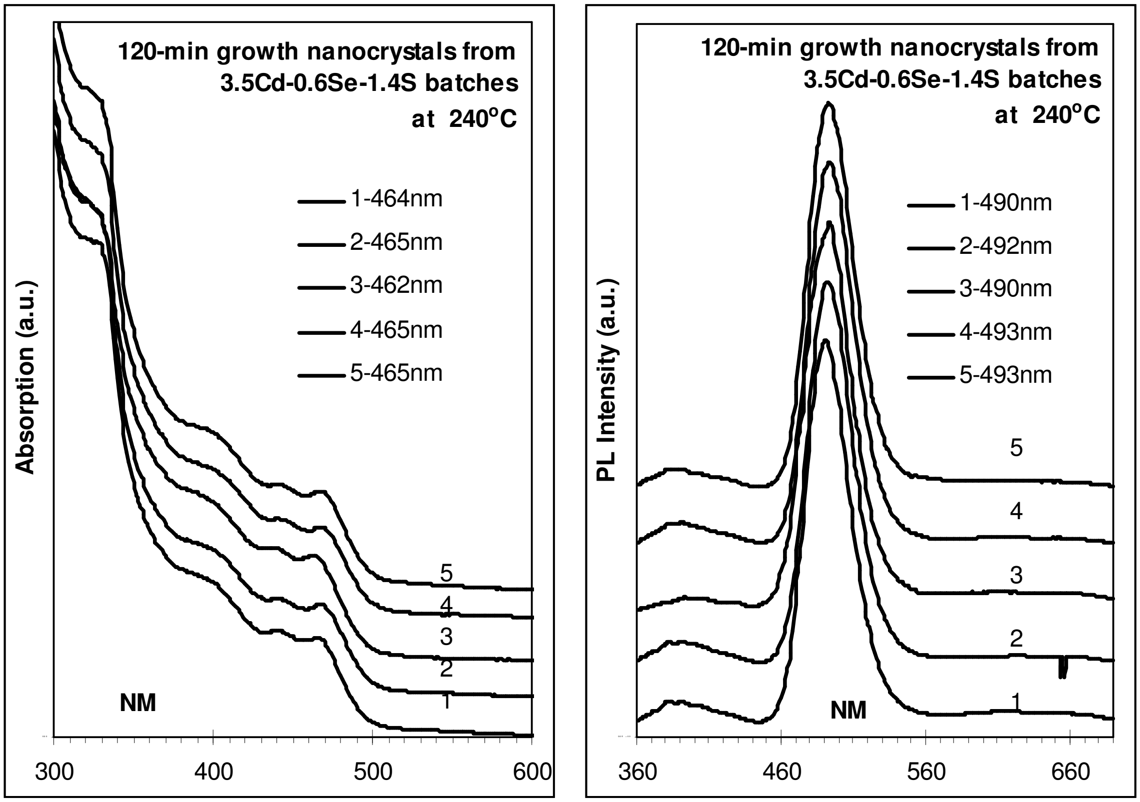

Figure S4: Whenever it was necessary to produce one QD sample with enough materials for structural characterization, such as XRD measurement, a large-scale synthesis, which is four-time scale of that shown in Table S1, was usually repeated a few times, with the same synthetic recipe and the same handling in the sample preparation. The optical properties of the resulting as-synthesized QD ensembles dispersed in toluene were monitored, such as UV-Vis absorption (left, offset) and photoemission (right, normalized and offset) of the five syntheses. The UV-Vis absorption and emission peak position were given; with the excitation wavelength of 350 nm, the PL FWHM is on the order of 37.5 – 39.0 nm and the quantum yield is estimated to be on the order of 6.0% - 7.0% with 400 nm excitation. The products exhibit similar absorption and emission; the products were purified separately and then combined for the structural characterization. The non-injection approach developed in our laboratories features great synthetic reproducibility and is easy to scale up. These synthetic batches started with feed molar ratios of 16S-to-1MBTS and 3.5Cd-to-0.6Se-to-1.4S; the growth of the nanocrystals was at 240°C for 120 min.

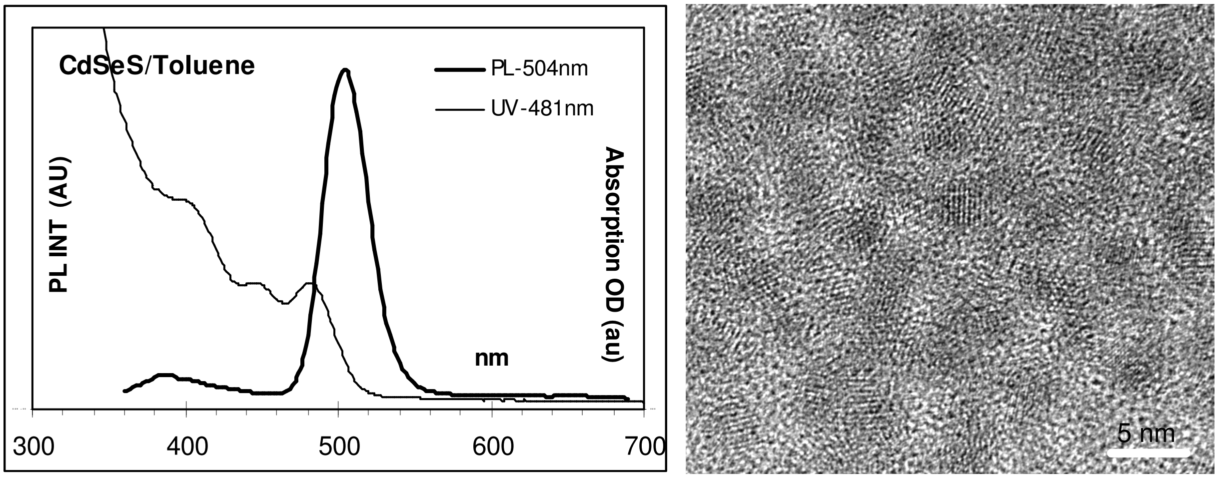

Figure S5: (left) The optical properties of the UV-Vis absorption spectrum (thin line) and PL emission spectrum (thick line) of the CdSeS nanocrystals from a large-scale synthetic batch, which is four-time scale of that shown in Table S1, with the feed molar ratios of 2Cd-to-1Se-to-1S and 13S-to-1MBTS. The nanocrystals had a growth period of 5 minute at 240 ^{o}C, and were dispersed in toluene; the excitation wavelength was 350 nm. The photoluminescent quantum yield (PL QY) of this CdSeS ensemble is estimated to be ca. 10%, with the excitation wavelength of 450 nm and the FWHM of ca. 33.9 nm. The absorption and emission peak positions are indicated. (right) One corresponding high-resolution TEM image with the scale bar of 5 nm, showing an average size of ca. 3.64 nm. The XPS and XRD pattern of this ensemble are shown in the manuscript Figures 5 and 6, with the composition of $CdSe_{0.45}S_{0.55}$.