Electronic Supplementary Information

Kinetic Studies on the Formation of Various II-VI Semiconductor Nanocrystals and Synthesis of Gradient Alloy Quantum Dots Emitting in the Entire Visible Range

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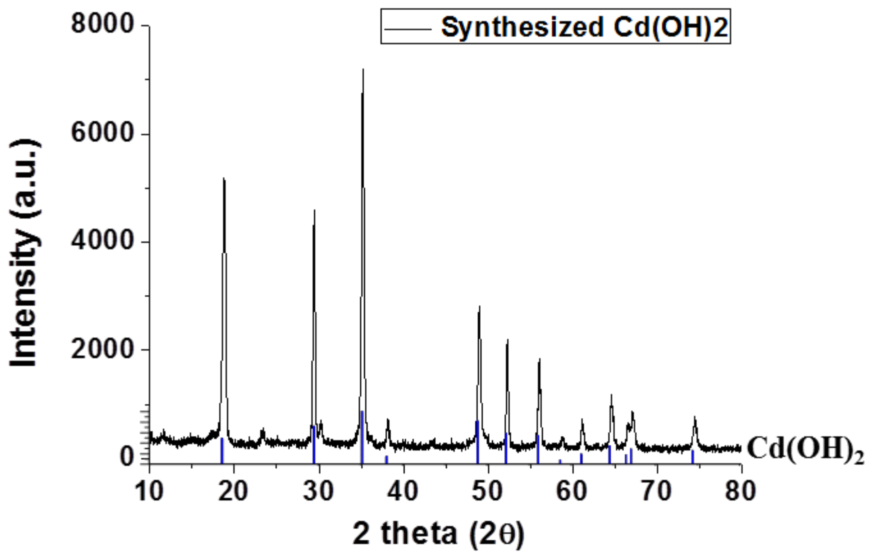

Fig. SI-1. Powder X-ray diffraction spectra of synthesized $Cd(OH)_2$ and reference XRD patterns of $Cd(OH)_2$ (blue).

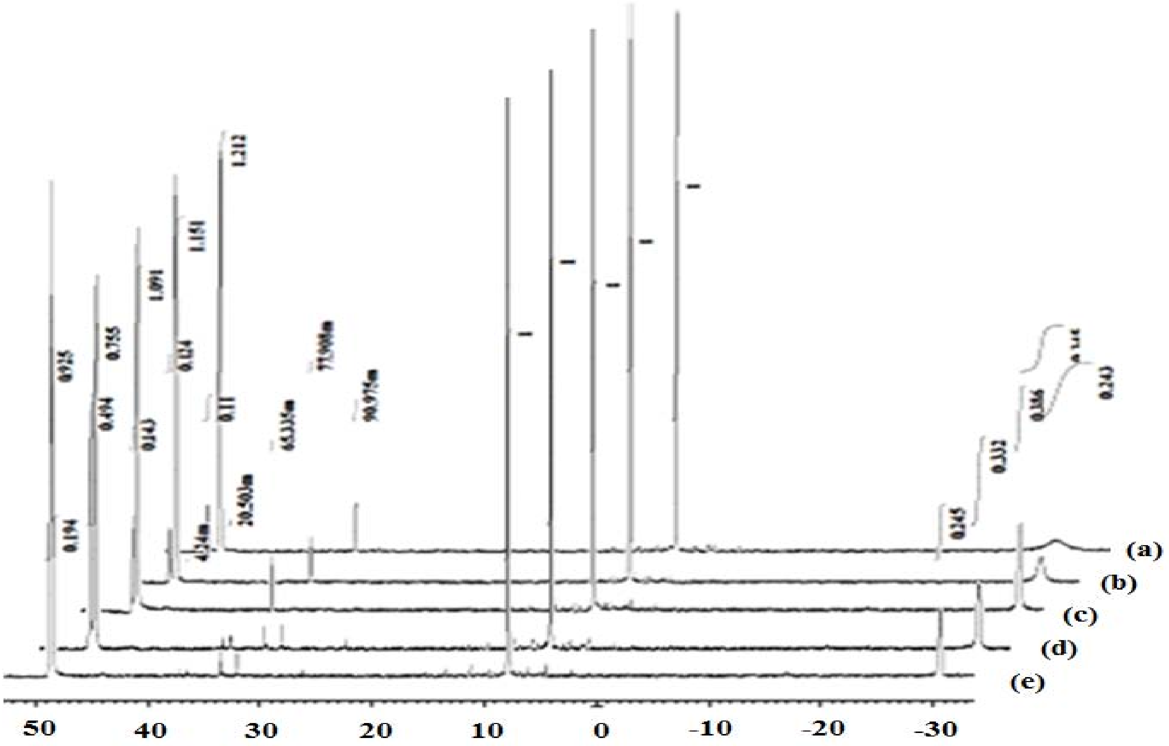

Fig. SI-2. ^{31}P NMR spectra under the reaction condition of Cd-OA:Zn-OA:TOPSe:TOPS = 0.4:4.0:0.4:4.0 at different time intervals. Spectra were collected at 0 s, 30 s, 60 s, 600 s, 1200 s, respectively. (δ = 7.3 ppm (standard), 35.8 ppm (TOPSe), 47.9ppm (TOPS), 48.0~49.6 ppm (TOPO), and ~ -31 ppm (TOP))

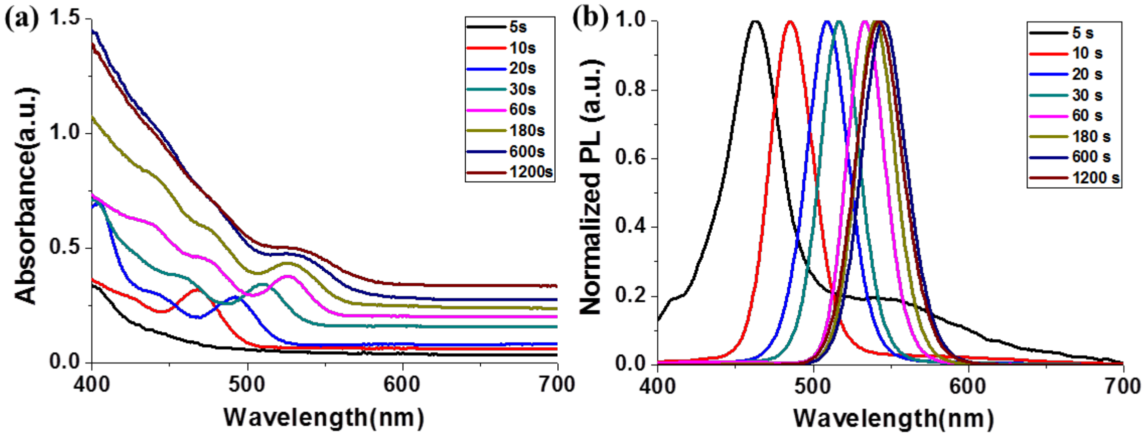

Fig. SI-3. (a) UV-Vis absorption and (b) PL spectra of the green-emitting gradient alloy QDs isolated at 5 s, 10 s, 20 s, 30 s, 60 s, 180 s, 600 s, and 1200 s, respectively.

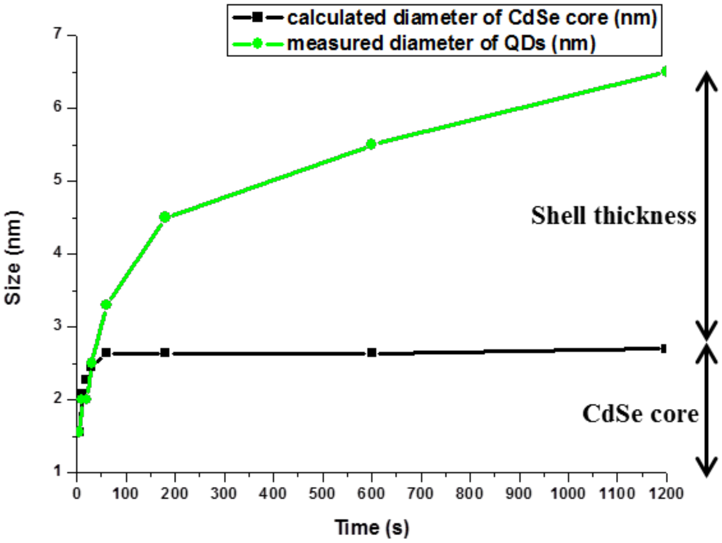

Fig. SI-4. Size evolution plot of the green-emitting gradient alloy QDs; total size was measured by TEM (green line) and effective CdSe core size was estimated from the first absorption peak (black line)

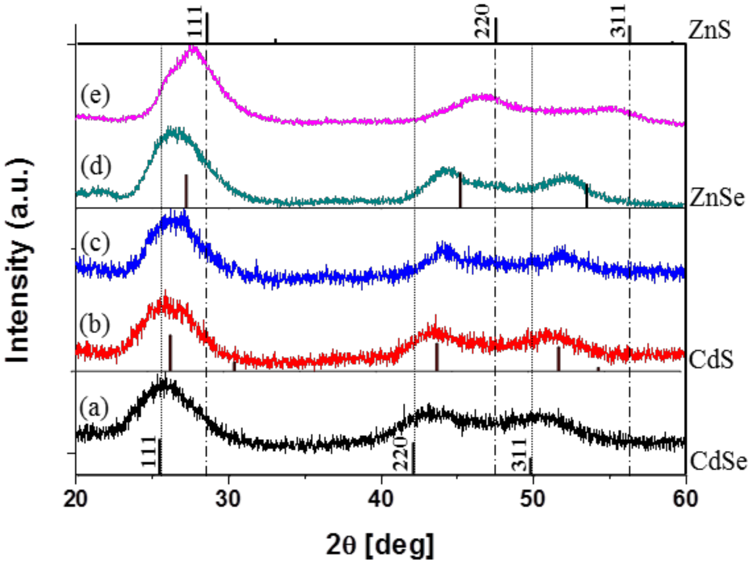

Fig. SI-5. Powder X-ray diffraction patterns of green-emitting gradient alloy QDs with reaction time at (a) 10 s, (b) 30 s, (c) 60 s, (d) 180 s, and (e) 600 s, respectively

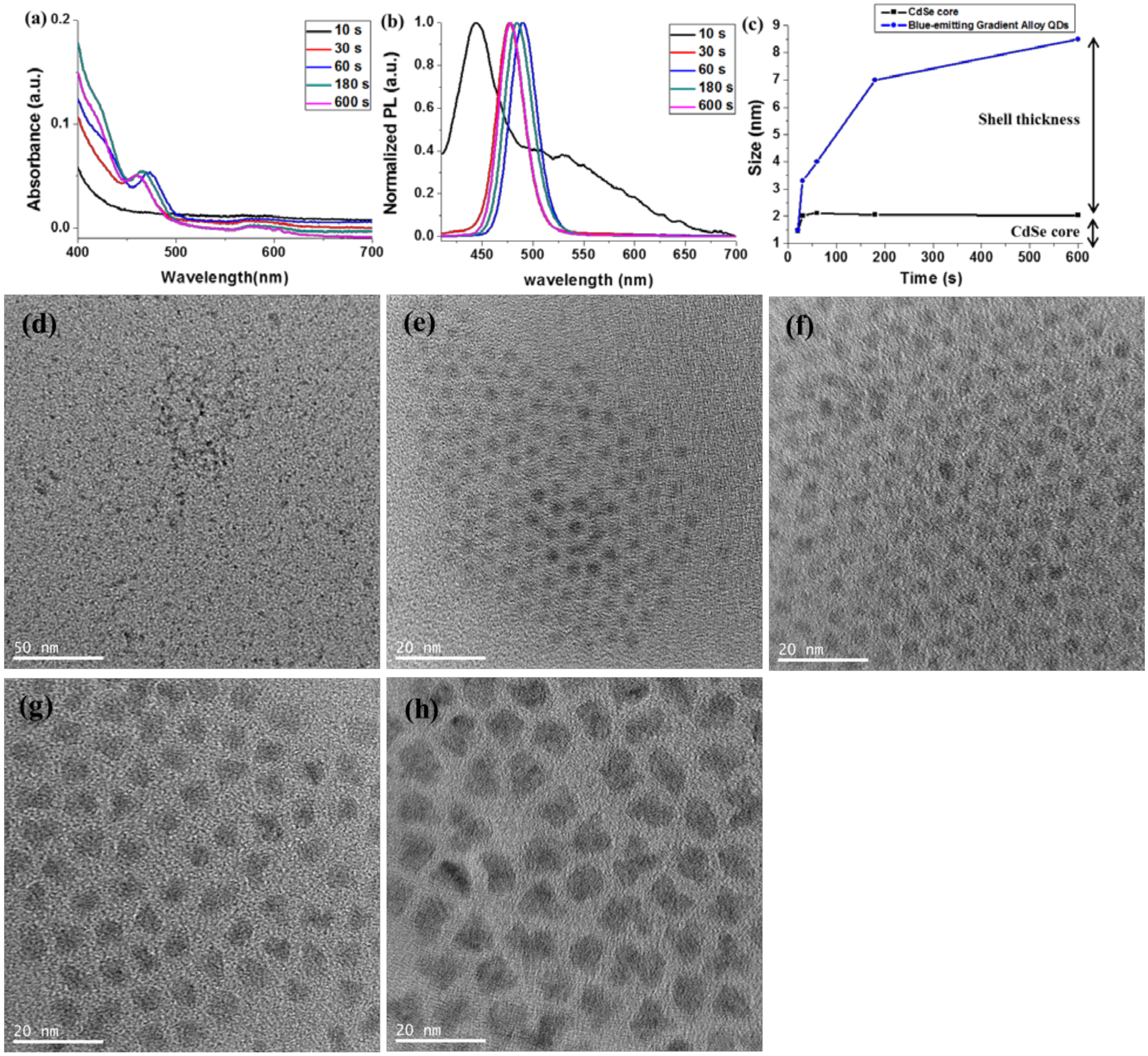

Fig. SI-6. (a) UV-Vis absorption, (b) PL spectra, (c) size evolution plot, and (d) TEM images of the blue-emitting gradient alloy QDs isolated at 10 s, 30 s, 60 s, 180 s, and 600 s, respectively.

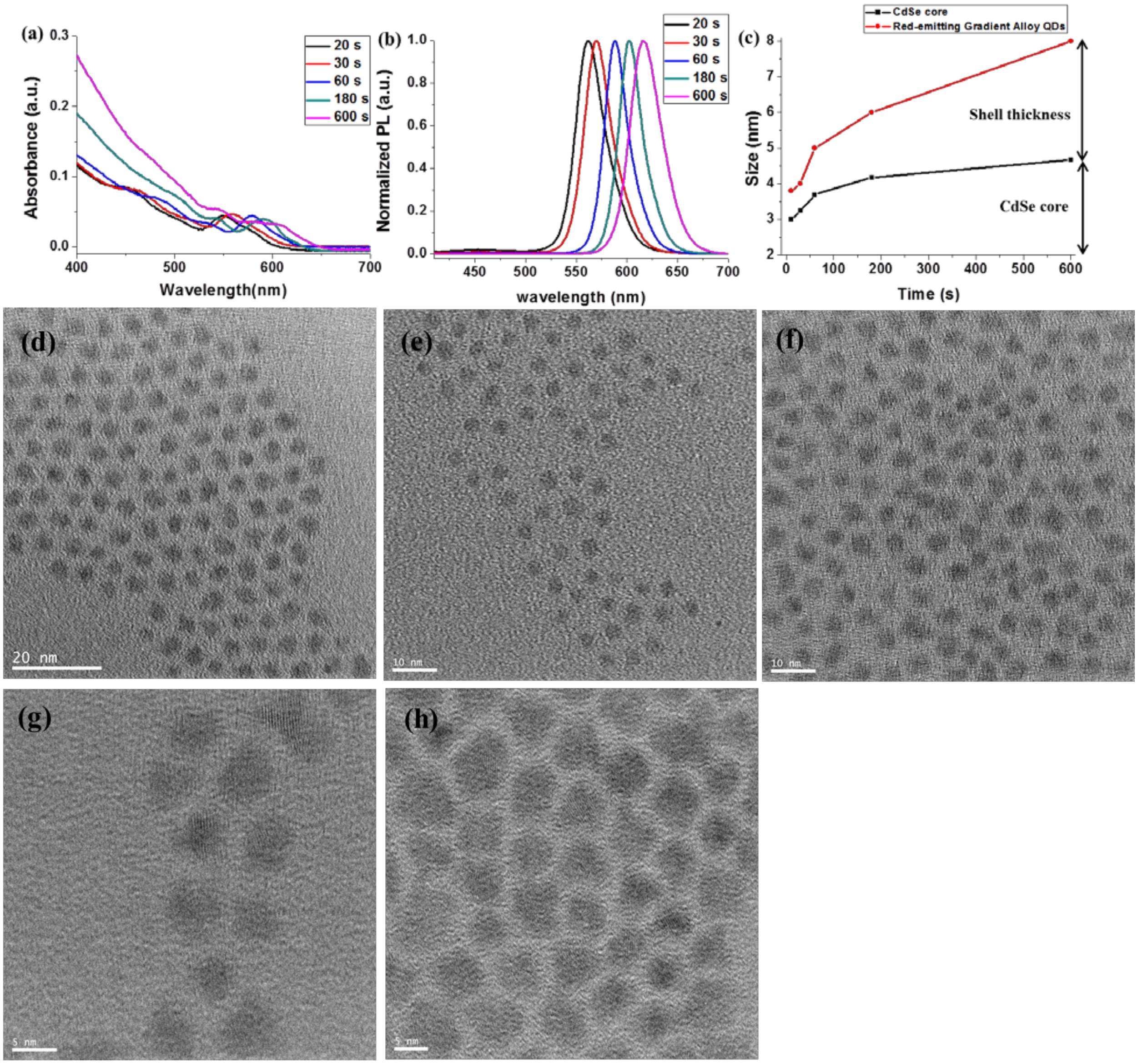

Fig. SI-7. (a) UV-Vis absorption, (b) PL spectra, (c) size evolution plot, and (d) TEM images of the red-emitting gradient alloy QDs isolated at 20 s, 30 s, 60 s, 180 s, and 600 s, respectively.

Calculation of consumption rate of TOP-E or formation rate of M-E (R_{obs})

The consumption rate of TOP-E and corresponding formation rate of metal chalcogenide were acquired by following equation. For consumption rate of TOP-E, it was obtained by dividing the changed amount of TOP-E by reaction time. Likewise, corresponding formation rate of metal chalcogenide was equivalent with the reversed value of TOP-E.

$R_{obs} = -\Delta[\text{TOP-E}]/t$ (Consumption rate of TOP-E); t = reaction time
$R_{obs} = +\Delta[\text{M-E}]/t$ (Formation rate of M-E); t = reaction time

Table SI-1. Experimentally observed consumption rates of TOP-E at the different time intervals; (a)-(d) indicated the numbers denoted in Fig. 2.

Measured species	**Reacted precursors**	**R_{obs} (mmol·s^{-1})**		
		0 – 10 s	**10 – 60 s**	**60 – 180 s**
TOP-Se	(a) Cd-OA/TOP-Se	4.1×10^{-2}	8.4×10^{-3}	1.3×10^{-4}
TOP-S	(a) Cd-OA/TOP-S	2.7×10^{-3}	2.4×10^{-3}	1.9×10^{-3}
TOP-Se	(b) Zn-OA/TOP-Se	6.1×10^{-4}	6.2×10^{-4}	6.5×10^{-4}
TOP-S	(b) Zn-OA/TOP-S	3.5×10^{-4}	3.5×10^{-4}	3.5×10^{-4}
TOP-Se	(c) Cd-OA/TOP-Se, TOP-S	6.0×10^{-2}	4.5×10^{-3}	2.8×10^{-4}
TOP-S	(c) Cd-OA/TOP-Se, TOP-S	2.1×10^{-3}	1.7×10^{-3}	1.0×10^{-3}
TOP-Se	(d) Zn-OA/TOP-Se, TOP-S	1.4×10^{-3}	1.3×10^{-3}	9.9×10^{-4}
TOP-S	(d) Zn-OA/TOP-Se, TOP-S	1.2×10^{-3}	1.0×10^{-3}	6.7×10^{-4}

Table SI-2. Experimentally observed consumption rates of TOP-E and growth rate of M-E at different time intervals; (a)-(b) indicated the numbers denoted in Fig. 4.

Measured Species	**Reacted Precursors**	**R_{obs} (mmol·s^{-1})**		
		0 – 10 s	**10 – 60 s**	**60 – 180 s**
TOPSe	(a) Cd-OA, Zn-OA/TOPSe, TOPS	3.5×10^{-2}	8.9×10^{-3}	1.8×10^{-3}
TOPS	(a) Cd-OA, Zn-OA/TOPSe, TOPS	2.0×10^{-3}	1.9×10^{-3}	1.6×10^{-3}
Cd	(b) Cd-OA, Zn-OA/TOPSe, TOPS	3.0×10^{-2}	8.5×10^{-3}	2.0×10^{-3}
Zn	(b) Cd-OA, Zn-OA/TOPSe, TOPS	6.1×10^{-4}	5.2×10^{-4}	5.1×10^{-4}

Table SI-3. Experimentally observed consumption rates of TOP-E and growth rate of M-E at different time intervals in the synthesis of the gradient alloy QD having the green emission color

Measured Species	Reacted Precursors	R_{obs} (mmol·s^{-1})			
		0 - 10 s	**10 - 60 s**	**60 - 180 s**	**180 - 600 s**
TOPSe	Cd-OA 0.4, Zn-OA 4.0/ TOPSe 0.4, TOPS 4.0	4.3×10^{-3}	1.8×10^{-3}	1.7×10^{-3}	1.0×10^{-3}
TOPS	Cd-OA 0.4, Zn-OA 4.0/ TOPSe 0.4, TOPS 4.0	2.6×10^{-3}	2.6×10^{-3}	2.6×10^{-3}	2.6×10^{-3}
Cd	Cd-OA 0.4, Zn-OA 4.0/ TOPSe 0.4, TOPS 4.0	1.1×10^{-2}	7.2×10^{-3}	2.0×10^{-3}	9.4×10^{-5}
Zn	Cd-OA 0.4, Zn-OA 4.0/ TOPSe 0.4, TOPS 4.0	1.3×10^{-3}	2.5×10^{-3}	8.4×10^{-3}	3.7×10^{-3}

Table SI-4. Effective CdSe core size was extracted from the first exciton peak of UV-Vis and the size of whole nanocrystals QDs was measured by TEM.

Time (s)	1st exciton peak (nm)	1st exciton peak (eV)	Size of the CdSe Core[1] (nm)	Size of the Gradient alloy QDs[2] (nm)	Shell thickness (nm)
5	400	3.09	1.5	n/a	n/a
10	468	2.64	2.1	n/a	n/a
20	492	2.52	2.2	2.5 ± 0.5	0.3 ± 0.5
30	510	2.43	2.3	3.3 ± 0.5	1.0 ± 0.5
60	526	2.35	2.6	4.5 ± 0.5	2.1 ± 0.5
180	526	2.35	2.6	5.5 ± 0.5	2.9 ± 0.5
600	526	2.35	2.6	6.5 ± 0.5	3.9 ± 0.5
1200	526	2.35	2.6	7.5 ± 0.5	4.9 ± 0.5

[1] Calculated from 1st exciton peak
[2] Measured by TEM

Calculation of effective CdSe core size

The synthesized gradient alloy QDs were composed of CdSe core and gradient shells so we could calculate the average diameter (D) of an CdSe core as follows.

$$\text{CdSe : } D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\,\lambda^3 + (1.6242 \times 10^{-3})\,\lambda^2 - (0.4277)\,\lambda + (41.57)$$

(λ = the wavelength of the first excitonic absorption peak in nm)

However, the value of CdSe at initial reaction time was slightly overestimated because the wavefunction of core probably penetrated into the shells; it represented expanded core. After formation of $ZnSe_yS_{1-y}/ZnS$ shells around CdSe core, the value would be accurate due to blocking of exciton wavefunction. The calculation results were summarized in Table SI-4.