Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.
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Supplementary Information to Accompany:

Kinetically controlled assembly of cadmium chalcogenide nanorods and nanorod heterostructures

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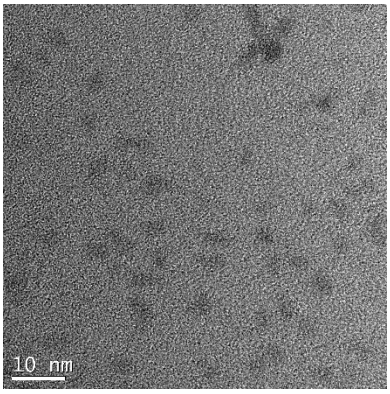

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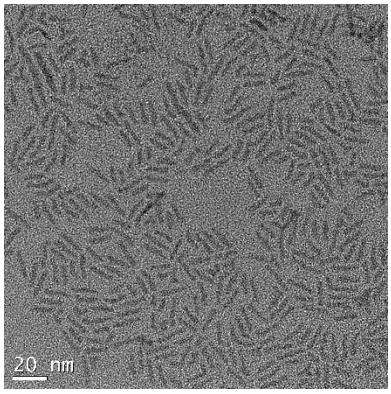

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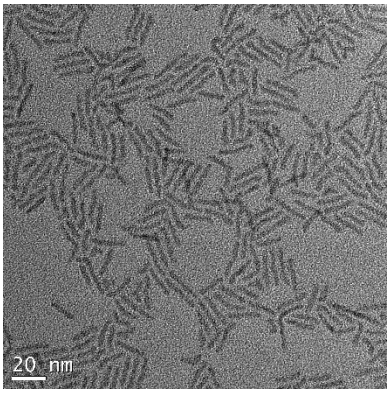

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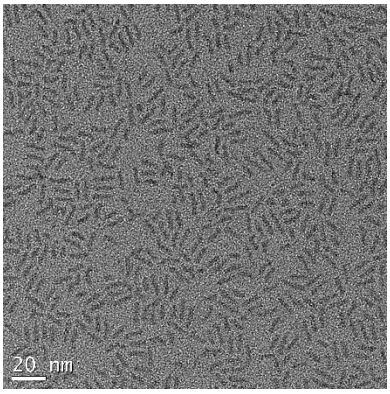

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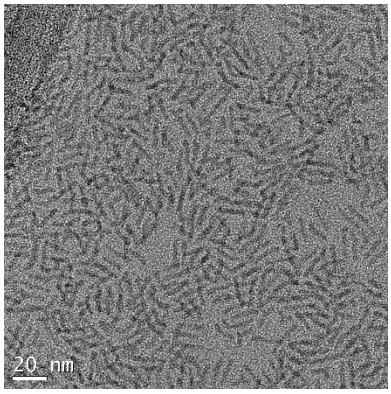

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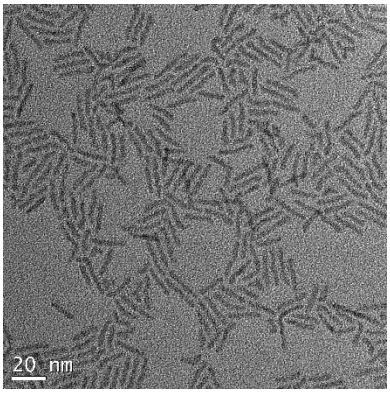

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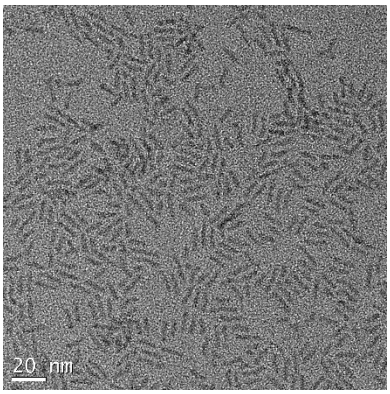

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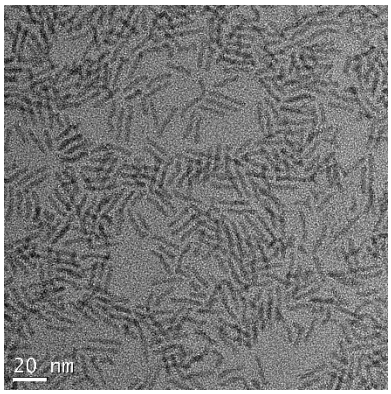

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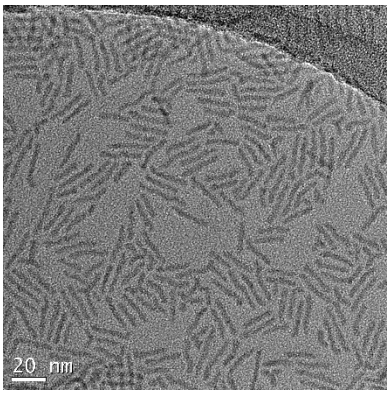

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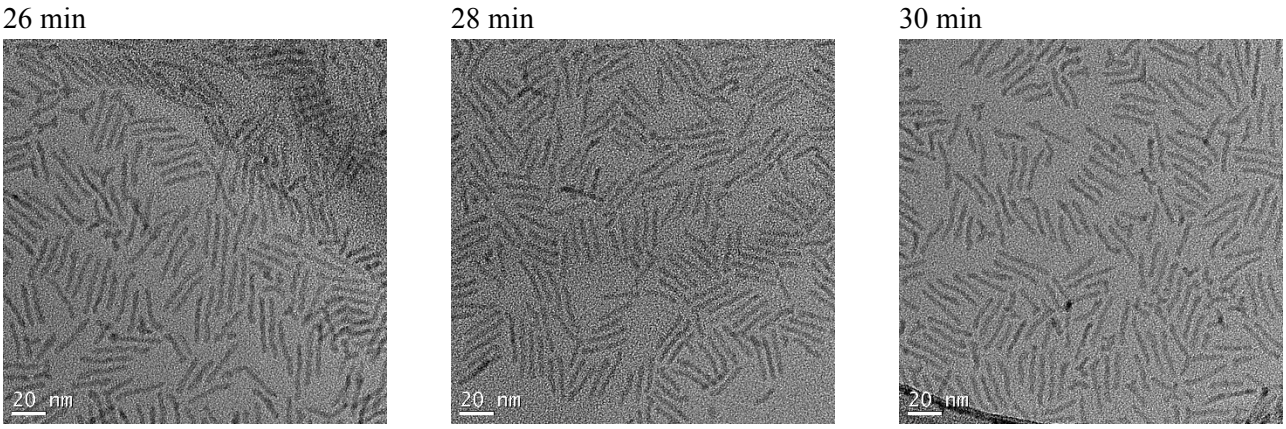
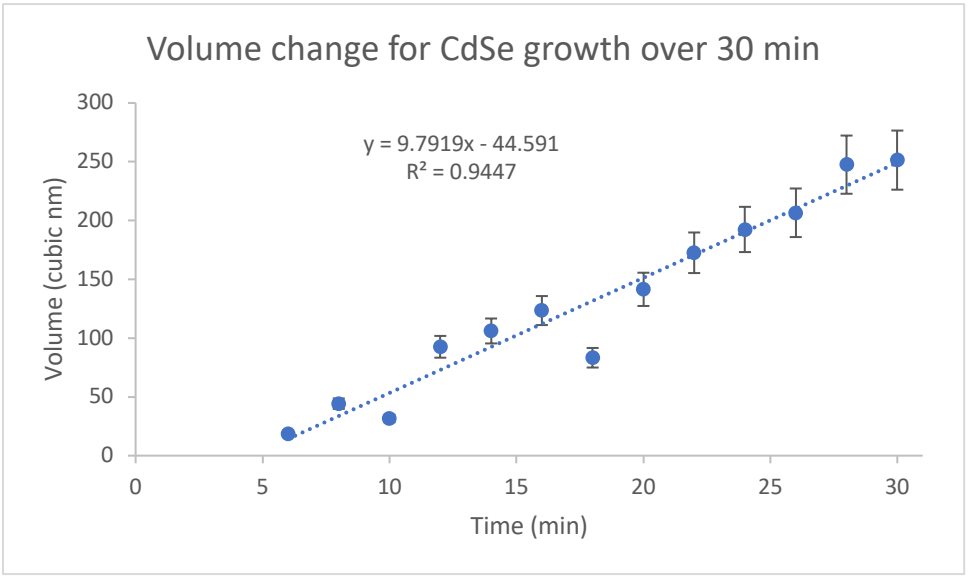


Figure S1. TEM images of unseeded CdSe nanorod growth corresponding with data reported in Figure 1 of the main text.

Example calculation to derive rates of rod growth for unseeded nanorods:



Equation from volume vs. time for unseeded CdSe nanorod growth: $y = 9.7919x - 44.591$

The slope, 9.7919, is the rate of volume added to a growing rod every minute.

The volume of a CdSe unit cell is 112.25 Å^3 and each unit cell is composed of 4 atoms (2 Cd and 2 Se)

Thus, $\left(\frac{9.7919\ nm^3}{min}\right)\left(\frac{1\ unit\ cell}{0.11225\ nm^3}\right)\left(\frac{2\ Cd\ or\ Se}{1\ unit\ cell}\right)\left(\frac{1\ min}{60\ s}\right) = 2.9\ monomers\ \ rod^{-1}s^{-1}$

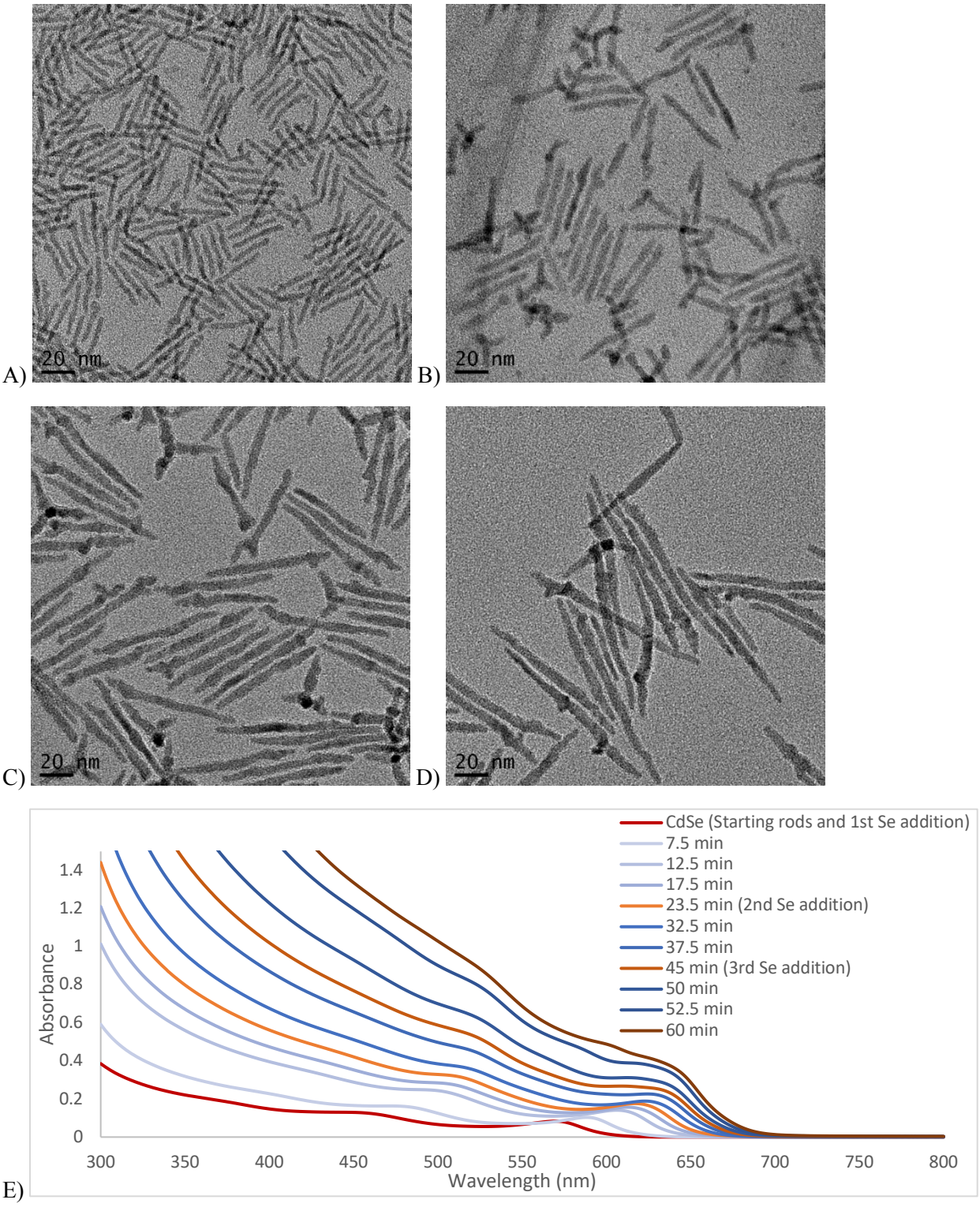
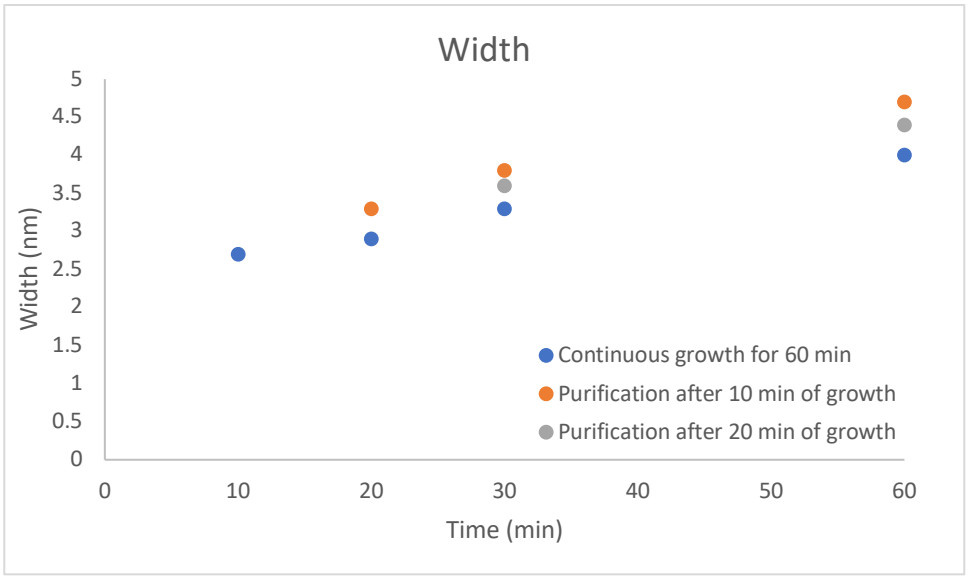


Figure S2. Progressive elongation of CdSe on 27.6 ± 2.9 nm by 2.9 ± 0.4 nm nanorods (A). The increased dimensions are 44.4 ± 6.5 nm by 4.4 ± 0.6 nm after 30 min (B), 69.8 ± 9.1 nm by 5.2 ± 0.8 nm after 30 min (C), and 99.3 ± 15.1 nm 5.9 ± 1.0 nm after 65 min (D). The increasing nanorod size the product of three subsequent additions of TOP-Se to a bath of excess cadmium tetradecylphosphonate (Cd-TDPA) precursor. UV-Vis of growing nanorods is also included (E).

A)



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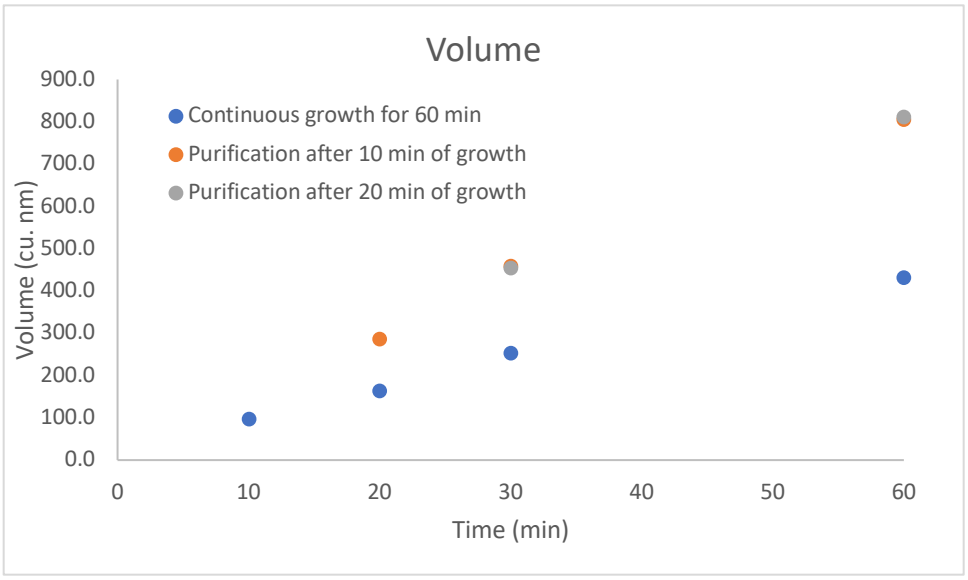
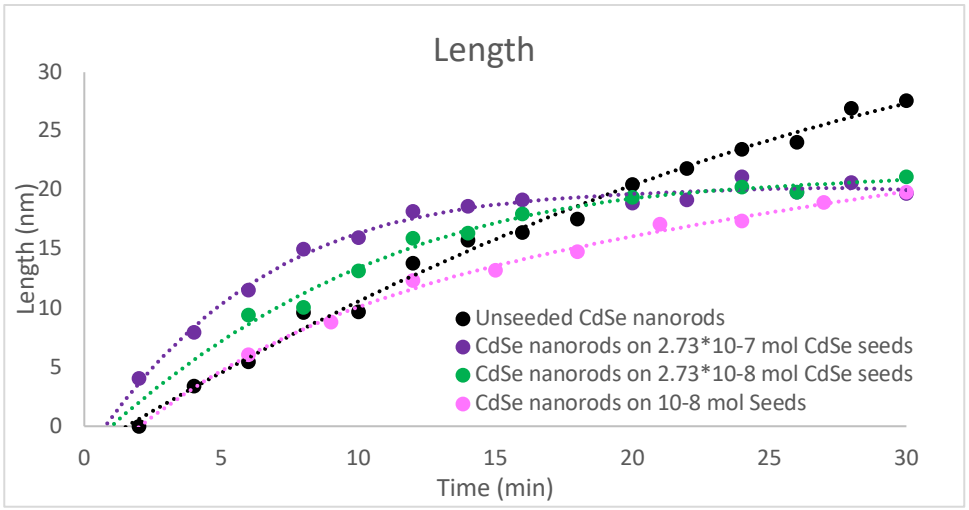


Figure S3. Width (A) and volume (B) vs time for the growth-purify-restart method of rod elongation corresponding to the same data set reported in Figure 2 of the main text.

A)



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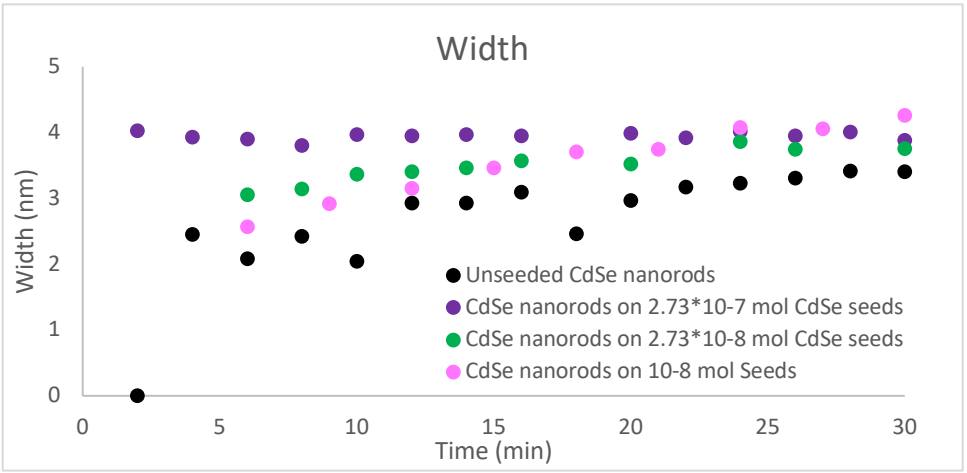

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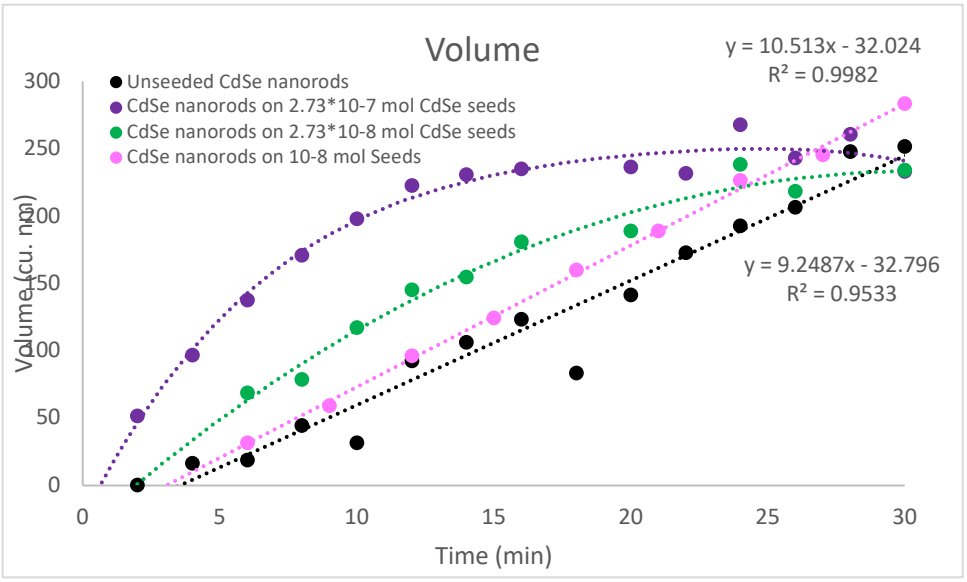

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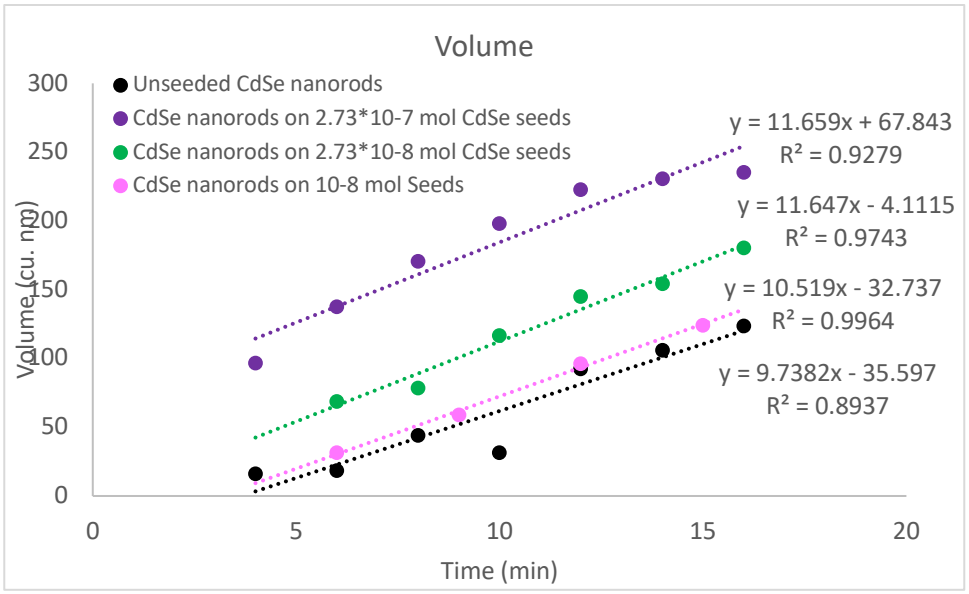
D)



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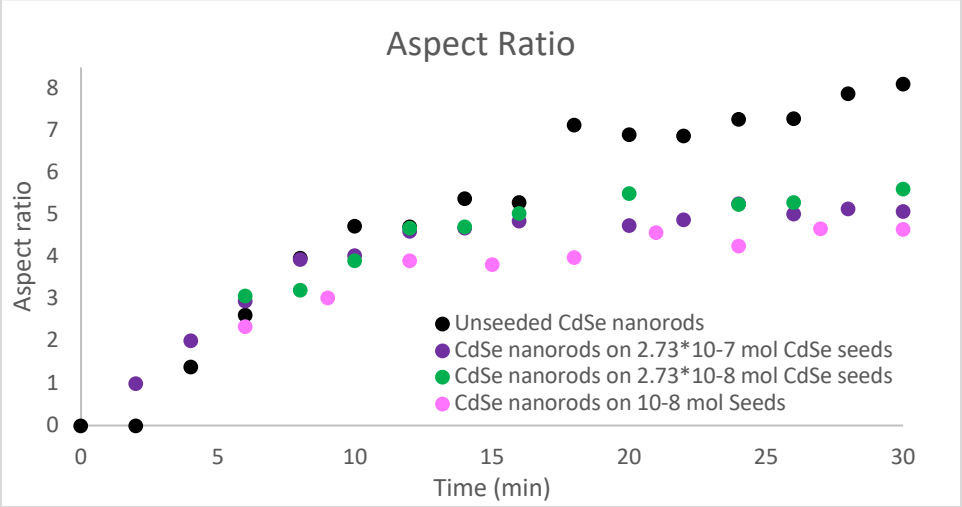
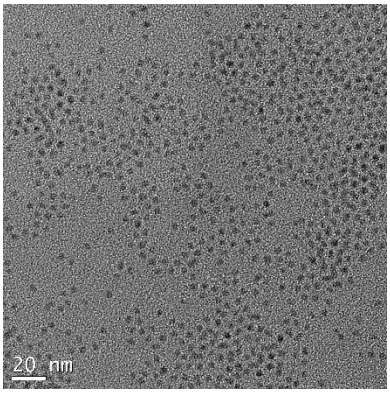


Figure S4. CdSe nanorod growth on CdSe seeds. Length (A), width (B), volume (C and D), and aspect ratio (E) are tracked over the duration of each reaction. (D) is a slope evaluation between 4-16 min, the period of time dominated by length growth, used to determine monomer addition rates for each seeded synthesis. Rod growth occurs at 2.9 monomers rod^{-1} s^{-1} for unseeded nanorods, 3.5 monomers rod^{-1} s^{-1} for$2.73*10^{-7}$ mol and $2.73*10^{-8}$ mol seeds.

2 min (CdSe seeds)



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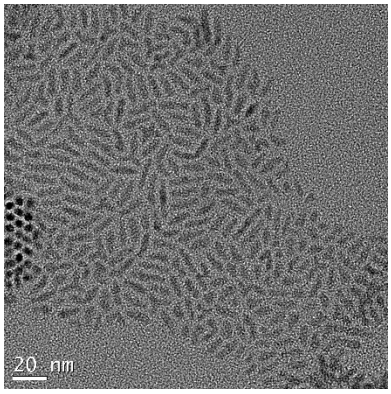

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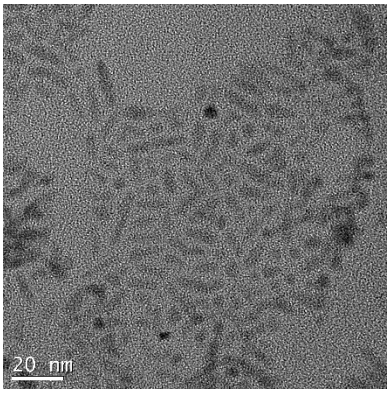

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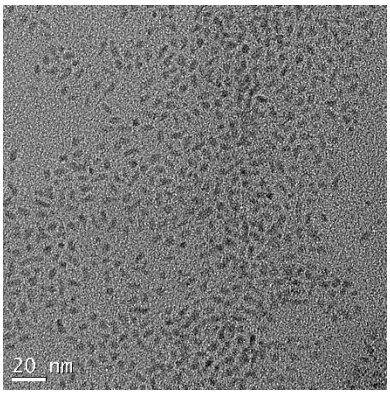

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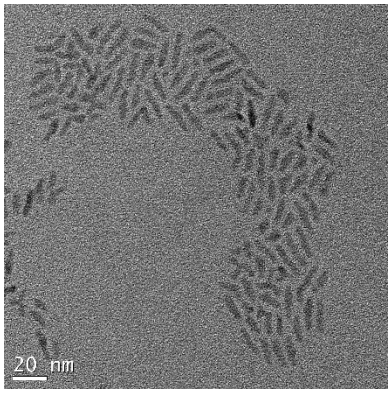

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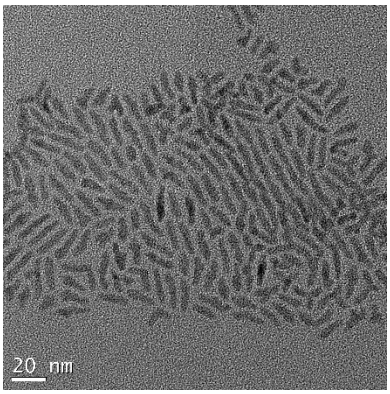

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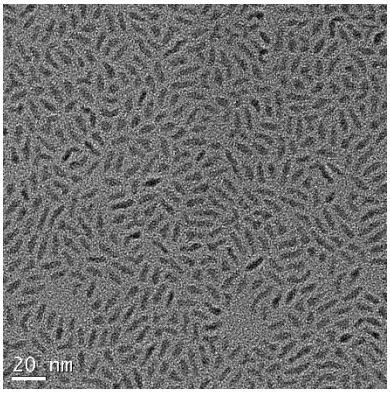

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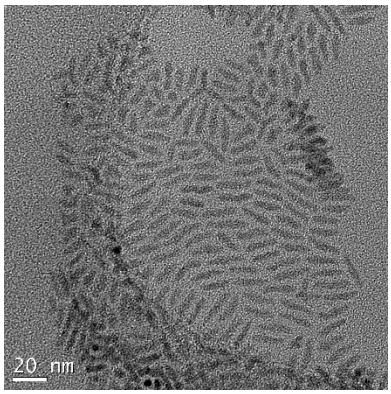

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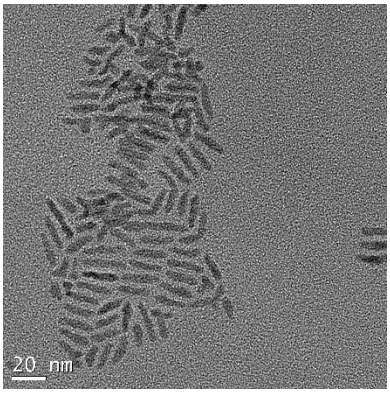

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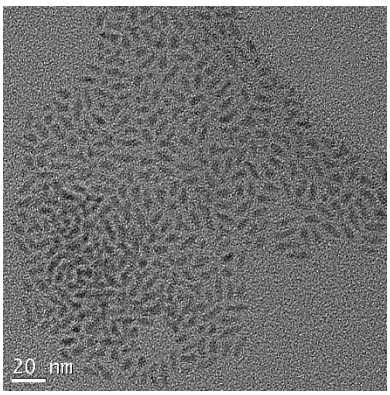

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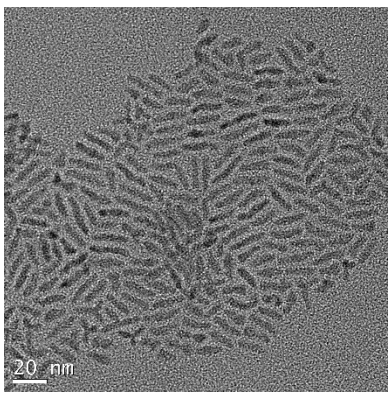

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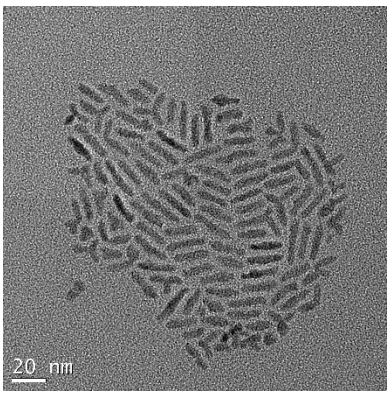


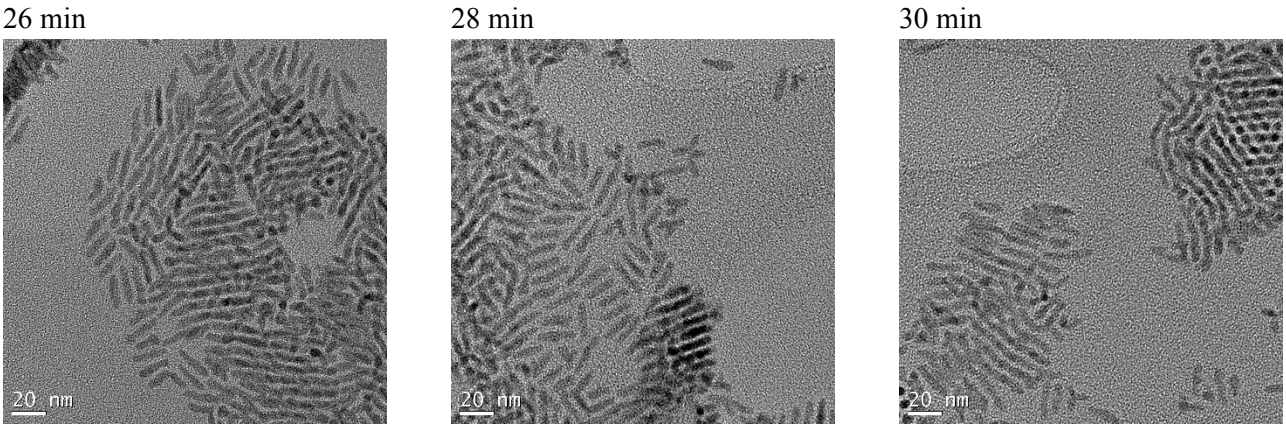


Figure S5. TEM images of growing CdSe nanorods upon $2.73*10^{-7}$ mol seeds.

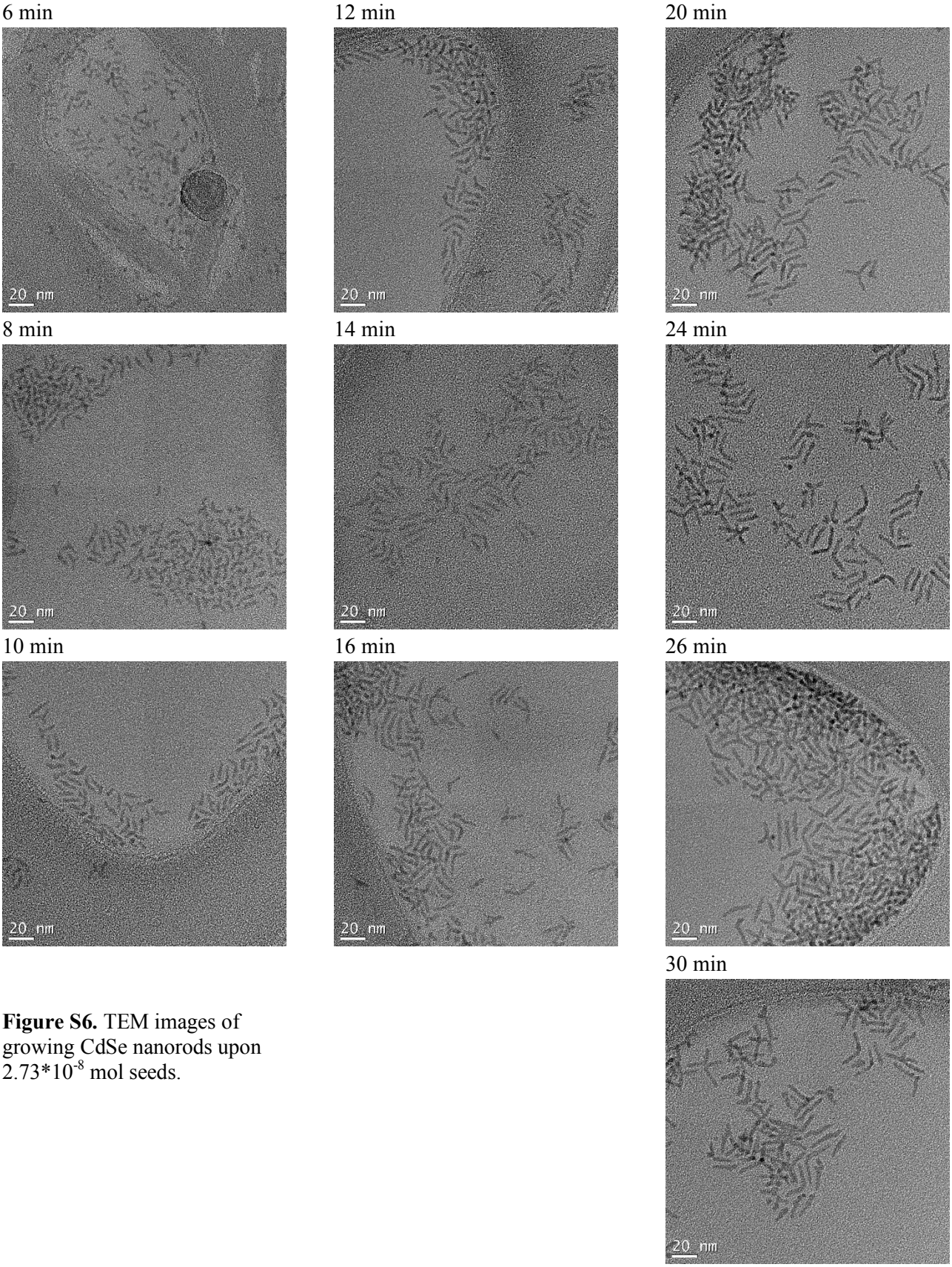
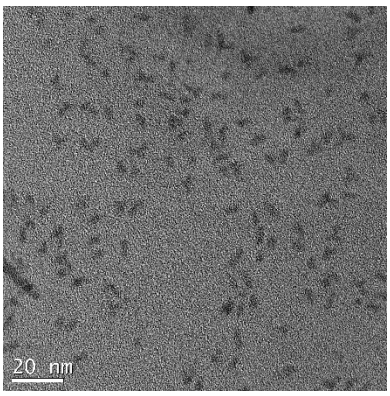


Figure S6. TEM images of growing CdSe nanorods upon $2.73*10^{-8}$ mol seeds.

6 min



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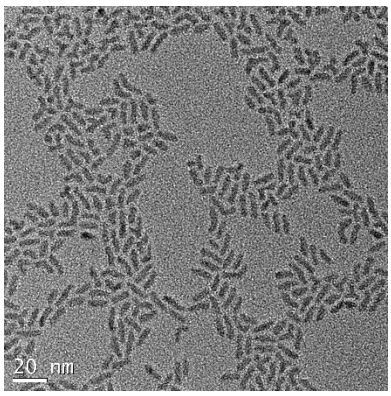

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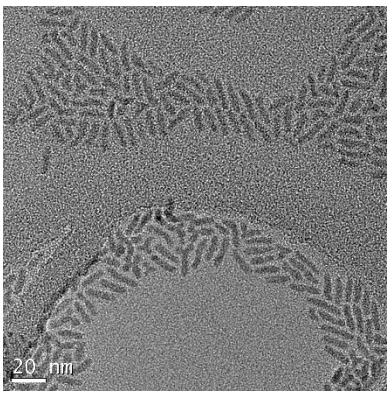

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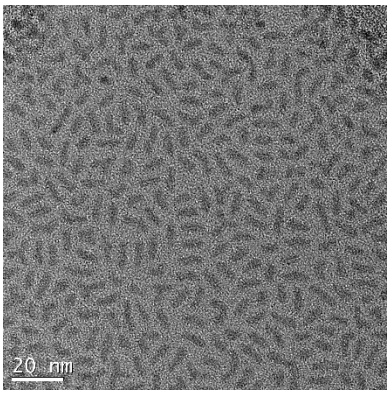

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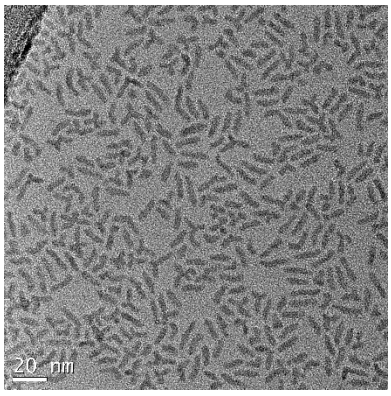

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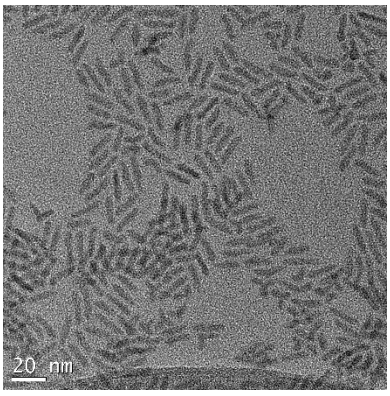

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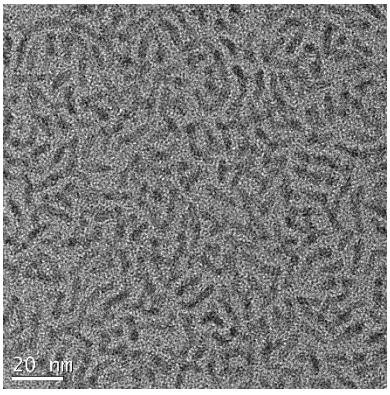

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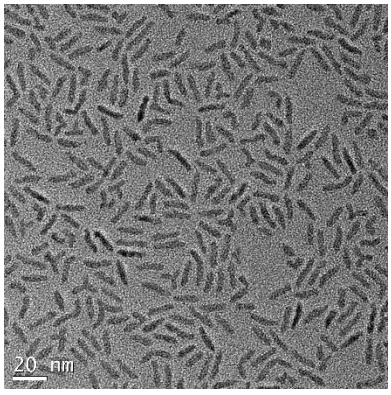

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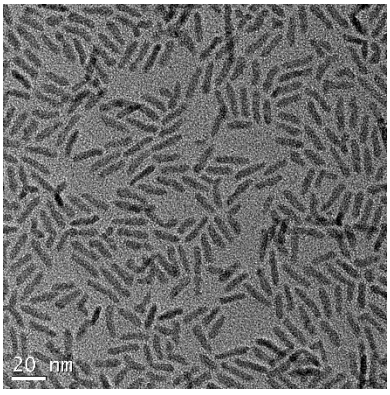

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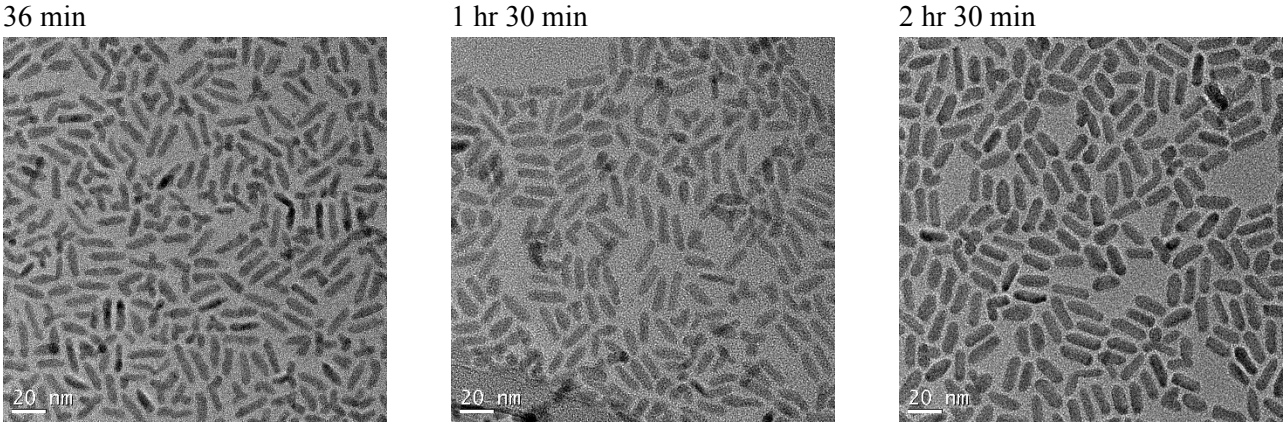

Figure S7. TEM images of growing CdSe nanorods upon $1.0*10^{-8}$ mol seeds.

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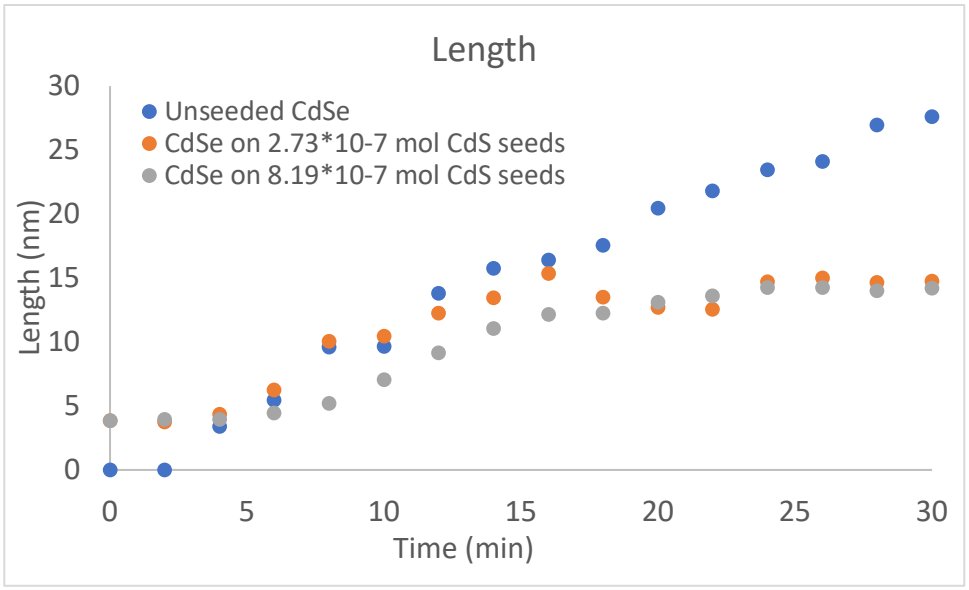

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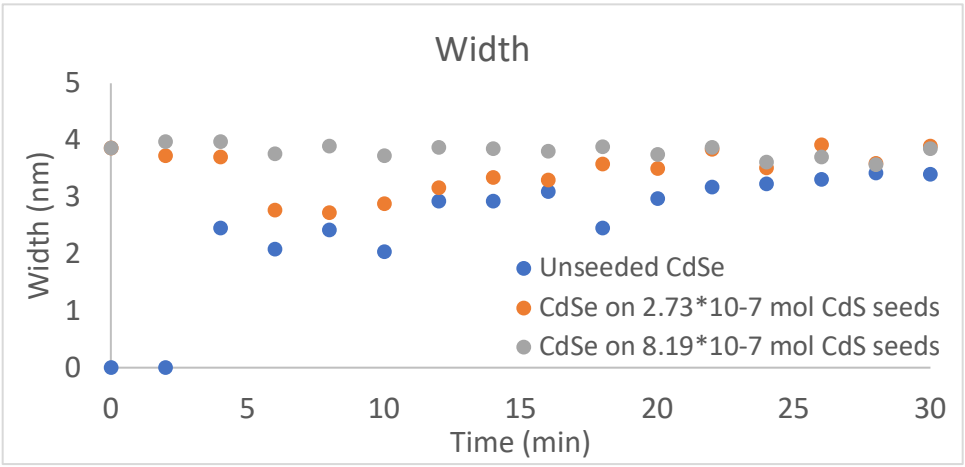

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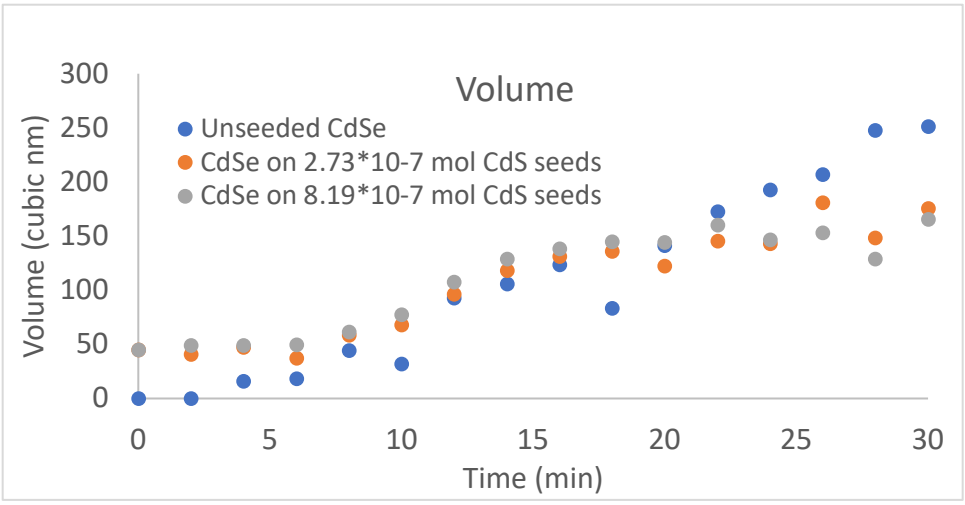
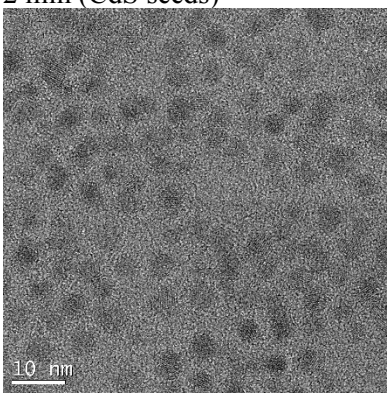


Figure S8. The length (A), width (B), and volume (C) profiles over time for CdSe nanorod growth when seeded with wurtzite CdS seeds.

2 min (CdS seeds)



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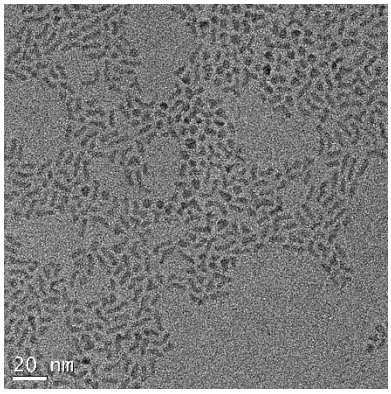

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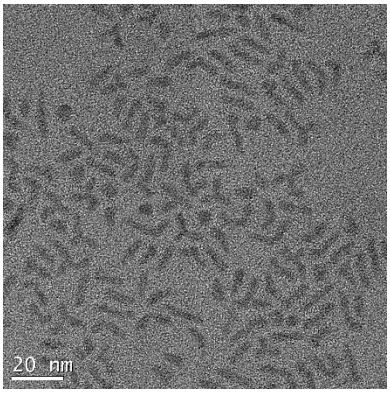

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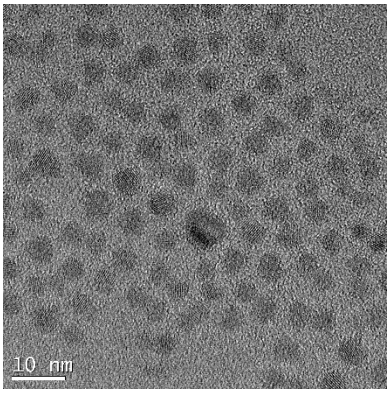

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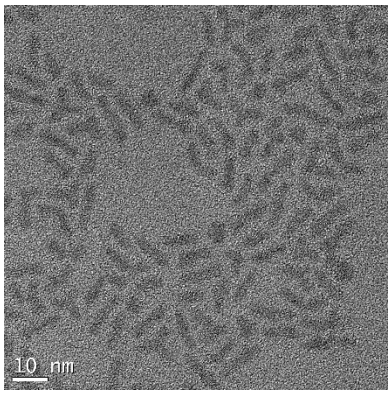

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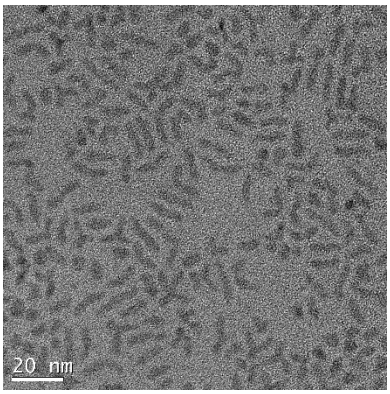

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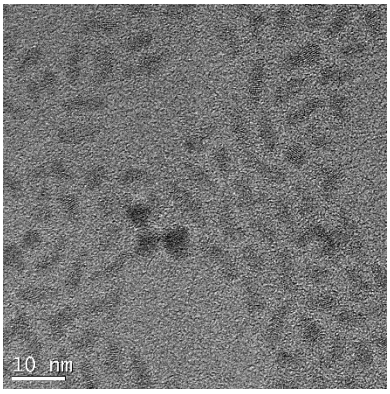

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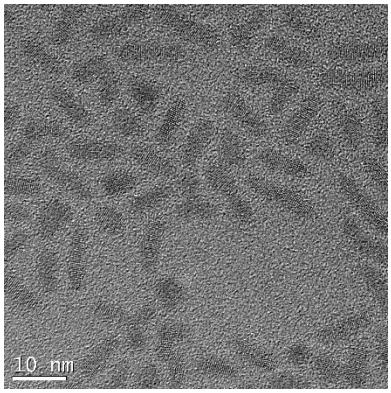
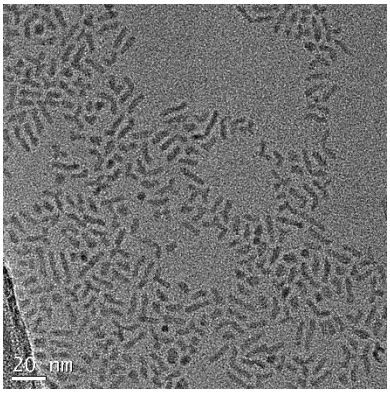
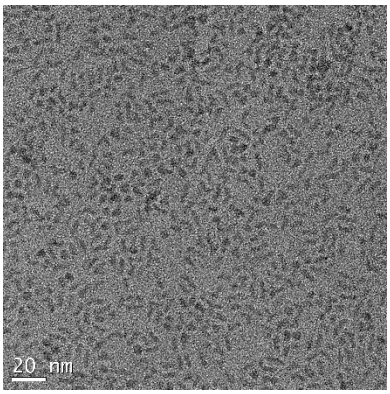


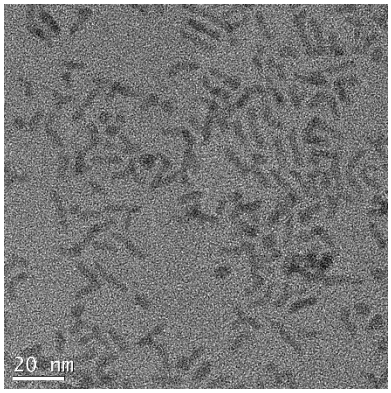
24 min



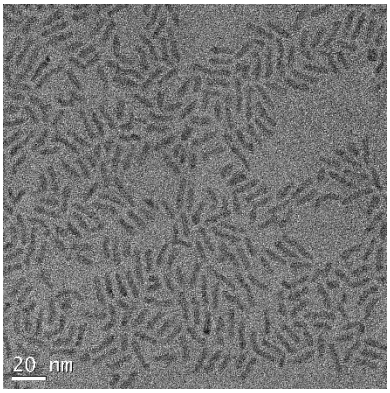
8 min



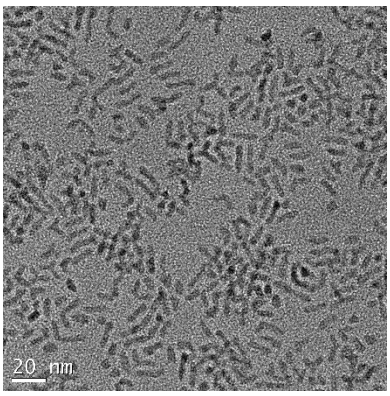
16 min



26 min



28 min



30 min

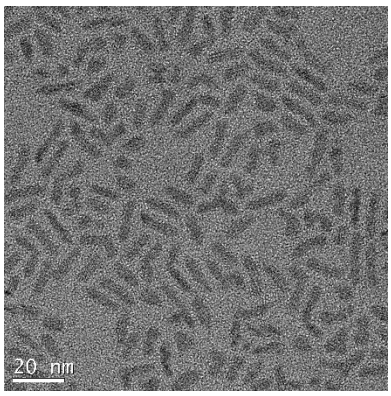
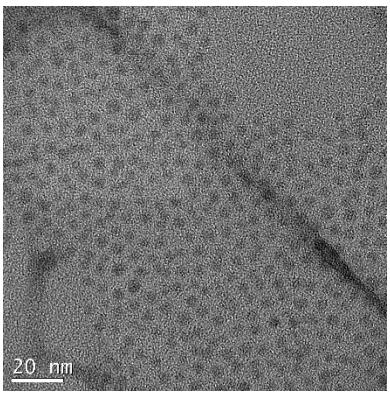
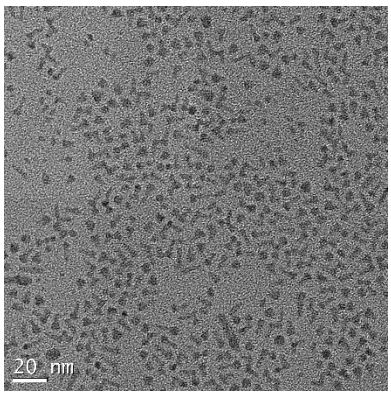


Figure S9. TEM images of CdSe nanorod growth on $2.73*10^{-7}$ mol CdS seeds.

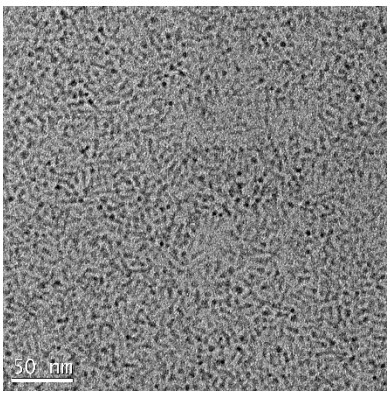
2 min



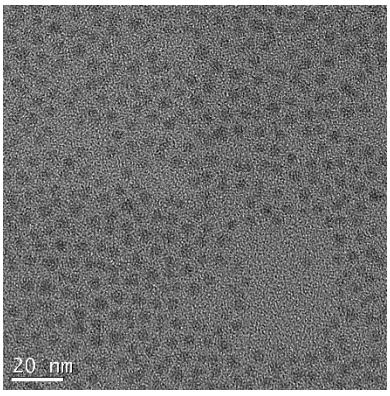
10 min



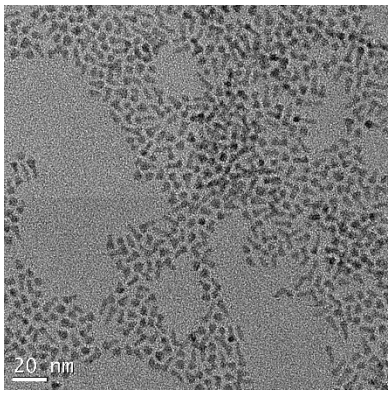
18 min



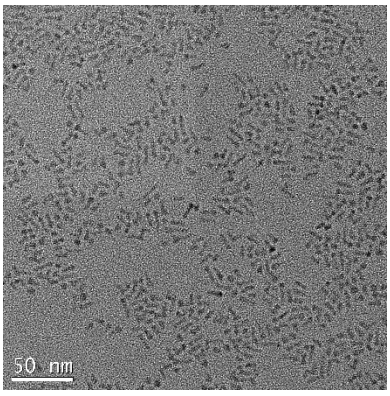
4 min



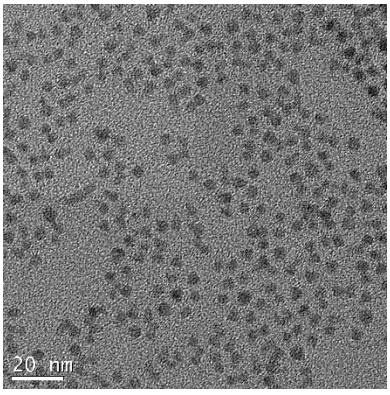
12 min



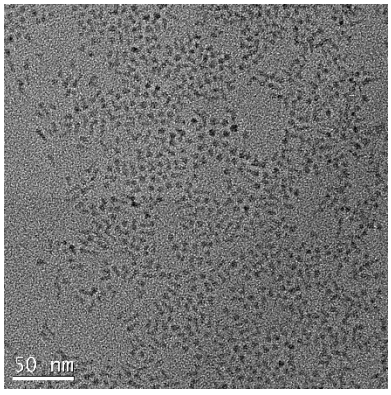
20 min



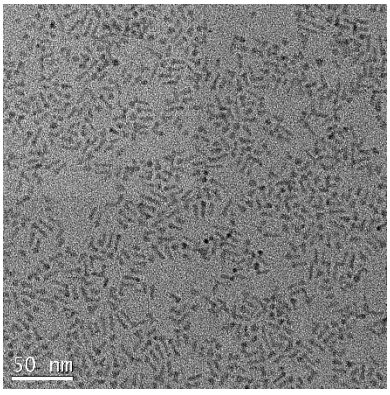
6 min



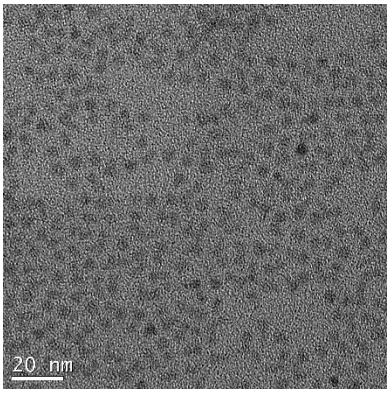
14 min



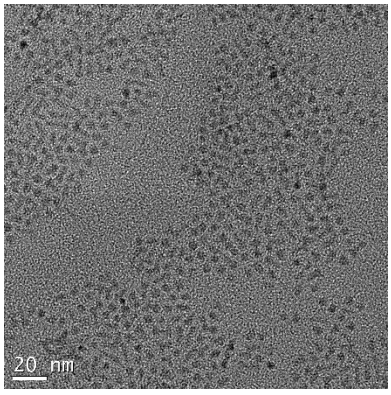
22 min



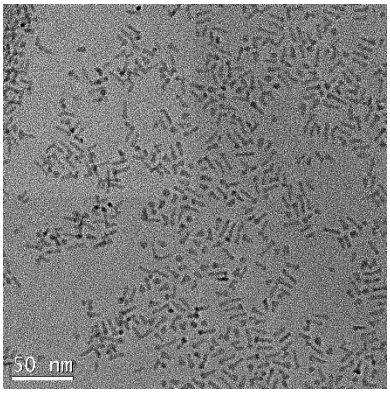
8 min



16 min



24 min



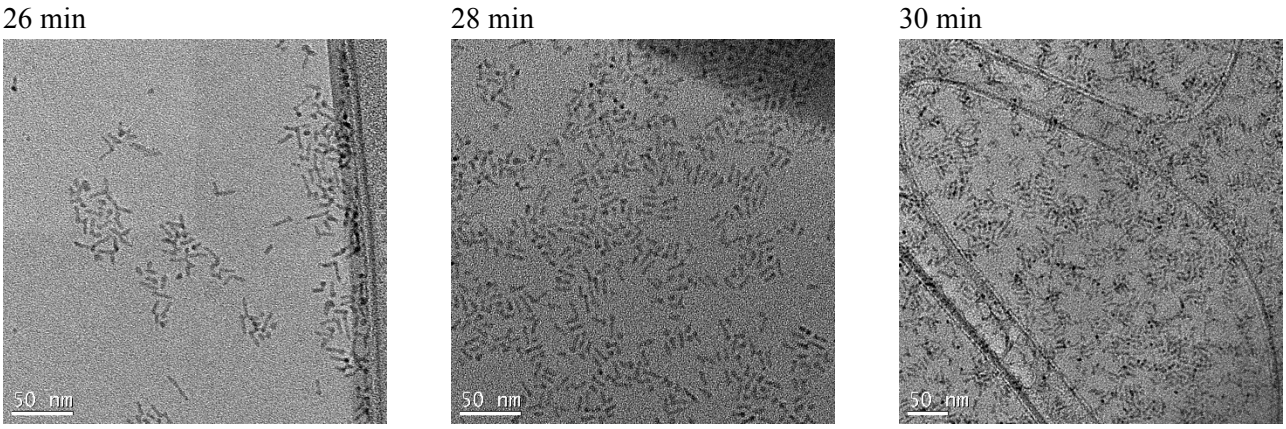
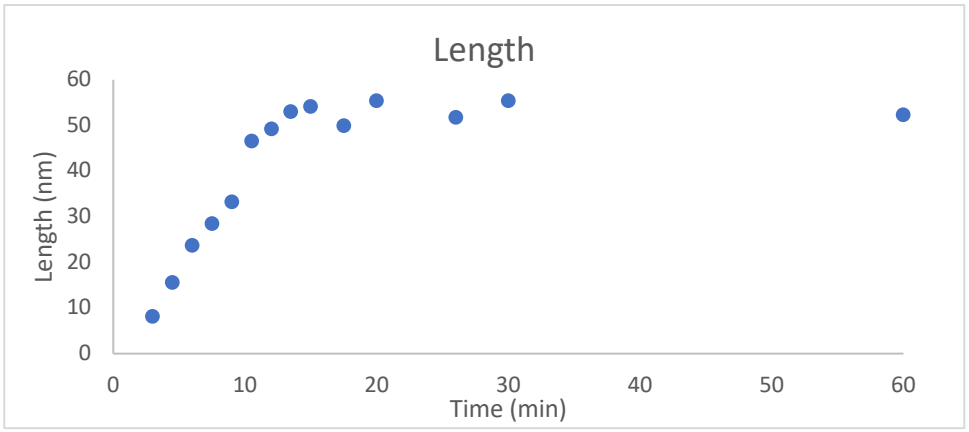
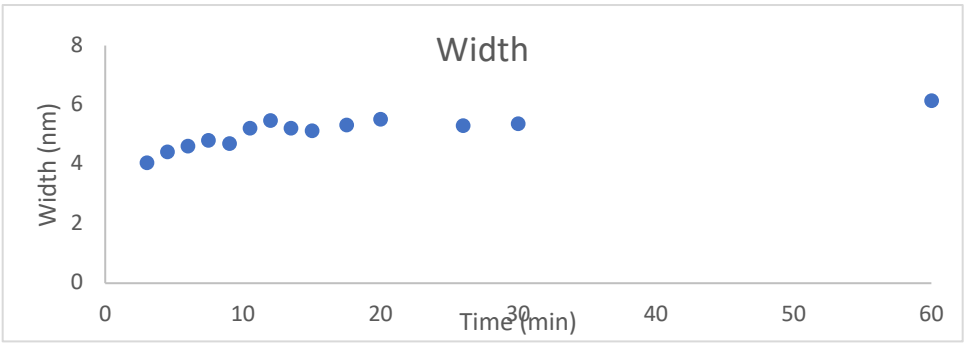


Figure S10. TEM images of CdSe nanorod growth on $8.19*10^{-7}$ mol CdS seeds.

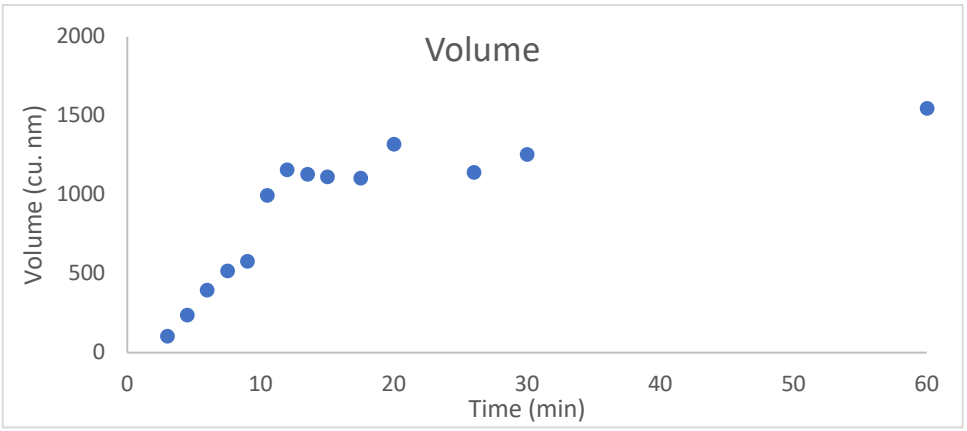
A)



B)



C)



D)

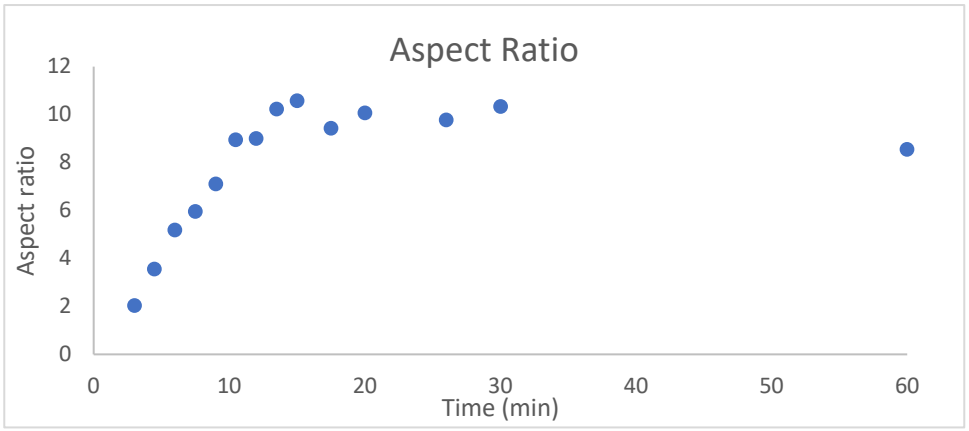
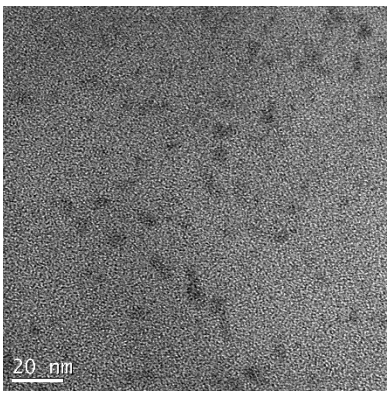
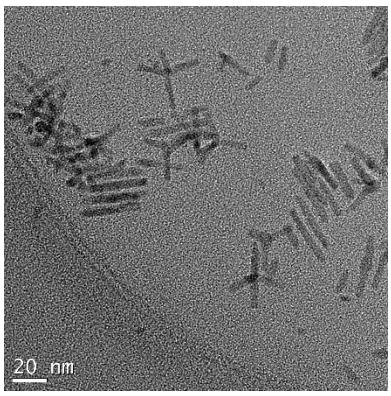


Figure S11. CdS growth on CdSe seeds: Length (A), width (B), volume (C), and aspect ratio (D) over time.

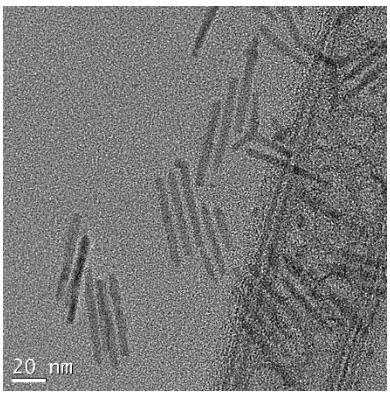
3 min



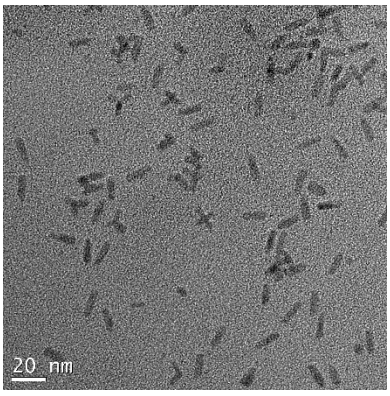
9 min



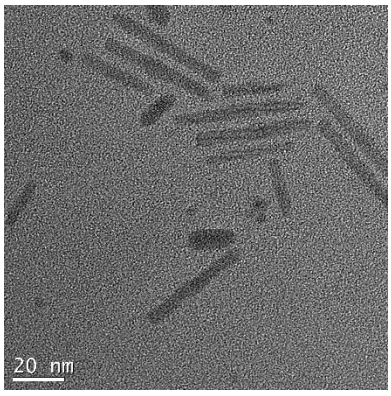
15 min



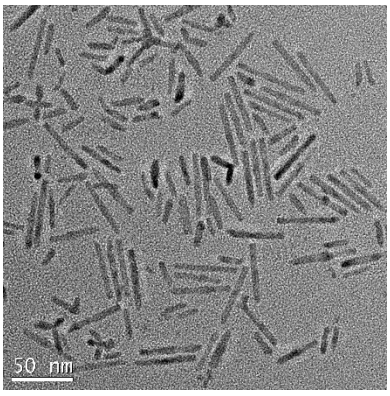
4.5 min



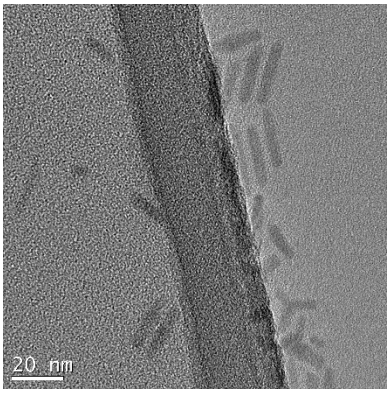
10.5 min



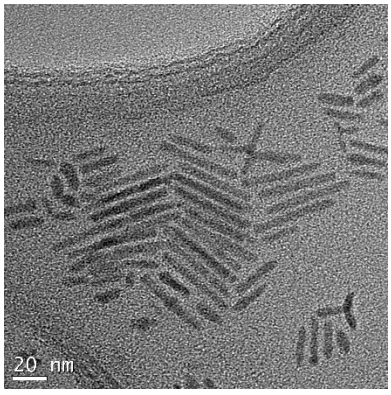
17.5 min



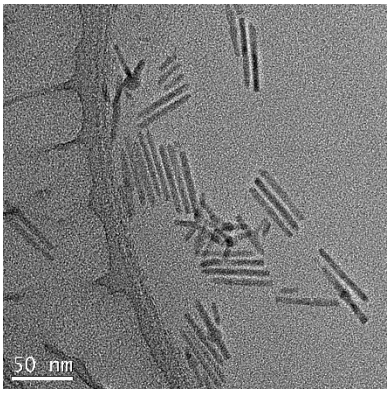
6 min



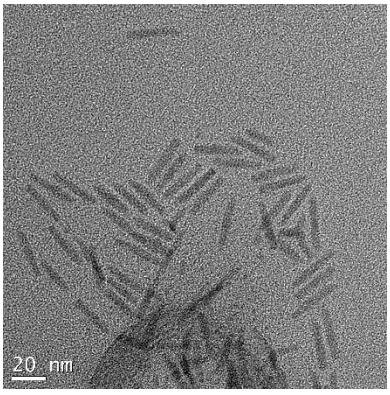
12 min



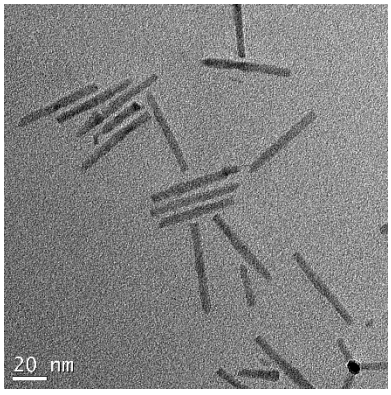
20 min



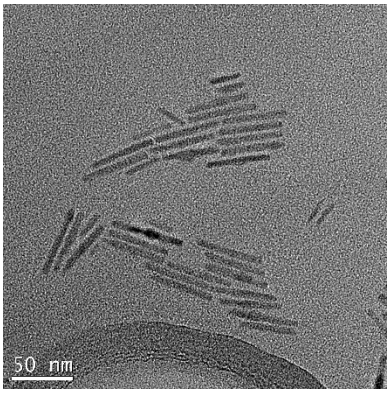
7.5 min



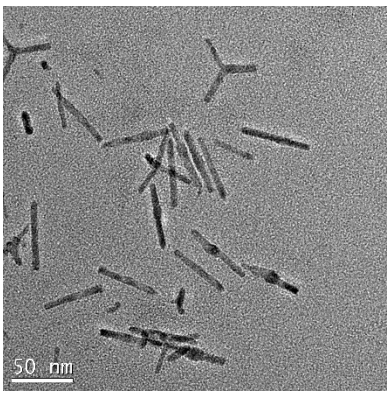
13.5 min



26 min



30 min



60 min

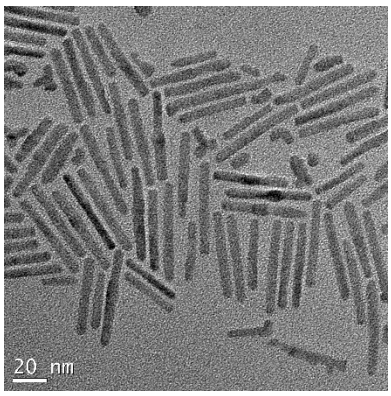
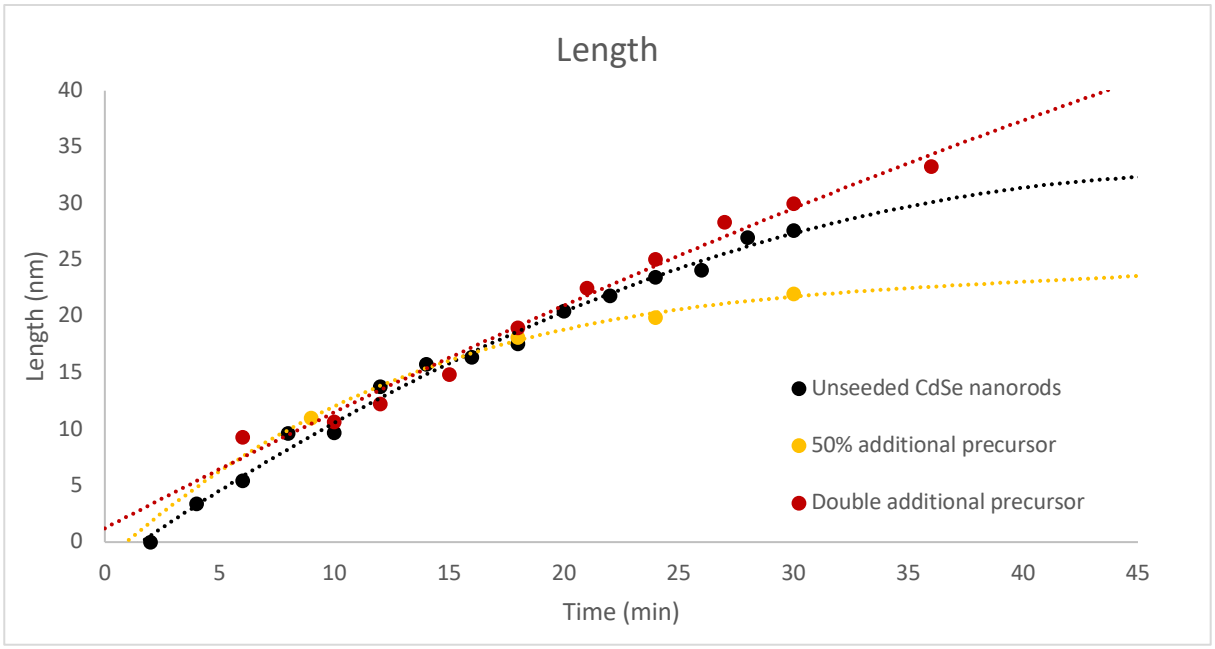
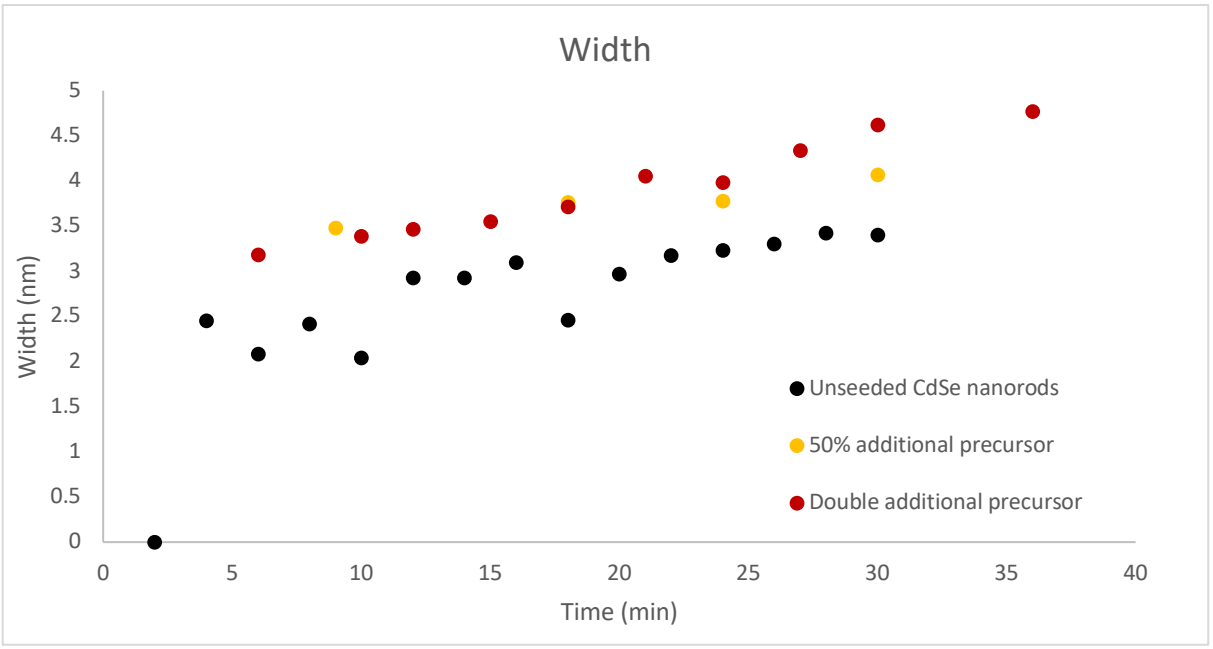


Figure S12. TEM images of the growing CdS nanorods on CdSe seeds.

A)

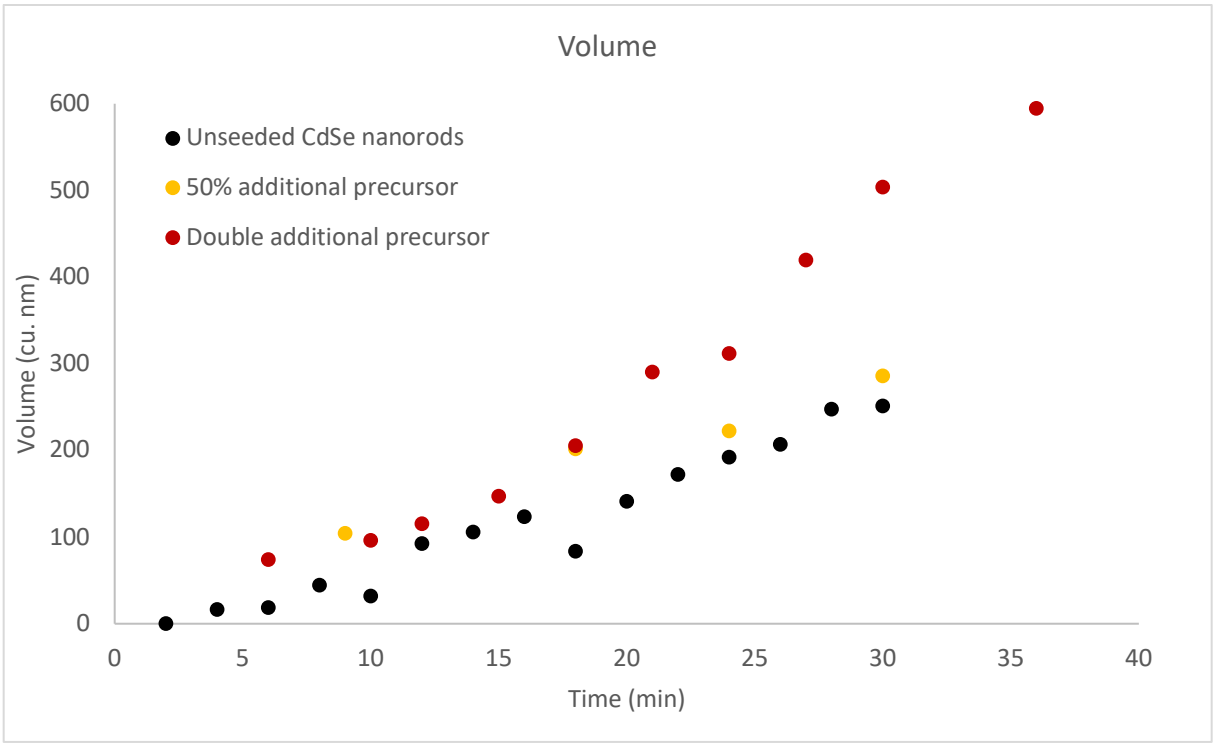


B)



(Continues on next page)

C)



D)

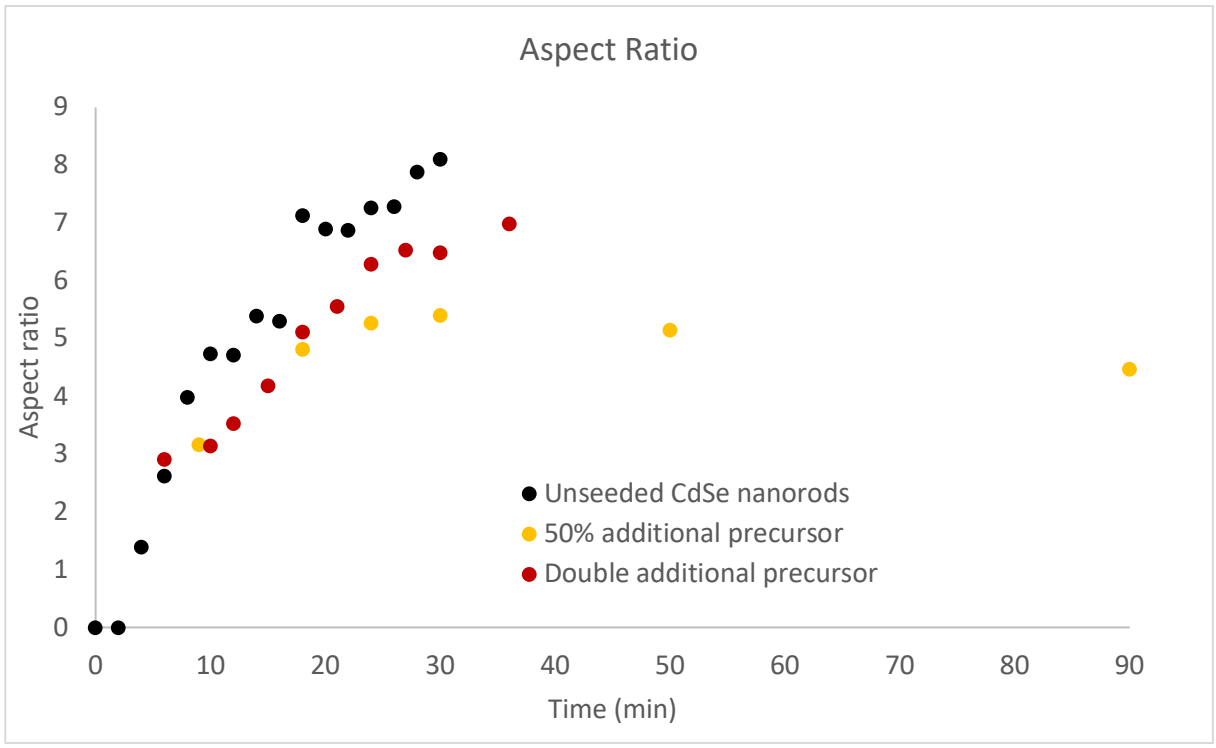


Figure S13. The length (A), width (B), volume (C), and aspect (D) profiles are tracked over time for CdSe nanorod growth facilitated by replenishment of additional precursor added all at once at 7 min 30 s.

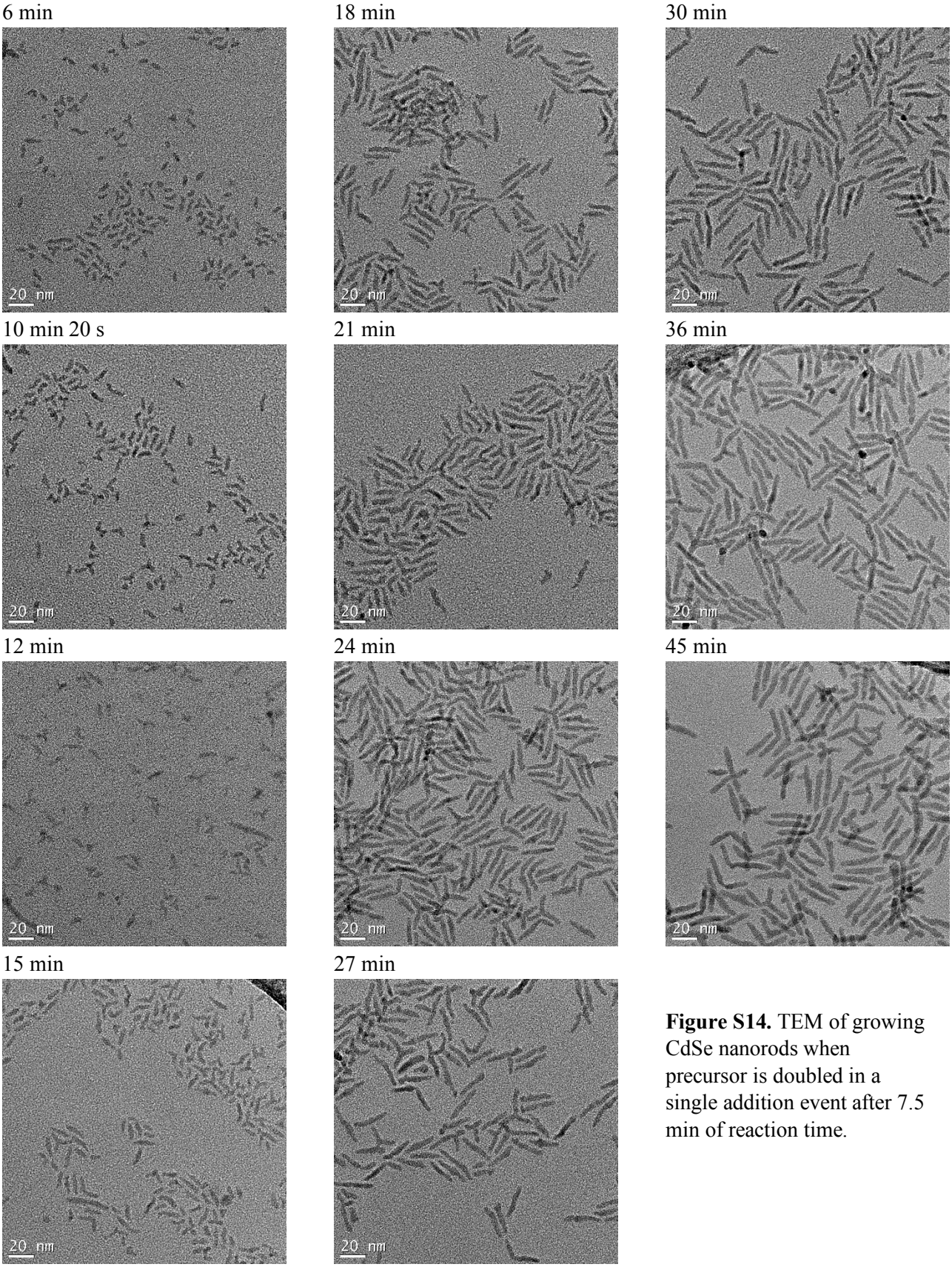


Figure S14. TEM of growing CdSe nanorods when precursor is doubled in a single addition event after 7.5 min of reaction time.

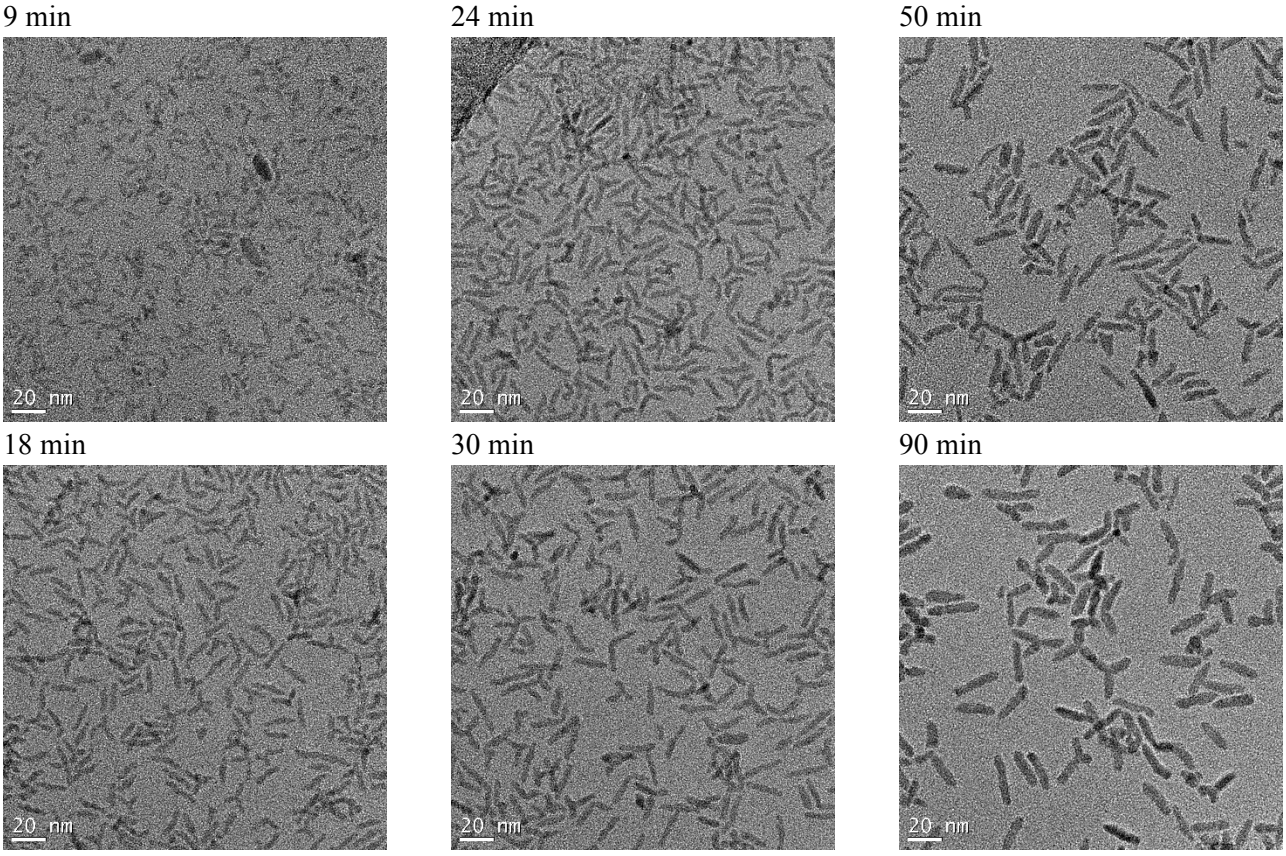
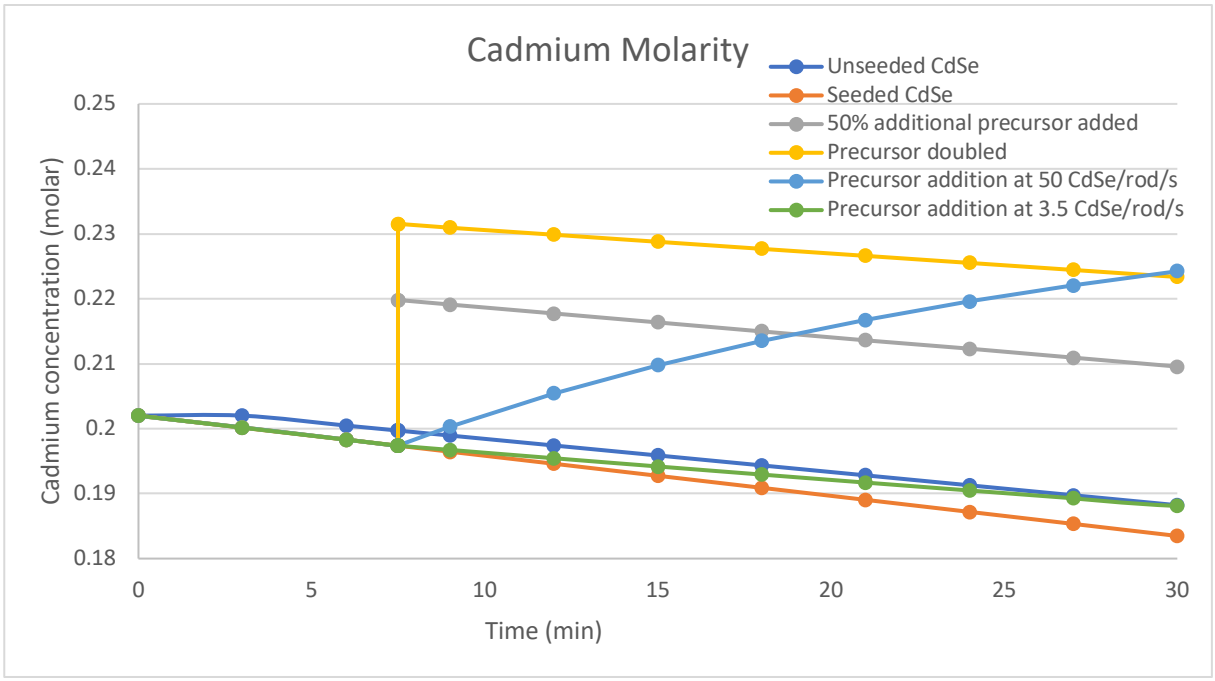
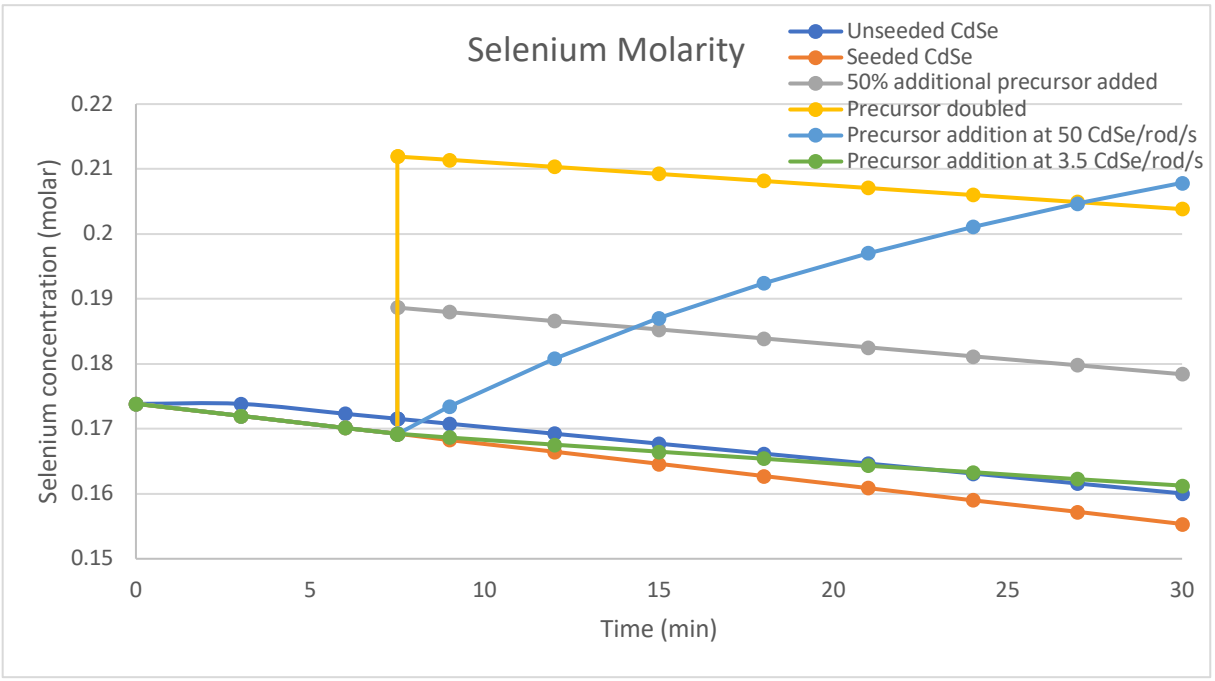


Figure S15. TEM of growing CdSe nanorods when 50% more precursor is added in a single event after 7.5 min of reaction time.

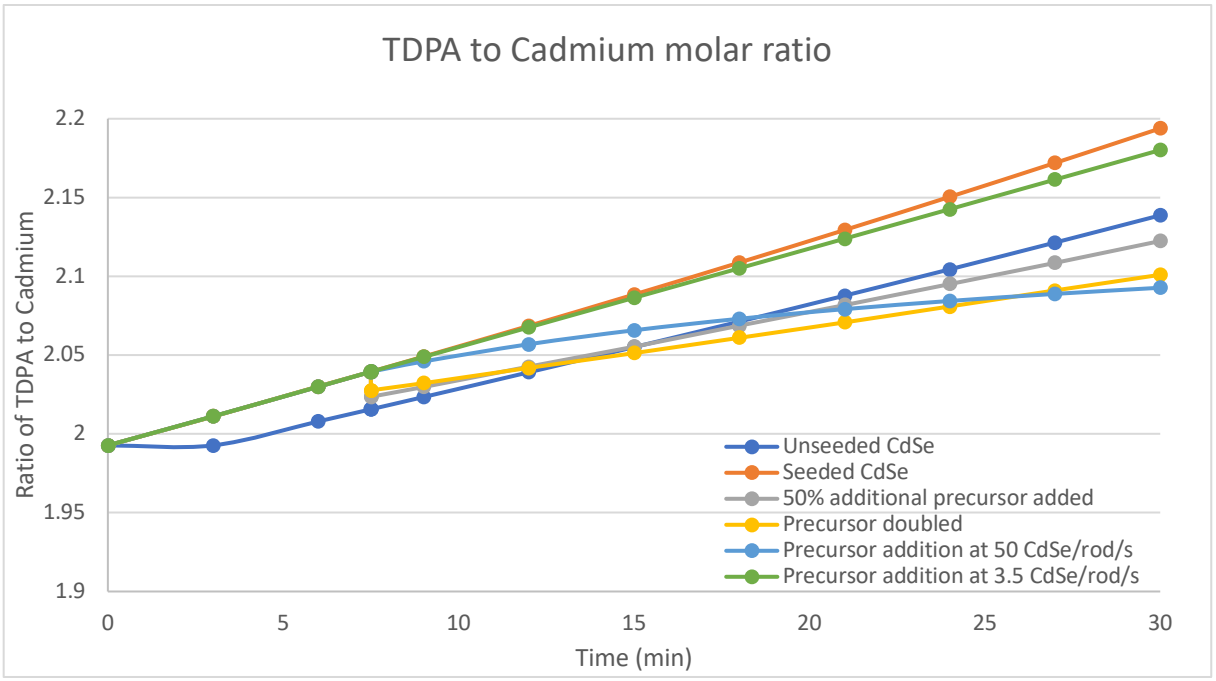
A)


Cadmium Molarity
Unseeded CdSe
Seeded CdSe
50% additional precursor added
Precursor doubled
Precursor addition at 50 CdSe/rod/s
Precursor addition at 3.5 CdSe/rod/s
Cadmium concentration (molar)
0.25
0.24
0.23
0.22
0.21
0.2
0.19
0.18
0
5
10
15
20
25
30
Time (min)

B)


Selenium Molarity
Unseeded CdSe
Seeded CdSe
50% additional precursor added
Precursor doubled
Precursor addition at 50 CdSe/rod/s
Precursor addition at 3.5 CdSe/rod/s
Selenium concentration (molar)
0.22
0.21
0.2
0.19
0.18
0.17
0.16
0.15
0
5
10
15
20
25
30
Time (min)

C)



D)

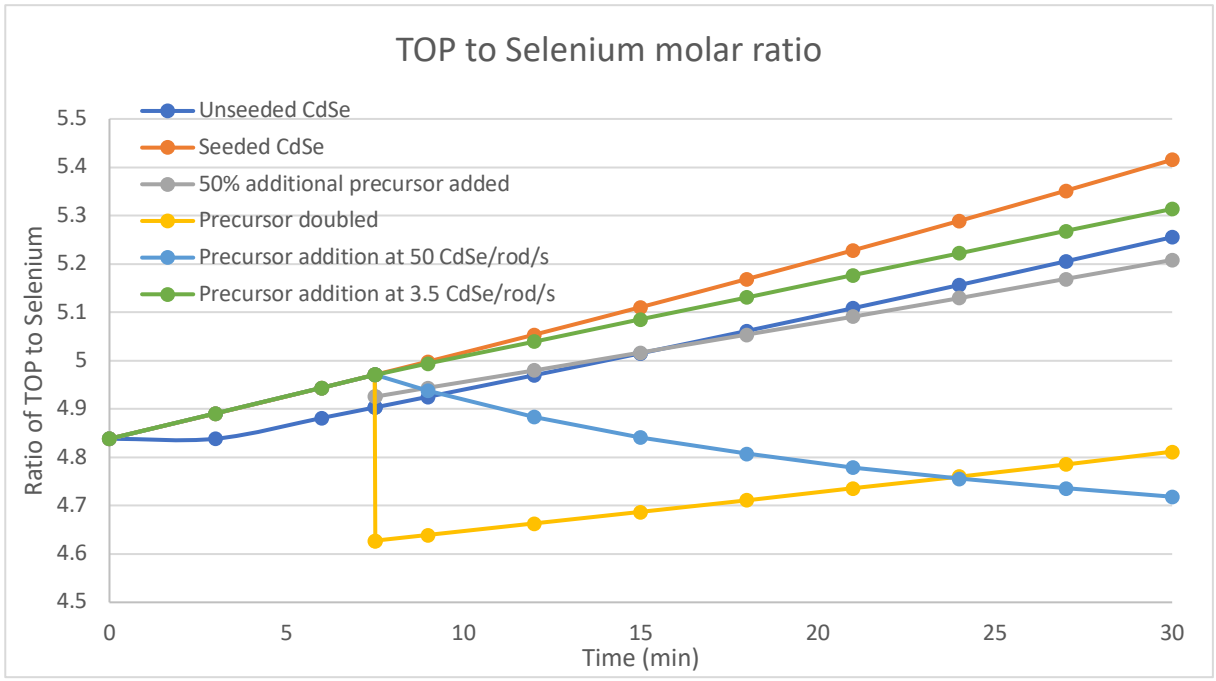
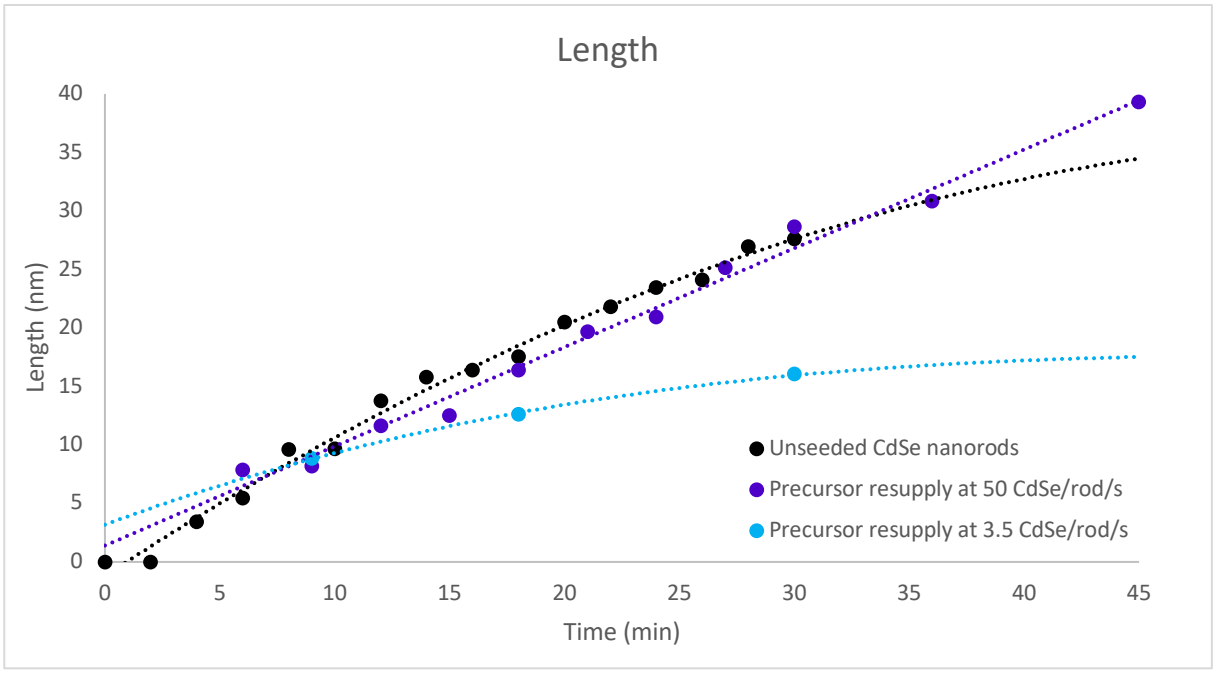
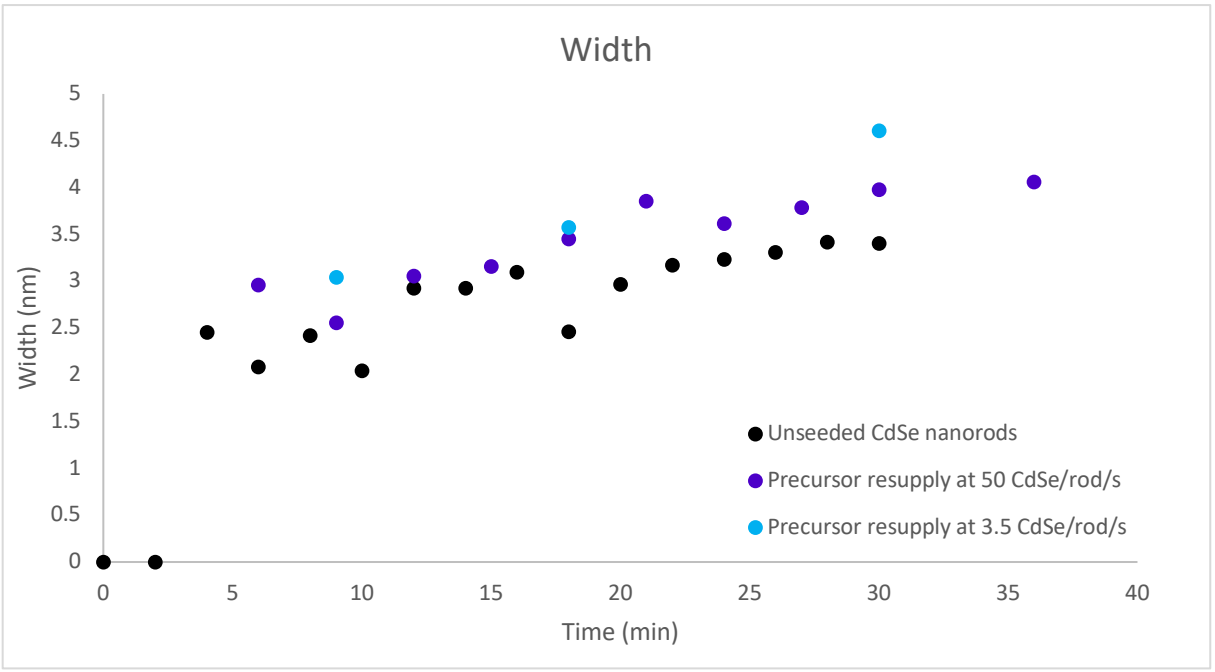


Figure S16. Evaluation of precursor concentrations and Cd/Se to ligand ratios to determine thresholds for extending the duration of the 1-D growth regime. Concentration of cadmium (A) and selenium (B) are shown with ligand to Cd/Se ratios for TDPA to Cadmium (C) and TOP to Selenium (D) are simulated over the first 30 min of the reaction assuming constant growth rates for the nanorods.

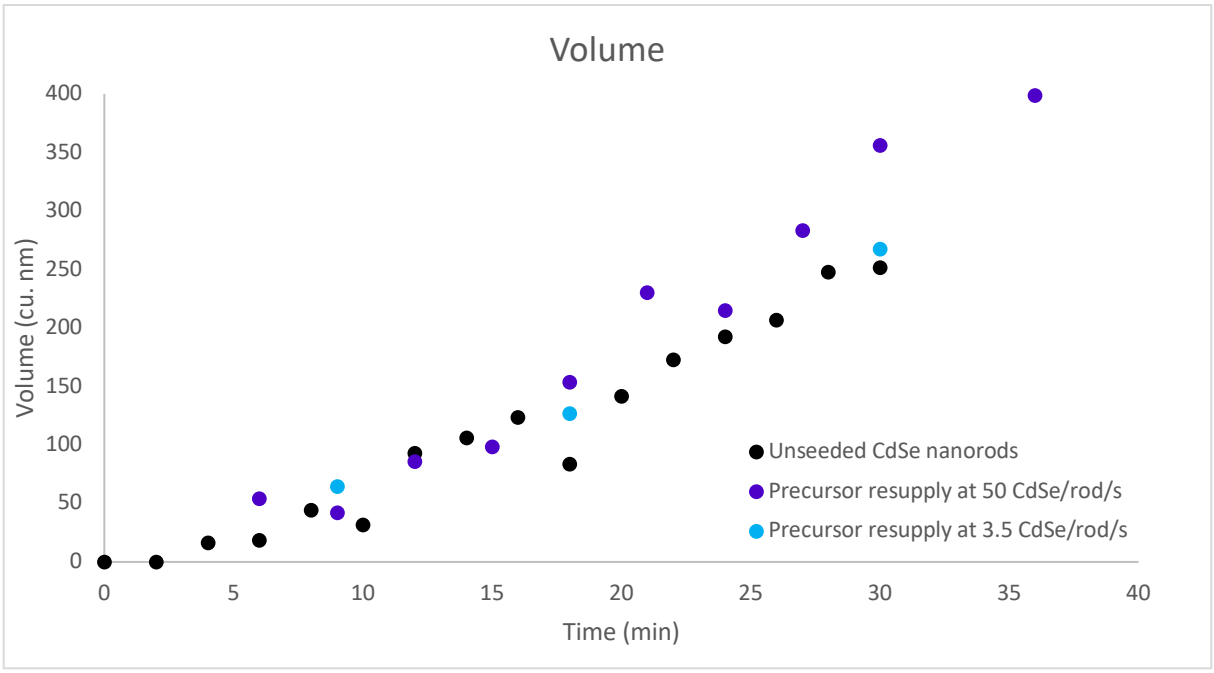
A)


Length
Length (nm)
Time (min)
Unseeded CdSe nanorods
Precursor resupply at 50 CdSe/rod/s
Precursor resupply at 3.5 CdSe/rod/s

B)


Width
Width (nm)
Time (min)
Unseeded CdSe nanorods
Precursor resupply at 50 CdSe/rod/s
Precursor resupply at 3.5 CdSe/rod/s

C)



D)

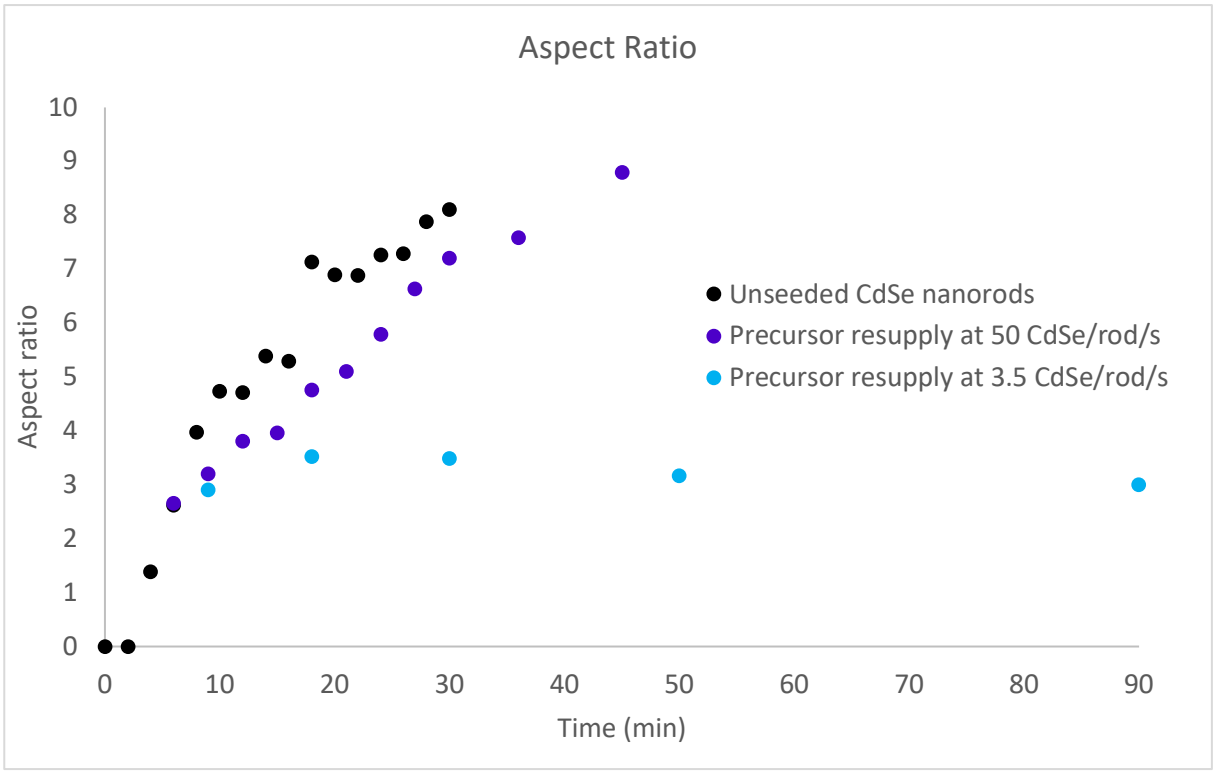


Figure S17. Replenishment of additional precursor: Length (A), width (B), volume (C), and aspect (D) profiles over time.

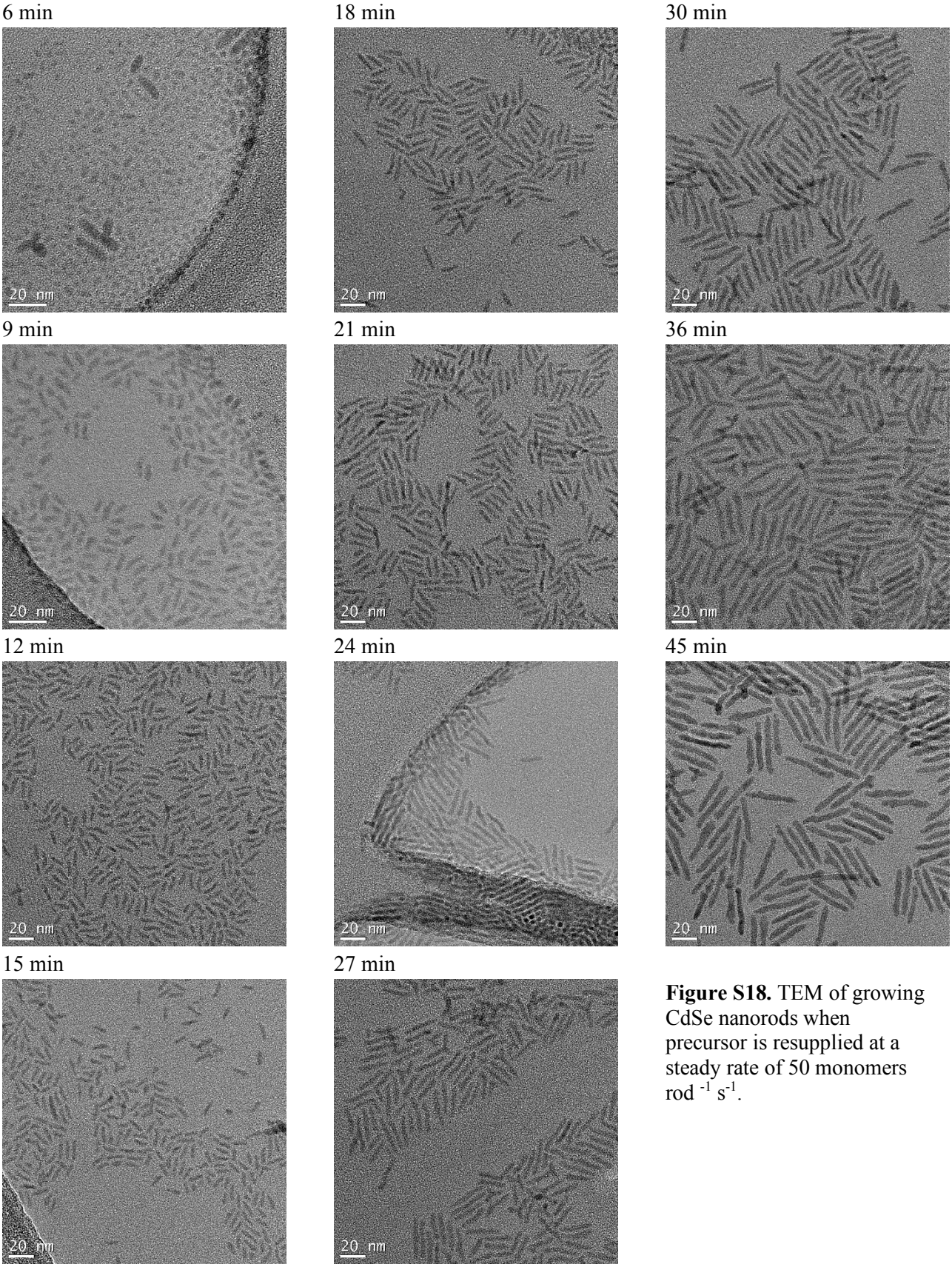


Figure S18. TEM of growing CdSe nanorods when precursor is resupplied at a steady rate of 50 monomers rod $^{-1}$ s^{-1}.

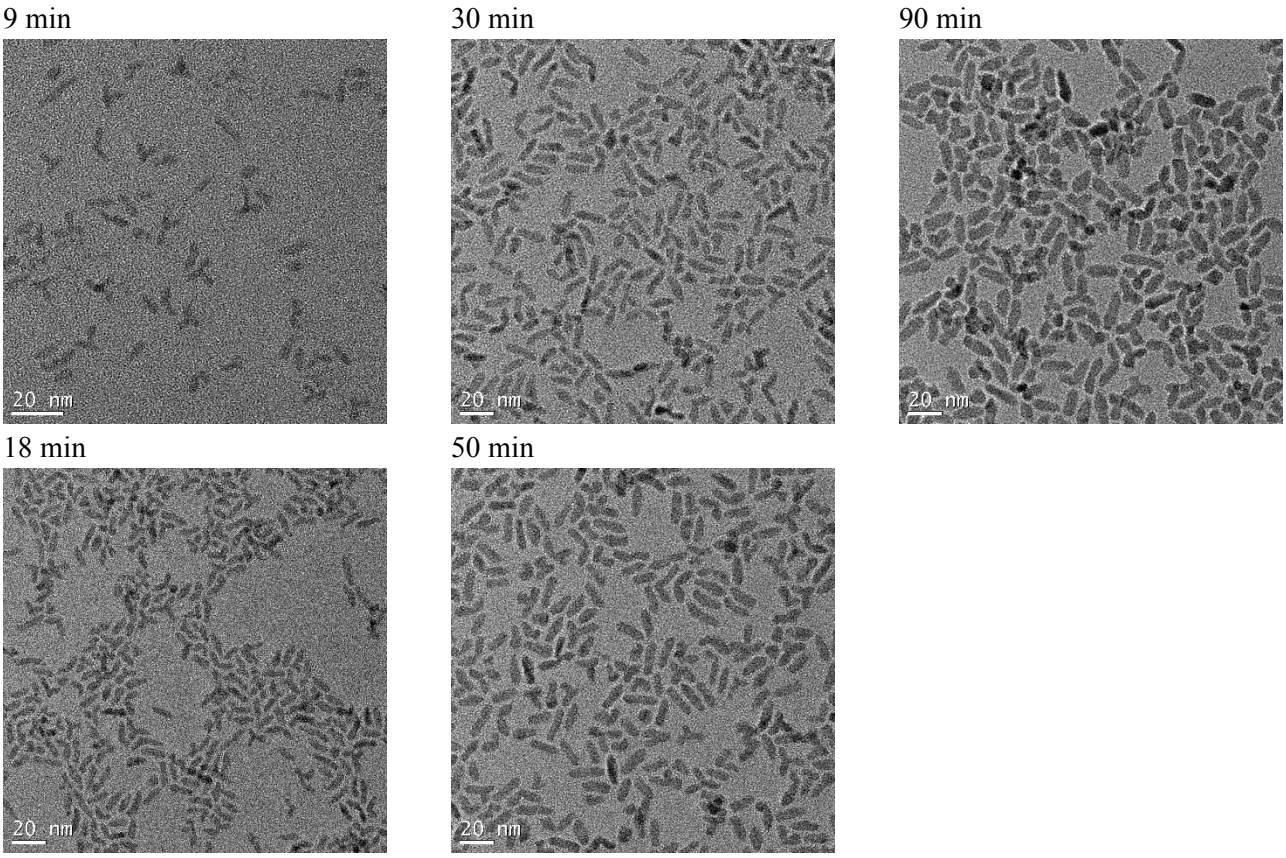
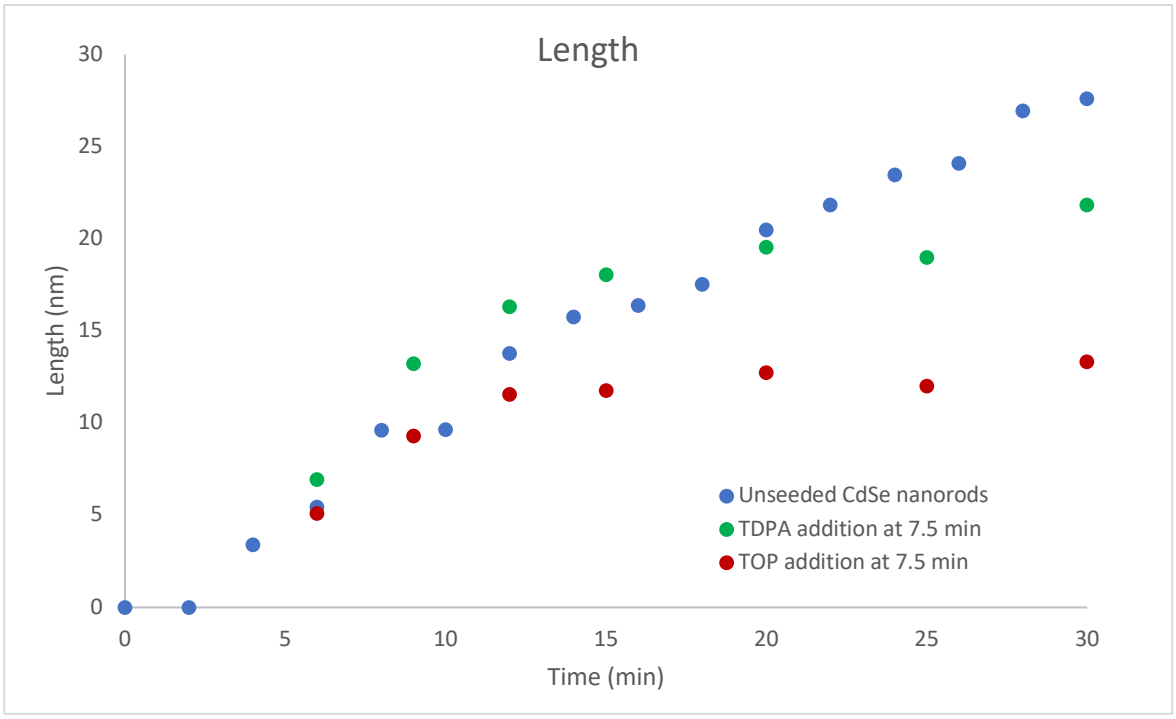
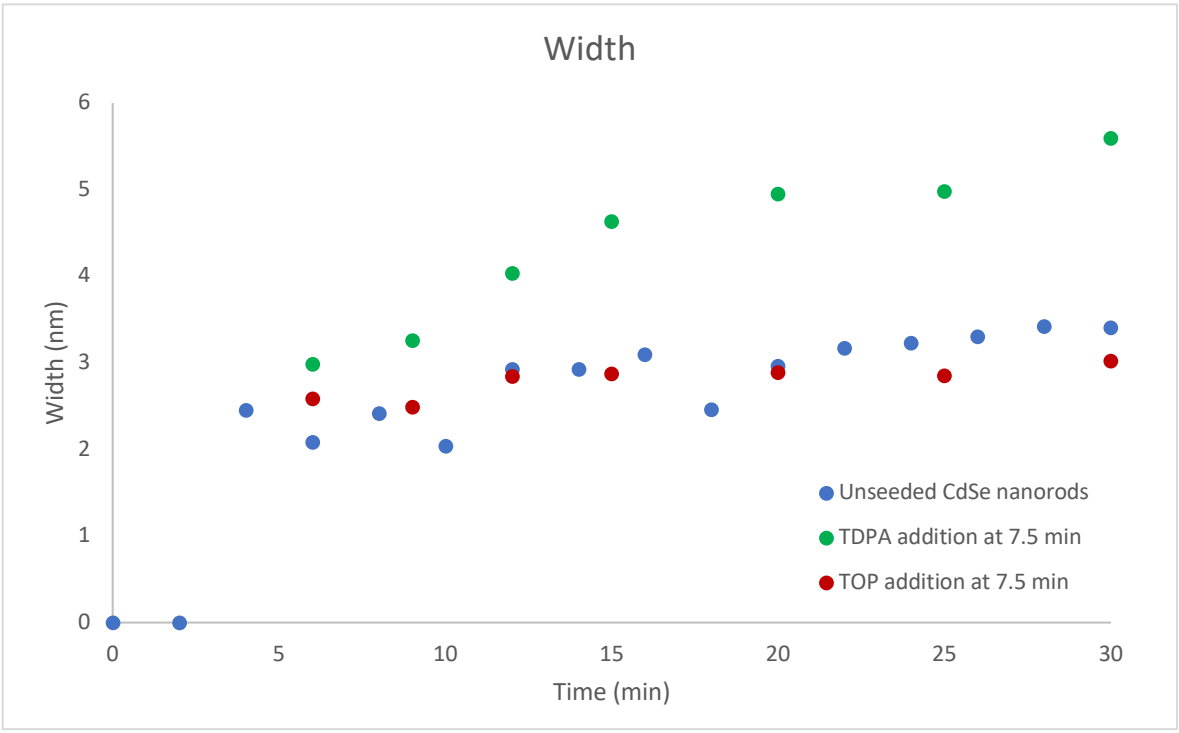


Figure S19. TEM of growing CdSe nanorods when precursor is resupplied at a steady rate of 3.5 monomers rod $^{-1}$ s^{-1}.

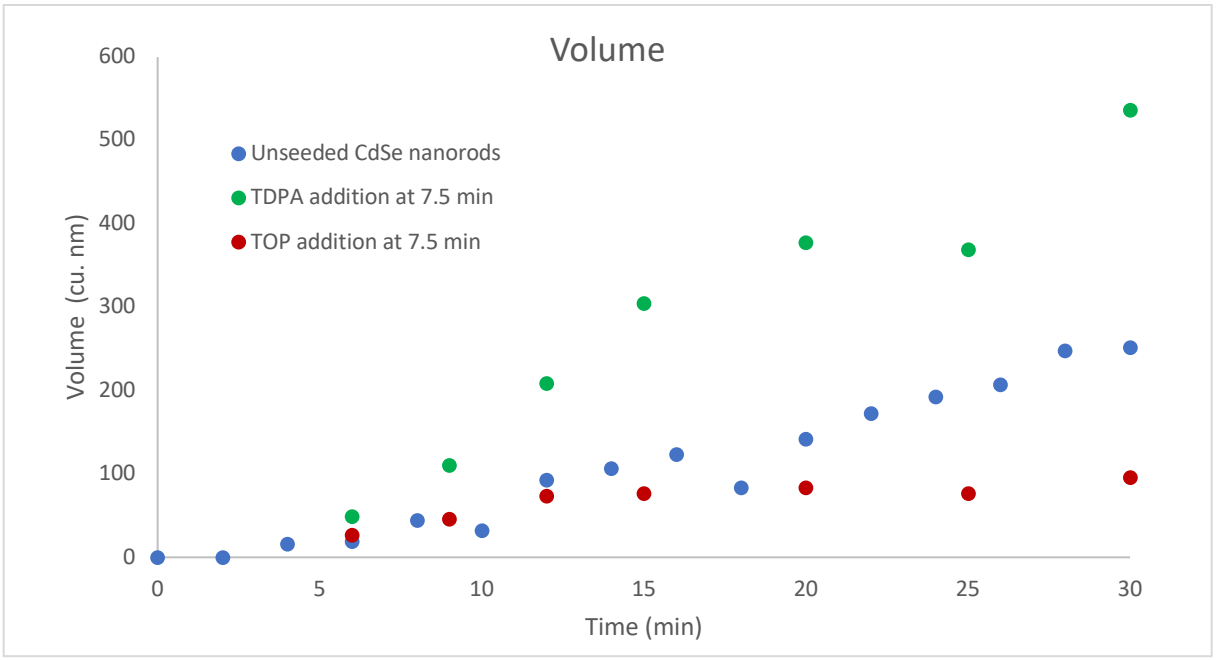
A)


Length
Length (nm)
Time (min)
0
5
10
15
20
25
30
Unseeded CdSe nanorods
TDPA addition at 7.5 min
TOP addition at 7.5 min

B)


Width
Width (nm)
Time (min)
0
1
2
3
4
5
6
0
5
10
15
20
25
30
Unseeded CdSe nanorods
TDPA addition at 7.5 min
TOP addition at 7.5 min

C)



D)

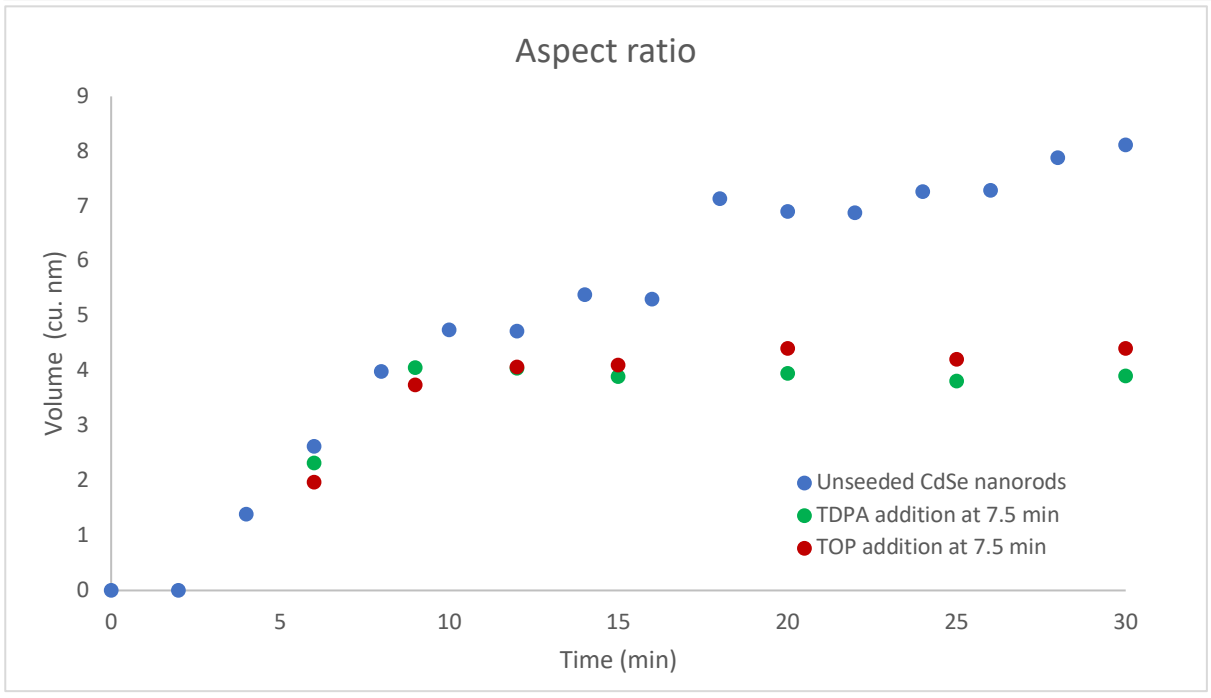


Figure S20. Additional TDPA or TOP added to growing CdSe nanorods. Additional TDPA, 0.14 g to push the TDPA:Cd ratio over 2.1:1, is added at 7.5 min to force premature exit from the 1-D growth regime. Likewise, additional TOP, 0.3 mL to push the TOP:Se ratio just over 5.1:1, is added at 7.5 min under otherwise identical growth conditions to typical CdSe nanorod growth. Length (A), width (B), volume (C), and aspect ratio (D) illustrate an early departure from the 1-D growth regime when TDPA or TOP is added to the growing nanorods.

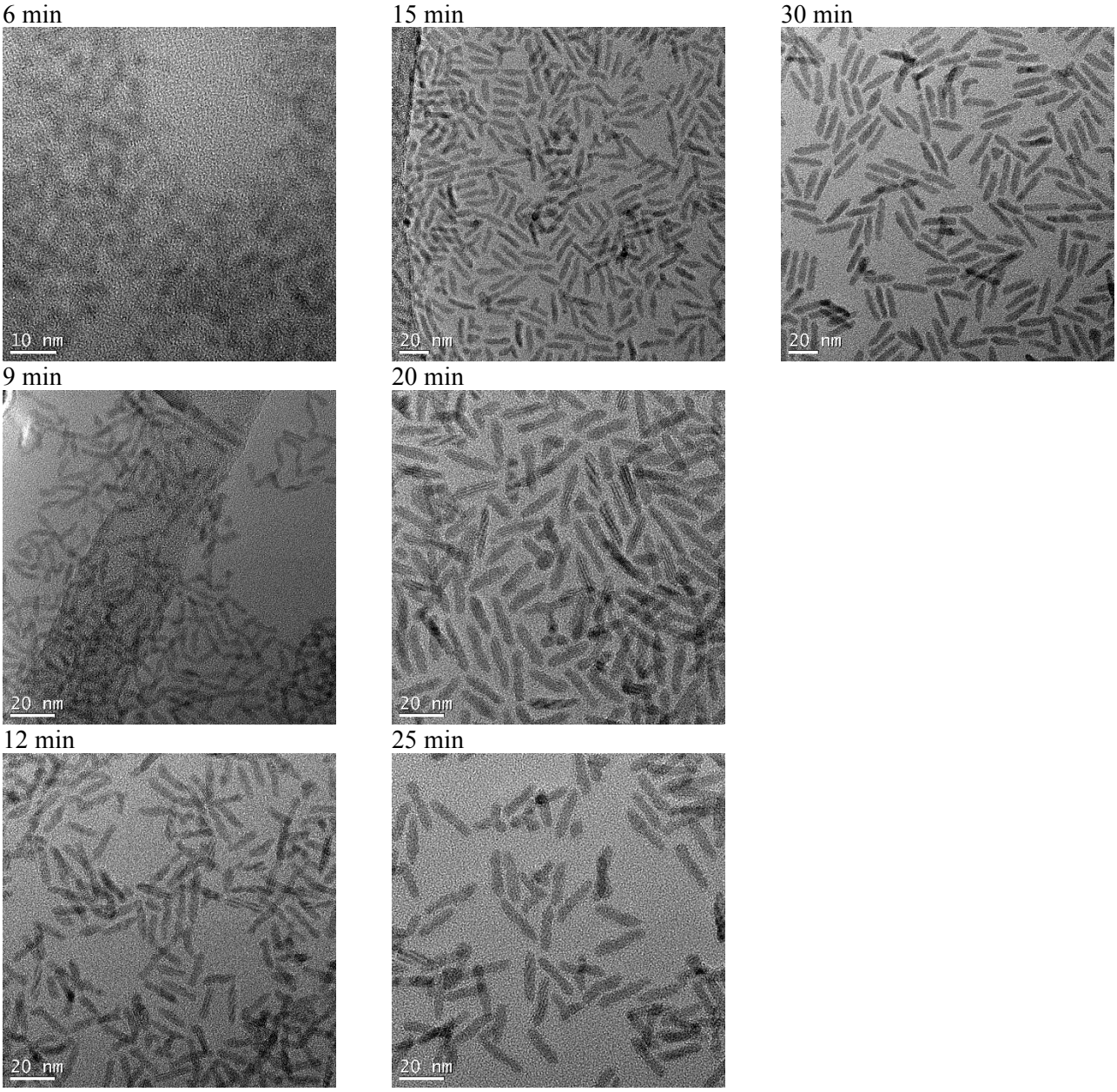


Figure S21. TEM of growing CdSe nanorods when extra TDPA is added at 7.5 min.

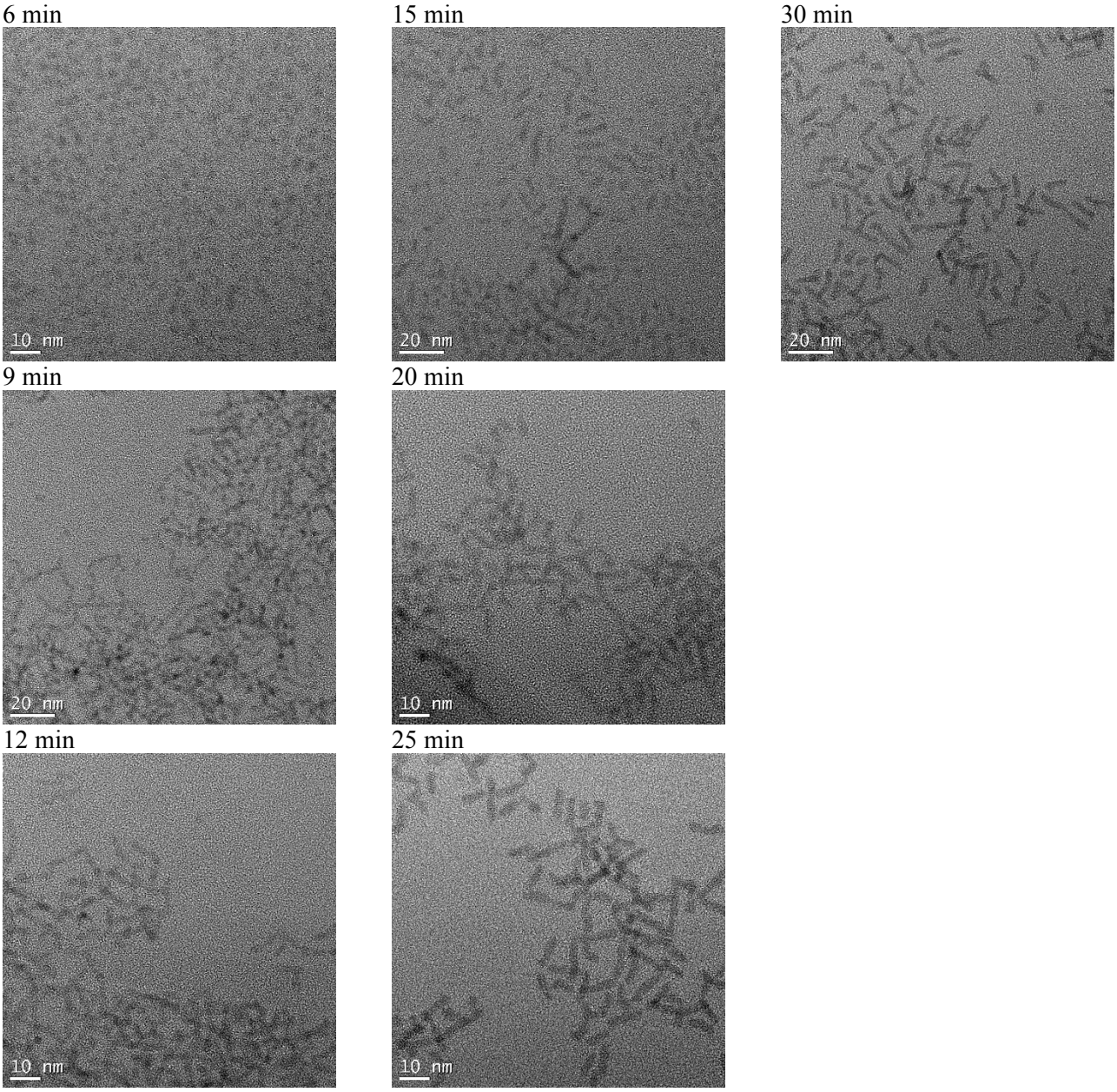


Figure S22. TEM of growing CdSe nanorods when extra TOP is added at 7.5 min.