Electronic Supplementary Information (ESI)

Symmetry breaking in semiconductor nanocrystals *via* kinetic-controlled surface diffusion: a strategy for manipulating the junction structure

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Calculation details

Specific surface area

$$S = \frac{A}{V * \rho}$$

S represents for specific surface area; *A* represents for surface area; *V* represents for volume; ρ represents for density of CdS (ρ = 4.626 × 10^6 g m^{-3}). Neglecting the small ZB cores/tips, the surface area could be estimated as follow:

$$A = \left[2 * \frac{\pi}{4}d^2 + \pi dl\right] \times R_1 + \left[\frac{\pi}{4}d^2 + \pi dl\right] \times (R_2 + R_3)$$

$$V = \pi\left(\frac{d}{2}\right)^2 l$$

Herein, *d* represents for the diameter of CdS nanorod; *l* represents for the length of CdS nanorod; R_1, R_2, R_3 for the ratio of one-armed, two-armed and three/four armed CdS nanorods.

Exposed facets percentage

Each ZB seed was enclosed by four {111} facets. To lower total surface energy, we regard each {111} facet as a round, whose diameter equaled to the diameter of nanorod. Therefore, the surface area of each facet would be:

$$A_{\{111\}} = \frac{\pi}{4}d^2$$

Supposing each WZ arm was a cylinder enclosed by {100} and {001} facets, the surface area of the {100} facets in one arm could be calculated as:

$$A_{\{100\}} = \pi dl$$

The surface area of the {001} facet in one arm, equaling to the surface area of one ZB {111} facet, also could be calculated as:

$$A_{\{001\}} = \frac{\pi}{4}d^2$$

Therefore, for monopod, the percentage of ZB {111} facet was:

$$P_{\{111\}-1} = \frac{3A_{\{111\}}}{3A_{\{111\}} + A_{\{100\}} + A_{\{001\}}}$$

For bipod, the percentage of ZB {111} facet was:

$$P_{\{111\}-2} = \frac{2A_{\{111\}}}{2A_{\{111\}} + 2A_{\{100\}} + 2A_{\{001\}}}$$

For tripod, the percentage of ZB {111} facet was:

$$P_{\{111\}-3} = \frac{A_{\{111\}}}{A_{\{111\}} + 3A_{\{100\}} + 3A_{\{001\}}}$$

For tetrapod, the percentage of ZB {111} facet was:

$$P_{\{111\}-4} = \frac{0}{4A_{\{100\}} + 4A_{\{001\}}}$$

And the percentages of WZ {100} and {001} facets for different shapes could be calculated by the same way.

Because of the difficulty to distinguish tripod and tetrapod in TEM images, we suppose these two forms had equal occupancy ratio. Therefore, for each sample, the percentage of ZB {111} facets could be estimated as:

$$P_{\{111\}} = P_{\{111\}-1} * R_1 + P_{\{111\}-2} * R_2 + P_{\{111\}-2} * \frac{R_3}{2} + P_{\{111\}-4} * \frac{R_3}{2}$$

And the percentages of WZ {100} and {001} facets for different samples could be calculated by the same way.

Surface oleylamine content

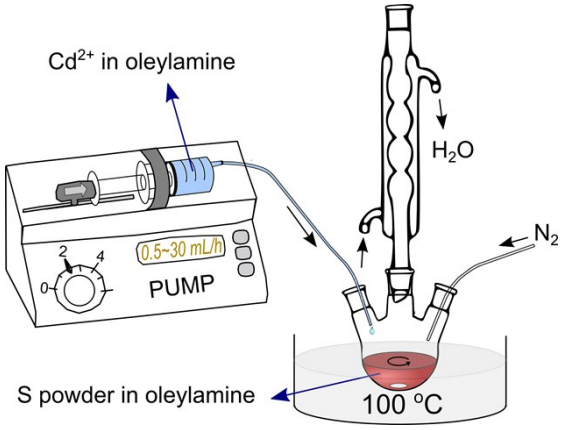
We calculated the surface oleylamine content using the following formula:

$$r_o = \frac{m_o}{m_{CdS} + m_o} = \frac{n_o * M_o}{\rho_{CdS} * V_{CdS} + n_o * M_o} = \frac{\frac{A_{CdS,100}}{A_{o,1} * N_A} * M_o}{\rho_{CdS} * V_{CdS} + \frac{A_{CdS,100}}{A_{o,1} * N_A} * M}$$

$$= \frac{\frac{1}{A_{S,1} * N_A} * M_o}{\rho_{CdS} * \frac{d}{4} + \frac{1}{A_{S,1} * N_A} * M_o}$$

Herein, r_o represents for the mass ratio of surface oleylamine; m_o represents for the mass of surface oleylamine; m_{CdS} represents for the mass of CdS nanocrystals; n_o represents for mole number of surface oleylamine molecules; M_o represents for the molar mass of oleylamine; ρ_{CdS} represents for density of CdS; V_{CdS} represents for volume of CdS nanocrystals; $A_{CdS,100}$

represents for {100} surface area of CdS nanocrystals; $A_{o,1}$ represents for area occupied by a single oleylamine headgroup; *d* represents for the diameter of CdS nanocrystals; *l* represents for the length of CdS nanorod. We supposed each surface S atom on CdS {100} facets bonded an oleylamine molecule, and $A_{CdS,100}$ therefore equal to the area occupied by each surface S atom on {100} facets, which is denoted as $A_{S,1}$ here. Because each hexagonal CdS cell ($a = b = 0.413$ nm, $c = 0.671$ nm) contains two S atoms, $A_{S,1} = ac/2 = 0.277$ nm^2. We set $\rho_{CdS} = 4.826 \times 10^6$ g m^{-3}, $d = 3.0$ nm (consider the similar diameters of the nanocrystals), $N_A = 6.022 \times 10^{23}$ mol^{-1}, $M_o = 267.5$ g mol^{-1}. Based on these data, r_o could be calculated as 31.7%.



Scheme S1. Schematic illustration of automated experimental set-up for the controlled growth of CdS nanocrystals by adjusting Cd^{2+} injection rate.

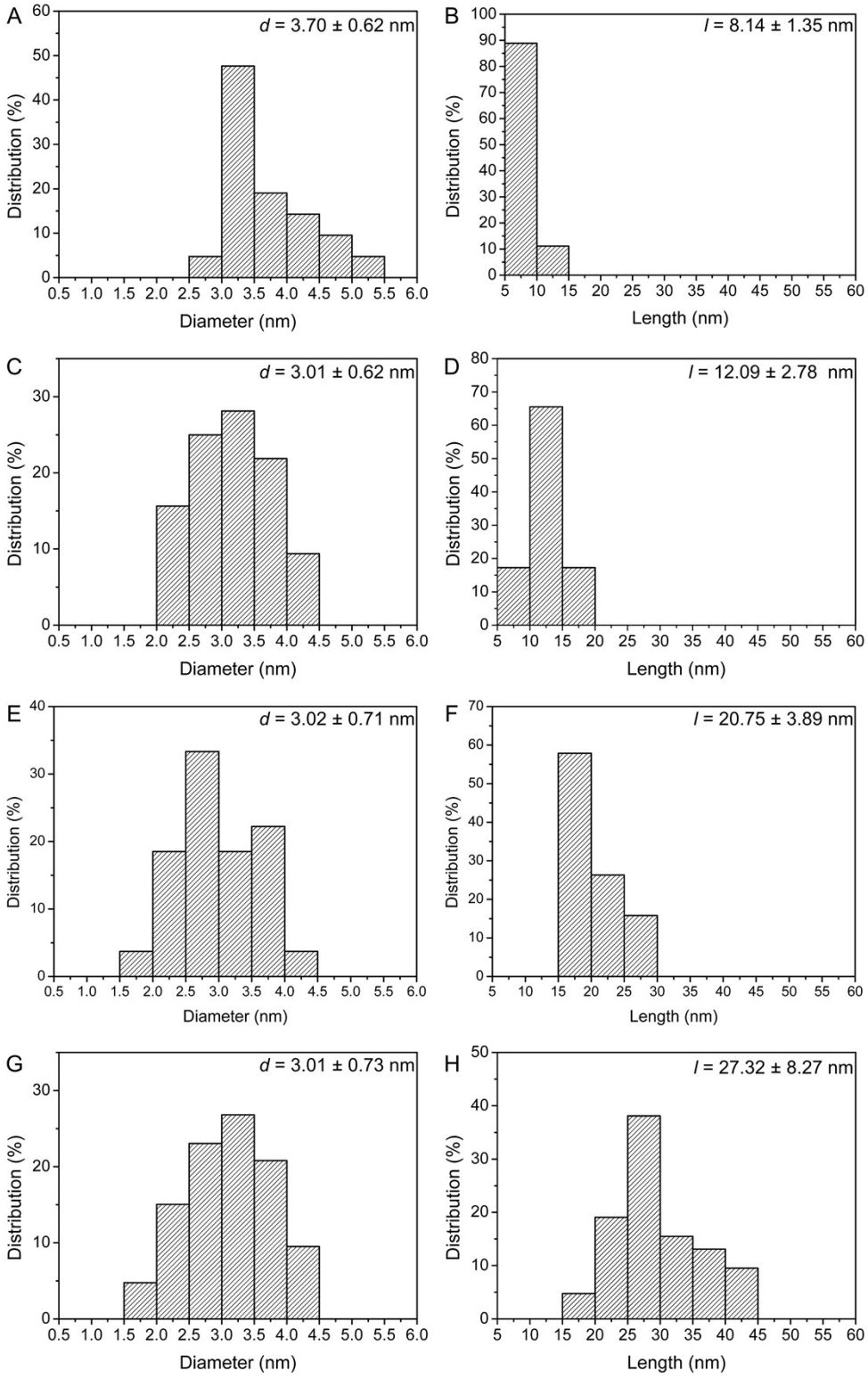


Fig. S1 Diameters and lengths histograms of different CdS samples, measured from TEM images. (A), (C), (E) and (G) are statistical diameters of CdS-1, CdS-2, CdS-3, CdS-4, respectively. (B), (D), (F) and (H) are the corresponding statistical arm lengths of CdS-1, CdS-2, CdS-3, CdS-4, respectively.

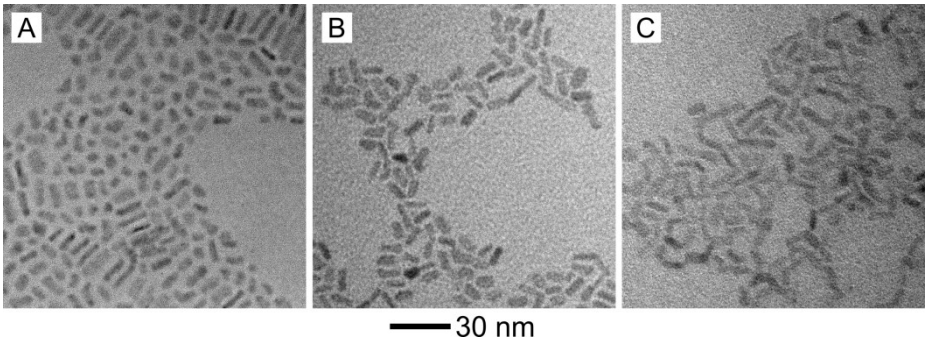


Fig. S2 TEM imgage of CdS nanocrystals synthesized by S solution injection to Cd2+ solution by rates of (A) one-shot injection, (B) 20 mL/h, (C) 1mL/h, respectively.

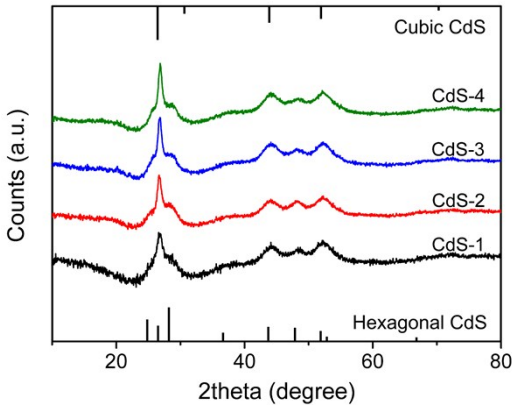


Fig. S3 XRD patterns of CdS nanocrystals and standard peaks of CdS.

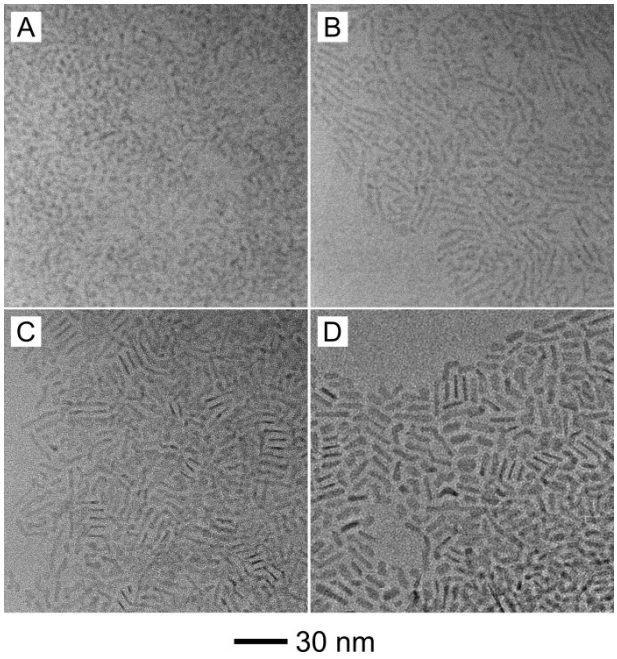


Fig. S4 TEM images of CdS-2, separating and sampling from the reaction at (A) 10 min, (B) 20 min, (C) 1 h and (D) 5 h. The scale bar of 30 nm applies to all the images.

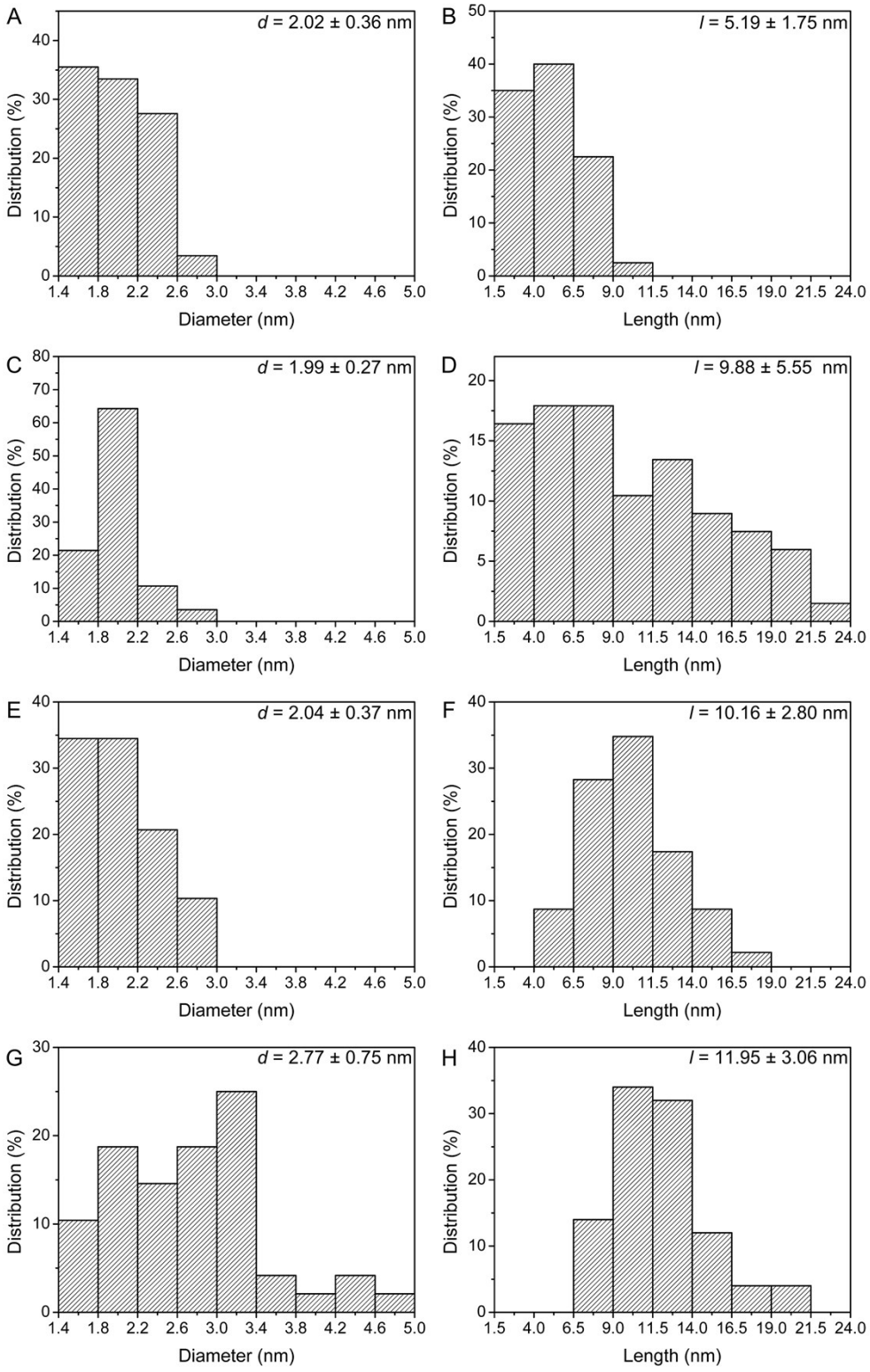


Fig. S5 Diameters and lengths measured from TEM images of CdS-2, sampled at different reaction stages. (A), (C), (E) and (G) are statistical diameters at 10 min, 20 min, 1 h, 5 h, respectively. (B), (D), (F) and (H) are the corresponding statistical arm lengths at 10 min, 20 min, 1 h, 5 h, respectively.

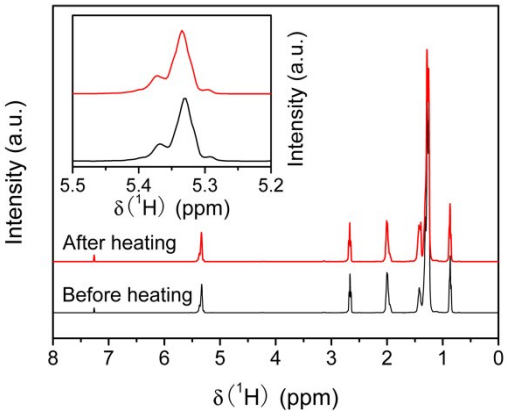


Fig. S6 ^{1}H NMR analysis of S-containing oleylamine solution, respectively for before heating and after heating for 20 hours. Inset shows the partial enlarged details of olefin protons.

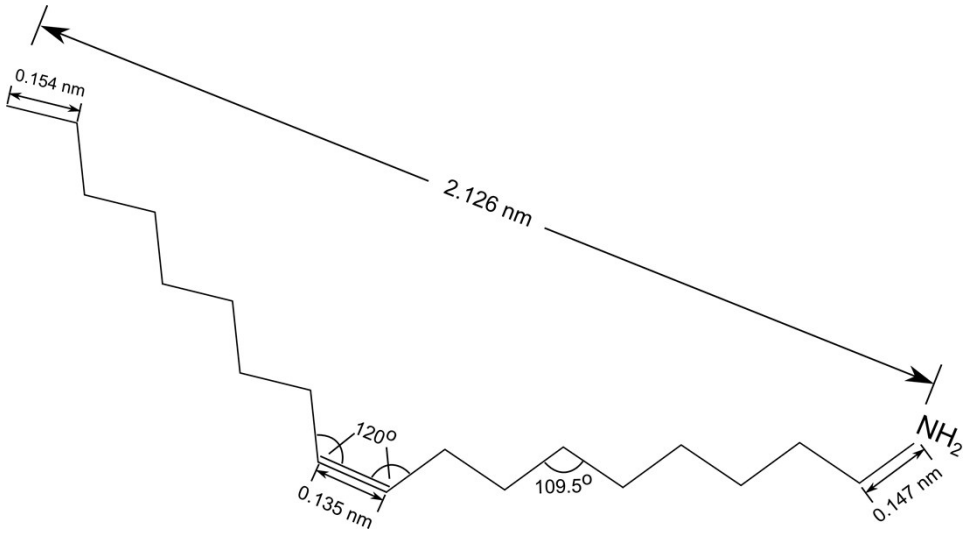


Fig. S7 Measured length of *cis*-form oleylamine.

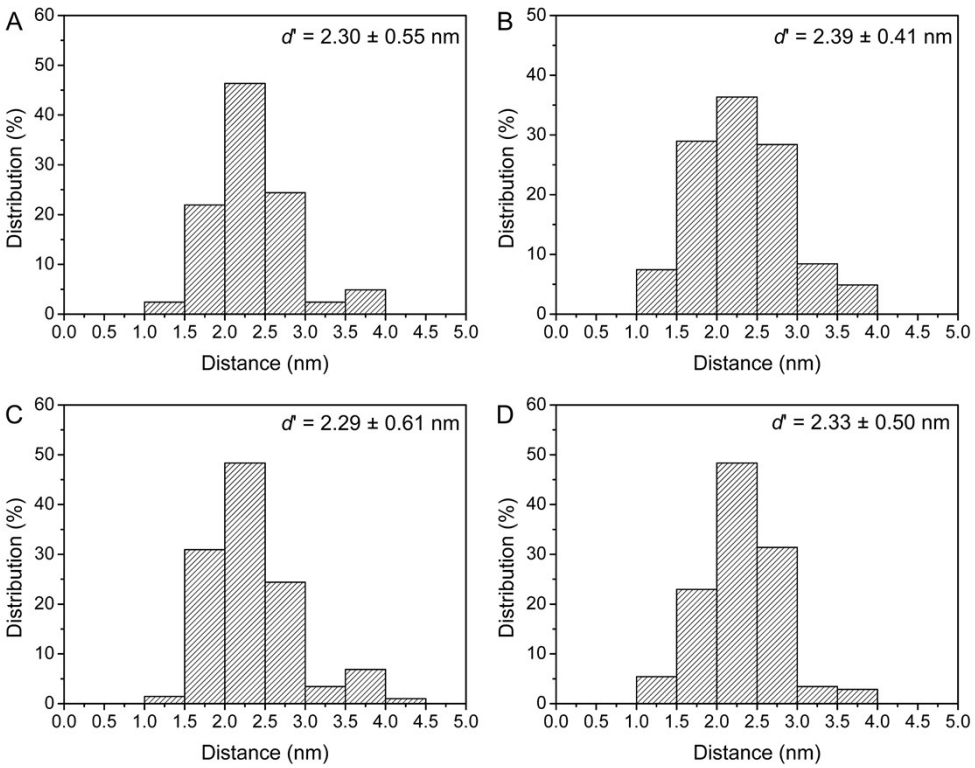


Fig. S8 Statistical distances between CdS-2 monopods measured from TEM images at different reaction stages. (A) 20 min, (B) 1 h, (C) 5 h, and (D) 20 h.

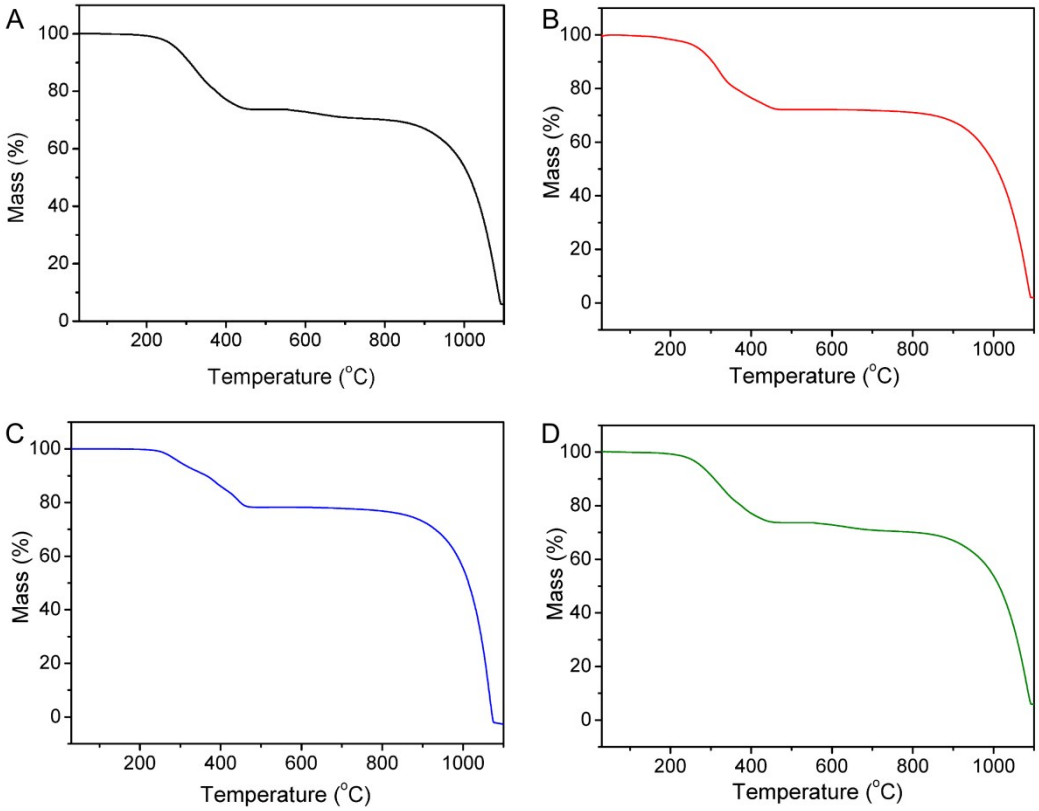


Fig. S9 Mass loss curves of (A) CdS-1, (B) CdS-2, (C) CdS-3, and (D) CdS-4.

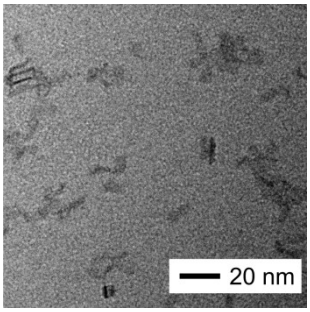
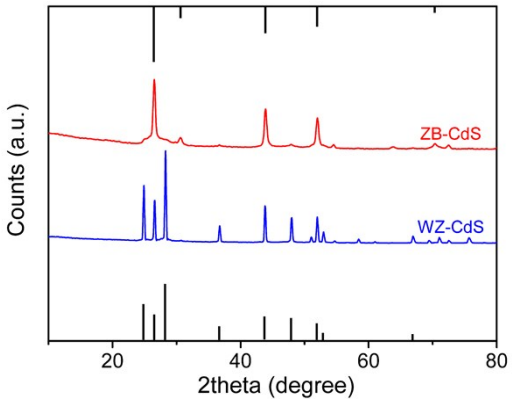


Fig. S10 TEM imgage of CdS nanocrystals synthesized under 80^{o}C by one shot Cd^{2+} injection.



Fg. S11 XRD patterns of ZB-CdS and WZ-CdS.

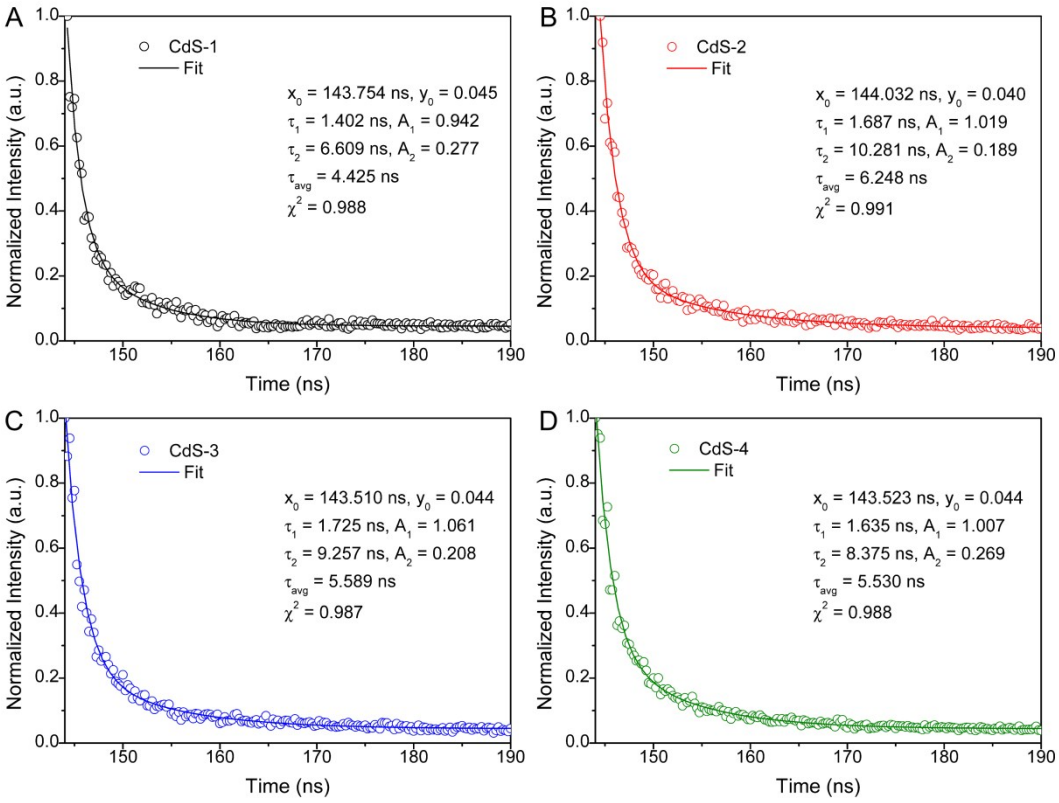


Fig. S12 PL transient fluorescence spectra of different CdS samples. The decay curves were fitted by the second order exponential decay function.

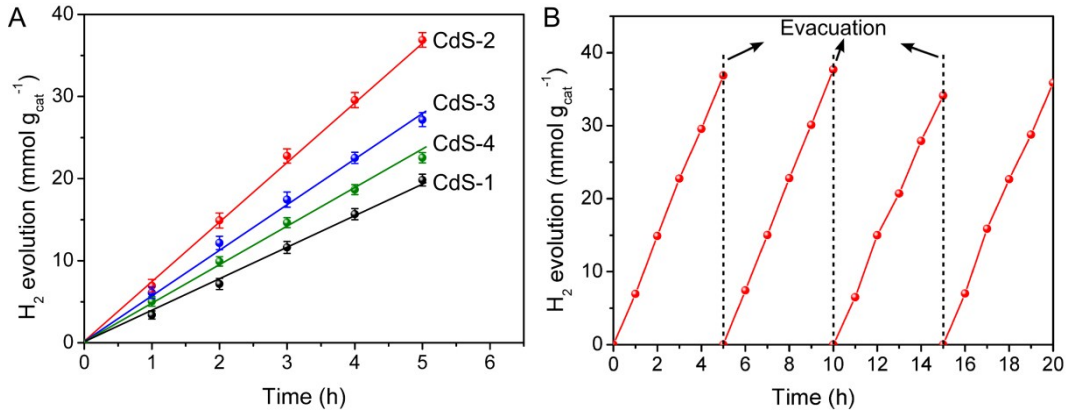


Fig. S13 (A) Time-course visible-light-driven photocatalytic hydrogen production activities of different CdS samples. Error bars are standard error values of three tests. (B) Time course for hydrogen generation over CdS-2.