Supplementary Materials for

Self-Assembled Colloidal Superparticles from Nanorods

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1. Materials and Methods

1.1 Chemicals. Trioctylphosphine oxide (TOPO, 99%), trioctylphosphine (TOP, 97%), tributylphosphine (TBP, 97%), tetraethoxysilane (TEOS 99%), sulfur (99%), octylamine (99%), poly(vinylpyrrolidone) (PVP, MW=55,000), and ethylene glycol (99%) were purchased from Aldrich. Cadmium oxide (CdO, 99.99%), selenium (Se, 200 mesh, 99.99%), and dodecyl trimethylammonium bromide (DTAB, 97%) were purchased from Alfa Aesar. Octadecylphosphonic acid (ODPA, 99%) and hexylphosphonic acid (HPA, 99%) were purchased from Polycarbon Inc. Polydimethylsiloxane (PDMS, Sylgard® 184 silicone elastomer) was purchased from Dow Corning. Dithiol-functionalized Tween-20 (Tween-20-SH) was synthesized according to a literature method (29). Nanopure® water (18 MΩ cm) was made by a Barnstead Nanopure Diamond system. All other solvents were purchased from Fisher Scientific International Inc.

1.2. Synthesis of 28.0-nm, 45.0-nm and 78.0-nm long CdSe/CdS core/shell nanorods. CdSe/CdS nanorods were prepared through a seed-growth method according to the literature method (30, 31). CdSe nanocrystal seeds of different sizes were used to grow CdSe/CdS nanorods with different sizes: 3.3-nm seeds for the growth of 28.0-nm nanorods (Fig. S1A); 3.0-nm seeds for the growth of 45.0-nm nanorods (Fig. S1B); and 2.6-nm seeds for the growth of 78.0-nm long nanorods (Fig. S1C). After growth at 350 ºC, reaction solutions were cooled to room temperature, and then nanorods were precipitated using a mixture of toluene and methanol (1:4, volume ratio). The precipitate
was redispersed in a toluene solution containing 8% octylamine and then was incubated for 20 min for nanorod surface treatment. Next, the nanorods were purified through three precipitation/redispersion cycles using methanol and hexane, respectively. The resulting nanorods are highly dispersible in nonpolar organic solvents such as hexane and toluene. Fourier transform infrared (FT-IR) spectroscopy shows the evidence that octylamine was functionalized onto the surface of CdSe/Cds nanorods (Fig. S2). Thermogravimetric analysis (TGA) confirms that octylamine was indeed on the nanorod surface (Fig. S3).

1.3. Synthesis of superparticles having multiple supercrystalline domains.
Multidomain superparticles (i.e., double-domed cylinders or irregular-multidomain particles) were synthesized using a literature method with minor modifications (15,16). In a typical synthesis, a chloroform solution containing CdSe/Cds nanorods with sizes of $l = 28.0 \pm 1.5$ nm and $d = 6.7 \pm 0.3$ nm, $l = 45.0 \pm 1.8$ nm and $d = 7.1 \pm 0.2$ nm, or $l = 78.0 \pm 2.1$ nm and $d = 5.4 \pm 0.3$ nm (10 mg/mL, 1 mL) was thoroughly mixed with the DTAB solution (5-30 mg/mL, 1 mL) by a vortex mixer. Afterwards, the chloroform was removed from the mixture by bubbling Ar at 40 °C, yielding a clear, yellow nanorod-micelle solution. Under vigorous stirring, this nanorod-micelle solution was injected into a three-neck flask with ethylene glycol (5.0 mL), and the mixture solution was further stirred at room temperature for 10 min. Then an aqueous solution containing Tween 20-SH (0.1 mM, 1 mL) was injected into the flask, and was stirred for 1 h. Colloidal superparticles were isolated from growth solution using centrifugation (3,200 rpm, 5 min). The yellow precipitate was redispersed in ethanol and the superparticles were further purified twice by centrifugation. The resulting superparticles are highly dispersible in polar solvents such as water, ethanol, and ethylene glycol. The average size of the resulting superparticles from the synthesis is dependent upon the amount of DTAB: a larger amount of DTAB led to the formation of smaller particles, and vice versa (Fig. S4).

1.4. Synthesis of needle-like, single-domain superparticles from CdSe/Cds nanorods. In a typical synthesis, octylamine (1 μL) was added into a chloroform solution containing CdSe/Cds nanorods ($l = 78.0 \pm 2.1$, $d = 5.4 \pm 0.3$ nm, 10 mg/mL, 1 mL), and the mixture was incubated for 6 days. Then, the resulting nanorod solution was
thoroughly mixed with a DTAB solution (20 mg/mL, 1mL) using a vortex mixer, followed by bubbling Ar to evaporate chloroform at 40 °C, yielding a clear, yellow nanorod-micelle aqueous solution. Under vigorous stirring, the nanorod-micelle aqueous solution was injected into a three-neck flask with ethylene glycol (5.0 mL). The mixture solution was further stirred at room temperature for 10 min, and then an aqueous solution containing Tween 20-SH (0.1 mM, 1 mL) was injected into the flask, and was stirred for additional 1 h. The resulting colloidal superparticles were isolated from the growth solution using centrifugation (3200 rpm, 5 min). The yellow precipitate was redispersed into ethanol and the superparticles were further purified twice by centrifugation. As-prepared superparticles are highly dispersible in polar solvents, and indefinitely stable in solvents with strong polarity such as water and ethanol. The superparticles exhibit a needle-like shape with an average diameter of 350±150 nm and an average length of 8±3 μm. The photoluminescence quantum yield of a typical superparticle sample is ~40% determined using Rhodamine 6G as the reference (30).

2. Supplementary Text, Supporting Figures, and Supporting Table

![Figure S1](image.png)

**Figure S1.** TEM images of CdSe/CdS nanorods: (A) length ($l$) = 28.0±1.5 nm, diameter ($d$) = 6.7±0.3 nm; (B) $l$ = 45.0±1.8 nm, $d$ = 7.1±0.2 nm, and (C) $l$ = 78.0±2.1 nm, $d$ = 5.4±0.3 nm
Figure S2. FT-IR spectrum of octylamine (A), CdSe/CdS nanorods with octylamine treatment (B), and CdSe/CdS nanorods without octylamine treatment (C). Characteristic N-H stretching IR peaks (at 3234 and 3302 cm\(^{-1}\)) appear in the spectrum of octylamine-treated nanorods (B).
Figure S3. (A) TGA data of octylamine-treated CdSe/CdS nanorods. (B) Derivative TGA spectrum shown in black and fitted by a red line. Peak positions for the weight-loss processes were indicated in the panel. We attribute the weight loss at 156 and 243 °C to the loss of weakly and strongly bonded octylamine (bp: 175-177 °C) ligands from the nanorod surface. The weight loss at 479 °C is associated with the loss of the high boiling point ligands including octadecylphosphonic acid as a major component and small amounts of hexylphosphonic acid, trioctylphosphine oxide, and trioctylyphosphine. In contrast, the CdSe/CdS nanorods without octylamine treatment exhibit only the weight loss at 479 °C as shown in panel C and D. (C) TGA data of the CdSe/CdS nanorods without octylamine treatment. (D) Derivative TGA spectrum shown in black and fitted by a blue line. The peak position for the weight-loss process was indicated in the panel.
Figure S4. TEM images of colloidal superparticles made from CdSe/CdS semiconductor nanorods with $l = 28.0$ nm, $d = 6.7$ nm, displaying an average size of $1,100 \pm 150$ nm (A), $650 \pm 60$ nm (B), $250 \pm 26$ nm (C), and $180 \pm 23$ nm (D).
Figure S5. TEM images of a cluster of four superparticles made from CdSe/CdS nanorods ($l = 28.0$ nm, $d = 6.7$ nm) at different tilting angles as indicated in each panel. The images show that these superparticles appear as double-domed cylinders at different tilting angles.
Table:

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**Figure S6.** A collection of high-magnification TEM images of domes in double-domed cylinder superparticles with a cylindrical domain radius (R) as indicated in each image. The constituent nanorods have $l = 28.0$ nm and $d = 6.7$ nm. Schemes of domes are listed with the number of layers ($i$) of stacked arches in the middle domain of each dome.
**Table S1. d-spacing and lattice constants of the lamellar and hexagonal lattice**

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<th>d(002)</th>
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<th>d(003)</th>
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**The SAXS pattern taken from double-domed cylinder superparticles with an average radius of 300 nm was integrated, yielding a spectrum shown in Figure 2M. The exact peak positions were determined via peak fitting (OriginPro® 8.5). The constant of the lamellar structure (l) was calculated using the equation (31):

\[
d_{00m} = \frac{l}{m}
\]

The constant of the hexagonal lattice (a) was calculated using the equation (31):

\[
\frac{1}{d_{(hk)}^2} = \frac{4}{3} \cdot \frac{h^2 + hk + k^2}{a^2}
\]
Figure S7. (A) Scheme of superparticle formation at equilibrium conditions. During nanorod-micelle decomposition, the leaving rates of DTAB from the side surface \((u_s)\) is similar to that from top/bottom faces \((u_t)\). This process results in nanorods with isotropic hydrophobicity, allowing colloidal crystallization of nanorods under an equilibrium condition. (i) Embryo formation, (ii) colloidal crystallization at an equilibrium condition, (iiiA) double-domed cylinder formation, and (iiiB) irregular-multidomain particle formation. (B) Scheme of superparticle formation at a non-equilibrium condition, where the rate of DTAB leaving from the side surfaces \((u_s)\) is smaller than that from top or bottom faces \((u_t)\). This difference in DTAB leaving rates causes the top/bottom of the nanorods to have higher solvophobicity than the side faces during nanorod-micelle decomposition, inducing “kinetic functional anisotropy.” This, in turn, leads to rapid growth of supercrystalline domains along nanorod long axes and the formation of needle-like superparticles. (i) Embryo formation, (ii) colloidal crystallization under non-equilibrium conditions, and (iii) needle-like superparticle formation.
2.1 Mechanistic study on superparticle formation. In general, the formation of multi-domain superparticles can undergo either (1) a nucleation-growth process or (2) an embryo-crystallization process. To distinguish between these formation mechanisms, we performed two sets of superparticle synthesis experiments using CdSe/CdS nanorods with sizes of \( l = 28.0 \pm 1.5 \text{ nm} \) and \( d = 6.7 \pm 0.3 \text{ nm} \). In the first set of experiments, a nanorod-micelle solution (~2 mL) was prepared with a CdSe/CdS nanorod chloroform solution (10 mg/mL, 2 mL) and a DTAB solution (20 mg/mL, 2 mL) according to the protocol described in section 1.2. Under vigorous stirring, 1 mL of the resulting nanorod-micelle solution was injected at a time zero into a three-neck flask containing ethylene glycol (5.0 mL). The mixture solution was further stirred at room temperature, and two aliquots (0.5 mL) were taken from the solution at reaction times of 1 and 10 min. At 11 min, the other part of the nanorod-micelle solution (~1 mL) was injected into the growth solution under stirring, and an aliquot was taken at the reaction time of 21 min. Each aliquot was kept in an aqueous solution containing Tween 20-SH (0.17 mM) for 5 min before the superparticles were isolated and purified for TEM measurement.

**Figure S8.** Typical TEM images of CdSe/CdS superparticles from the aliquots taken at (A) 1 min, (B) 10 min, and (C) 21 min.

TEM observations show that the size and size distribution of superparticles in these three aliquots are near identical (Fig. S8). The results suggest that the superparticle growth did not undergo a nucleation-growth process, but instead underwent an embryo-crystallization process. If the formation of multi-domain superparticles undergoes an
embryo-crystallization process, then the second injection of nanorod micelle solution should increase the amount of resulting superparticles.

To quantitatively determine whether the second injection increase the amount of superparticles, we performed the second set of experiments. The experiments were carried out using identical experimental parameters in the synthesis described above, but no aliquots were taken during superparticle growth. For the single-injection synthesis, an aqueous solution containing Tween 20-SH (0.1 mM, 1 mL) was injected into the reaction solution at 10 min, and the resultant mixture was stirred for 1 h. For the double-injection synthesis, an aqueous solution containing Tween 20-SH (0.1 mM, 1.2 mL) was injected into the reaction solution at 21 min, and the resultant mixture was stirred for 1 h. The results from gravimetric analyses show that the amount of the resulting superparticles in the double injection synthesis is 1.9±0.2 times higher than that in the single injection synthesis (note that the standard deviation was calculated using the results from three parallel superparticle syntheses). In addition, TEM observations show that the size and size distribution of superparticles from these two syntheses have no measurable difference.

Taken together, the results from all these experiments are consistent with an embryo-crystallization mechanism. In addition, kinetic studies using synchrotron-based, time-resolved, small angle X-ray scattering spectroscopy are being undertaken to further reveal the detailed mechanisms behind the embryo-crystallization process during the formation of multidomain supercrystalline particles from CdSe/CdS core/shell nanorods.

2.2. Numerical Simulations

2.2.1. 2D packing factor for nanorod assembly on a cylinder base. The packing factor (Φ) can be determined via calculating the surface area of the void part (S_{void}) in the cylinder base (Fig. S9), and given by

$$\Phi(R, i, j) = \frac{\pi \cdot R^2 - S_{\text{void}}}{\pi \cdot R^2} = 1 - \frac{S_{\text{void}}}{\pi \cdot R^2}$$ \hspace{1cm} \text{Eq. S1}

$$S_{\text{void}} = S(i) + S(j) + S_0$$ \hspace{1cm} \text{Eq. S2}
S(i) is the sum of void areas caused by horizontally aligned rods (Fig. S9), which is determined by i, and Y_p—the base length of each void area (p is the index number of each void area, given by 1, 2,..., u, and u+1; and $u = \text{int} \left[ \frac{i}{2} \right] + 1$).

**Figure S9.** Diagram of nanorod packing on the top of a cylinder base with a radius of R. The maximization of 2D packing factor ($\Phi$) requires nanorods to be packed into three domains with orthogonally related nanorod alignment directions: the middle domain (in blue) and the side domains (in green). The angles $\theta$ and $\phi$ related to i and j are defined.

When i is even:

$$S(i) \approx 4 \times \left( \frac{1}{2} \times (l \cdot Y_1 + l \cdot Y_2 + l \cdot Y_3 + \cdots + l \cdot Y_w) \right)$$

$$= 2 \cdot l \cdot ((Y_1 + Y_2 + Y_3 + \cdots + Y_w))$$

$$= 2 \cdot L \cdot R \cdot (1 - \cos \theta) \quad \text{Eq. S3}$$
When $i$ is odd:

$$Y_i = R \cdot (1 - \cos \sin^{-1}(\frac{0.5 \cdot l}{R})) \quad \text{Eq. S4}$$

$$S(j) \approx 4 \times \left(\frac{1}{2} \times (l \cdot Y_1 + l \cdot Y_2 + l \cdot Y_3 + \cdots l \cdot Y_w)\right) = 2 \cdot l \cdot \left((Y_1 + Y_2 + Y_3 + \cdots Y_w) - l \cdot Y_1\right) = 2 \cdot l \cdot R \cdot (1 - \cos \theta) - l \cdot R \cdot \left[1 - \cos \left(\sin^{-1}(\frac{0.5 \cdot l}{R})\right)\right] \quad \text{Eq. S5}$$

When $j$ is even:

$$S(j) \approx 4 \times \left(\frac{1}{2} \times (l \cdot X_1 + l \cdot X_2 + l \cdot X_3 + \cdots l \cdot X_w)\right)$$

$$= 2 \cdot l \cdot \left((X_1 + X_2 + X_3 + \cdots X_w)\right) = 2 \cdot l \cdot R \cdot (1 - \cos \phi) \quad \text{Eq. S6}$$

$S(j)$ is the sum of void areas introduced by vertically aligned rods (Fig. S9), which is determined by $j$, and $X_q$—the base length of each void area ($q$ is the index number of each void area, given by 1, 2, ... $w$, and $w+1$; and $w = \text{int} \left[\frac{j}{2}\right] + 1$)

When $j$ is odd:

$$X_1 = R \cdot (1 - \cos \sin^{-1}(\frac{0.5 \cdot l}{R})) \quad \text{Eq. S7}$$

$$S(j) \approx 4 \times \left(\frac{1}{2} \times (l \cdot X_1 + l \cdot X_2 + l \cdot X_3 + \cdots l \cdot X_w)\right) = 2 \cdot l \cdot \left((X_1 + X_2 + X_3 + \cdots X_w)\right) - l \cdot X_1 = 2 \cdot l \cdot R \cdot (1 - \cos \phi) - l \cdot R \cdot \left(1 - \cos \left[\sin^{-1}(\frac{0.5 \cdot l}{R})\right]\right) \quad \text{Eq. S8}$$

$S_0$ is the area of the void created by both horizontally and vertically aligned rods (Fig. S9),

$$S_0 \approx 4 \times \frac{1}{2} \cdot X_{w+1} \cdot Y_{u+1} = 2 \cdot X_{w+1} \cdot Y_{u+1} \quad \text{Eq. S9}$$

Where, $X_{w+1} = R \cos \phi - R \sin \theta$, and $Y_{u+1} = R \cos \theta - R \sin \phi$

In general, all the mathematical possible packing configurations are allowed when $2 > \frac{R}{l}$, and thus one only needs to compare the packing factor between each packing
configuration when \( \frac{R}{l} \geq 2 \). Under this conduction, the contribution of 
\( (1 - \cos \left[ \sin^{-1} \left( \frac{0.5 - l}{R} \right) \right] ) \) is negligible in the calculation of the packing factor. Therefore, combining Eqs. S1 through S9 yields a simple expression of the parking factor (\( \Phi \)).

\[
\Phi(R, i, j) = 1 - \frac{2 \cdot l}{\pi R} \cdot (2 - \cos \varphi - \cos \theta) - \frac{2}{\pi} \cdot (\cos \varphi - \sin \theta) \cdot (\cos \theta - \sin \varphi)
\]

Eq. S10

where \( \theta \) and \( \varphi \) can be determined by \( R \) and integers \( i \) and \( j \):

\[
\sin \theta = \frac{i \cdot l}{2 \cdot R} \quad (i = 1, 2, 3, \ldots \text{Int}\left(\frac{2 \cdot R}{l}\right))
\]

Eq. S11

and

\[
\sin \varphi = \frac{j \cdot l}{2 \cdot R} \quad (j = 1, 2, 3, \ldots \text{Int}\left(\frac{2 \cdot R \cdot \sin \theta}{l}\right))
\]

Eq. S12

The packing factor (\( \Phi \)) as a function of \( i \) at a \( j \) associated with maximized nanorods packing in the two side domains is given by

\[
\Phi(i) = \max_j (\Phi(R, i))
\]

Eq. S13

For each \( i \), the \( j \) value is determined using integer linear regression and calculated using a Matlab program (MATLAB® 7.0.1). As an example, the plot of \( \Phi(i) \) for \( R = 160 \) nm is shown in Figure 3B in the main text.

2.2.2. The size relationship between two domes in a given double-domed cylinder.
In a double-domed cylinder with a given volume and a minimal surface area, the question on the size relationship of its two domes is mathematically equivalent to a question on how the two domes are related to each other in their size when the two domes have a minimal total surface area and a fixed total volume. To answer the second question, we can simply calculate the total surface area and volume of two domes using two partial spheres with heights of \( H_t \) and \( H_b \) and identical base radii of \( R \) (Fig. S10).
Figure S10. Proposed DDC model: radius of cylinder (R), the height of top dome (H_t), and the bottom dome (H_b)

The total volume of the domes (V_d) is given by

\[ V_d = \frac{\pi}{6} \cdot H_t \cdot (3R^2 + H_t^2) + \frac{\pi}{6} \cdot H_b \cdot (3R^2 + H_b^2) \]  

which can be rearranged into the following equation:

\[ H_t(3R^2 + H_t^2) + H_b(3R^2 + H_b^2) - \frac{6V_d}{\pi} = 0 \]  

The total surface area of the domes (S_d) is given by:

\[ S_d = \pi \cdot (R^2 + H_t^2) + \pi \cdot (R^2 + H_b^2) \]  

The necessary condition for the existence of a minimal value of S_d can be found using Lagrange multipliers, and a Lagrange function is defined by

\[ f(H_t, H_b, \lambda) = \pi(R^2 + H_t^2) + \pi(R^2 + H_b^2) + \lambda \cdot \left[ H_t(3R^2 + H_t^2) + H_b(3R^2 + H_b^2) - \frac{6V_d}{\pi} \right] \]  

where \( \lambda \) is the Lagrange multiplier.
For Sd having a critical point (e.g. local extrema and saddle point), the following equations are given by

\[
\begin{align*}
\nabla_{H_t} f &= 2\pi \cdot H_t + \lambda \cdot (3R^2 + 3H_t^2) = 0 \quad \text{Eq. S18} \\
\nabla_{H_b} f &= 2\pi \cdot H_d + \lambda \cdot (3R^2 + 3H_d^2) = 0 \quad \text{Eq. S19} \\
H_t \cdot (3R^2 + H_t^2) + H_b \cdot (3R^2 + H_b^2) - \frac{6V_d}{\pi} &= 0 \quad \text{Eq. S15}
\end{align*}
\]

Second partial derivatives of the Lagrange function are given by

\[
\begin{align*}
\frac{\partial f^2}{\partial H_t H_b} &= 2\pi + 6\lambda \cdot H_t = A \quad \text{Eq. S20} - i \\
\frac{\partial f^2}{\partial H_t H_b} &= 0 = B \quad \text{Eq. S20} - ii \\
\frac{\partial f^2}{\partial H_t H_b} &= 2\pi + 6\lambda \cdot H_b = C \quad \text{Eq. S20} - iii
\end{align*}
\]

The second partial derivative test for the Lagrange function is given by

\[
A \cdot C - B^2 = (2\pi + 6\lambda \cdot H_t) \cdot (2\pi + 6\lambda \cdot H_b) \quad \text{Eq. S21}
\]

Combining and simplifying Eqs. S18 and S19 yields

\[
(H_t - H_b) \cdot (R^2 - H_t \cdot H_b) = 0 \quad \text{Eq. S22}
\]

Therefore, two conditions are required for Sd to have a critical point: (1) \(H_t = H_b\), and (2) \(H_t \cdot H_b = R^2\).

(1) For \(H_t = H_b = H\), solving Eqs. S18 or S19 yields

\[
\lambda = -\frac{2\pi \cdot H}{3R^2 + 3H^2} \quad \text{Eq. S23}
\]

Combining Eqs. S21 with S23 yields

\[
A \cdot C - B^2 = \left[2\pi \cdot \left(1 - \frac{2H^2}{R^2 + H^2}\right)\right]^2 \geq 0 \quad \text{Eq. S24}
\]
Therefore, if $H < R$, then $A > 0$, and $AC - B^2 > 0$. According to the extreme value theorem, the total surface area of domes ($S_d$) is the minimum when $H_t$ is equal to $H_b$.

If $H > R$, then $A < 0$, and $AC - B^2 > 0$. According to the extreme value theorem, the total surface area of domes ($S_d$) is maximum when $H_t$ is equal to $H_b$.

If $H = R$, then $AC - B^2 = 0$, and the second partial derivative test is inclusive under this condition.

(2) For $H_t \cdot H_b = R^2$ ($H_t \neq H_b$), solving Eq. S18 yields

$$\lambda = -\frac{2\pi H_t}{3R^2 + 3H_t^2}$$

Eq. S25

Combining Eqs. S21 and S25 yields

$$A \cdot C - B^2 = -2\pi^2 \times \frac{(H_t + R)^2}{H_t^2 + R^2} \times \frac{(H_t - R)^2}{H_t^2 + R^2} < 0$$

Eq. S26

Therefore, the total surface area of domes ($S_d$) is a saddle point under this condition.

In summary, the necessary conditions for the total surface area of two domes to be a minimum are (i) $H_t = H_d = H$, and (ii) $H < R$. 
Figure S11. Schematic illustration of the definition of relative curvatures in a double-domed cylinder structure: (A) dome ($\kappa_d$) and (B) cylindrical domain ($\kappa_c$). $R_{od}$ is given by $R_{od} = \frac{H^2 + R^2}{2H}$. $R_d$ is the radius of the curve of a dome, and thus (in A) $\kappa_d$ is 1 when $R_d = R_{od}$, whereas (C) $\kappa_d$ is 0 when $R_d \to \infty$. $R_{oc}$ is given by $R_{oc} = \sqrt{\left(\frac{1}{2} n \cdot l\right)^2 + R^2}$. In addition, for a double-domed cylinder having a minimized surface energy, the maximum value of H equals to R, and thus $0 \leq \kappa_d \leq 1$. $R_c$ is the radius of the curve of cylinder side wall, and thus (in B) $\kappa_c$ is 1 when $R_c = R_{oc}$, whereas (in D) $\kappa_c$ is 0 when $R_c \to \infty$. (E) $\kappa_d > 1$ when $R_d < R_{od}$. In this case, the dome does not fully cover the cylinder base. (F) $\kappa_c > 1$ when $R_c < R_{oc}$. In this case, the superparticle appears as a cylinder with a ring.
Figure S12. The six typical morphologies of numerically simulated superparticles built with a total number (N = 17,425) of constituent rods (l = 28.0 nm and d = 6.7 nm). The superparticle structure is defined with seven variables (n, i, j, R, H, κc, and κd). (A) seven-domain double-domed cylinder (n, i, j ≠ 0; κc = 0; and κd = 1); (B) Seven-domain sphere (n, i, j ≠ 0; κc = 1; and κd = 1); (C) Right cylinder (n ≠ 0; i, j = 0; and κc = 0); (D) Single-domain sphere (n ≠ 0; i, j = 0; and κc = 1); (E) Three-domain double-domed cylinder (n = 0; i, j ≠ 0; and κd = 0); (F) Three-domain spheres (n = 0; i, j ≠ 0; and κd = 1).
2.2.3. Equilibrium structure of a superparticle via surface-area minimization. In thermodynamically controlled colloidal crystallization of CdSe/CdS nanorods, a superparticle adopts the structure with a minimized Gibbs free energy, which includes contributions from bulk free energy and surface energy. When the surface-energy term is dominant, the minimization of superparticle surface area dictates the morphology and supercrystalline domain configuration of the superparticle. Surface area minimization requires constituent nanorods to have a maximized packing density and to pack in a configuration that is associated with the minimized superparticle surface area. A maximized nanorod packing density in a superparticle also minimizes the bulk free energy of the particle.

**Figure S13.** (A) Proposed model of a seven-domain superparticle, (B) Right-angle side view of the particle, (C) Scheme of the middle domain in a dome, which consists of multilayer stacked arches, and (D) Scheme of a side domain in a dome, which consists of multiplayer stacked partial arches.
To minimize superparticle surface area, we propose that the superparticle is constructed with blocks of hexagonal-close-packed nanorods (Fig. S13). The superparticle consists of multiple supercrystalline domains and is characterized by nine parameters: \( n, i, j, R, H, l, d, \kappa_c, \) and \( \kappa_d \), where \( l \) and \( d \) are the building block parameters, \( n, i, \) and \( j \) are superparticle domain parameters, \( R \) and \( H \), are superparticle dimension parameters, and \( \kappa_c, \) and \( \kappa_d \) are superparticle morphology fine-tuning modifiers (see Fig. S11 for detailed definition of \( \kappa_c \) and \( \kappa_d \)). The superparticle adopts seven-domain structures when all \( n, i, \) and \( j \) are nonzero (Fig. S12, A and B), adopts single domain structures when \( n \) is nonzero and \( i \) and \( j \) are zero (Fig. S12, C and D), and adopts three-domain structures when \( n \) is zero and \( i \) and \( j \) are nonzero (Fig. S12, E and F).

In the calculation of surface area of a superparticle with given \( N \) (the total number of constituent nanorods), we assume that the 3D nanorod packing factor (\( \psi \)) in the superparticle is 90.69\%, the packing density in a structure with single-domain, hexagonal-close-packed nanorods. In other words, we ignore the decrease of \( \psi \) caused by the formation of grain boundaries between supercrystalline domains inside the superparticle. The assumption holds good when \( N \) is larger than 110. Therefore, for a given \( N \), the volume of the superparticle can be presented by

\[
V(N) = \frac{N \cdot \pi \cdot d^2 \cdot l}{4 \cdot \psi}
\]  

**Eq.S27**

Then \( V(N) \) is the sum of the volume of the cylinder domain and domes, and can be given by: \( V(N) = V_c + 2 \times V_d \), where \( V_c \) and \( V_d \) are the volume of the cylinder domain and a dome, respectively. The value of \( V_c \) is zero when \( n = 0 \), while \( V_d \) is zero when \( i \) and \( j \) are zero.

In general, the surface area of the superparticle is a nine-variable function of \( n, i, j, R, H, l, d, \kappa_c, \) and \( \kappa_d \), wherein the contribution of \( d \) can be ignored when \( d \ll l \). Thus, superparticle surface area (\( S \)) can be generally presented by

\[
S(n, i, j, R, H, l, \kappa_c, \kappa_d) = S_c + 2 \times S_d
\]  

**Eq.S28**
where $S_c$ and $S_d$ are the surface areas contributed from the cylindrical domain and a dome, respectively. $S_c$ is zero when $n$ is zero, whereas $S_d$ is zero when $i$ and $j$ are zero.

### 2.2.3.1. Calculation of $V_c$ and $S_c$

The volume and surface area of the cylinder domain are calculated by summation of the contributions from each disk in the domain (Fig. S13). To assist the calculation, we introduce a new parameter: $R_p$ (the radius of the disks in the cylinder domain) is given by

$$R_p = \sqrt{R^2 + \kappa_c \cdot \left(\frac{p}{2} \cdot l\right)^2}, \quad p = 0, 1, \ldots, \text{int} \left[\frac{n}{2}\right]$$

**Eq. S29**

When $n$ is even, $V_c$ and $S_c$ are given by

$$V_c = 2 \times \sum_{p=0}^{\frac{n}{2}} \pi \cdot R_p^2 \cdot l$$  \quad **Eq. S30**

$$S_c = 2 \times \kappa_c \cdot \left(\frac{\pi \cdot n}{2} \cdot l\right)^2 + 2 \times \sum_{p=0}^{\frac{n}{2}} 2 \cdot \pi \cdot R_p \cdot l$$  \quad **Eq. S31**

When $n$ is odd, $V_c$ and $S_c$ are given by
\[ V_c = \pi \cdot l \cdot (R^2 + \kappa_c \cdot \left(\frac{n-1}{2} \cdot l \right)^2) + 2 \times \sum_{0}^{\frac{n-1}{2}} \pi \cdot R_p^2 \cdot l \] \hspace{1cm} \text{Eq. S32}

\[ S_C = 2 \times \kappa_c \cdot \left(\pi \cdot \frac{n-1}{2} \cdot l^2 \right) + 2 \times \sum_{0}^{\frac{n-1}{2}} 2 \cdot \pi \cdot R_p \cdot l \] \hspace{1cm} \text{Eq. S33}

### 2.2.3.2. Calculation of \( V_d \) and \( S_d \):

The volume and surface area of a dome are calculated by summation of the contributions from the middle and two side domains (Fig. S15), which are given by

\[ V_d = V_{dm} + V_{ds} \] \hspace{1cm} \text{Eq. S34}

where \( V_{dm} \) and \( V_{ds} \) are the volume of the middle and two side domains.

\[ S_d = S_{dm} + S_{ds} \] \hspace{1cm} \text{Eq. S35}

where \( S_{dm} \) and \( S_{ds} \) are the surface area of the middle and two side domains.

(1) **Calculation of \( V_{dm} \) and \( S_{dm} \).** The middle domain consists of multiple stacked arches made of hexagonally packed nanorods. Theses arches have different heights and different curvatures in the directions parallel and perpendicular to their radial direction (Fig. S15, A to C). We assume that the relative curvature in their radial direction \( (\kappa_{dr}) \) is 1 because of the minimization of surface area (Fig. S15D). The relative curvature perpendicular to the arch radial direction is \( \kappa_d \) with a value between 0 and 1, which determines the relationship among the heights of the arches in this domain. To simplify the calculation, we divide the middle domain into two identical zones (Zone 1 and 2, see Fig. S15A).

The volume and surface area are given by

\[ V_{dm} = \sum_{1}^{u} V_u \] \hspace{1cm} \text{Eq. S36}
Figure S15. (A) Proposed model for the middle domain of a dome, which consists of multilayered stacked arches and is defined with $i$, $H$, and $\kappa_d$. Two identical zones were separated to assist the calculation of the volume and surface area of this domain. (B) Right-angle side view of the domain showing that the arches have different heights labeled with $H_{dmu}$, where $u$ is an index given from $1$, $2$,… $\text{int}\left(\frac{i}{2}\right)$. (C) Proposed model of the arches in the domain. To assist the calculation, the arch radius ($r_u$) and angles ($\alpha_u$) are defined in the panel. (D) Side view of the arch with highest height where $H_{dm1} = H$. The radius of the base ($a_1 = R$) and arch ($r_1$) are labeled.
\[
S_{dm} = \sum_{i=1}^{u} S_{u} + 0.5 \times ( (a_{1} - \sin \alpha_{1}) \cdot r_{1}^2 - (a_{uf} - \sin \alpha_{u}) \cdot r_{uf}^2 ) \quad \text{Eq. S37}
\]

Where \(uf= \text{int}(\frac{i}{2})\); \(V_{u} = \frac{1}{2} \times l \cdot r_{u}^2 \cdot (a_{u} - \sin \alpha_{u})\); \(S_{u} = a_{u} \cdot r_{u} \cdot l\);

\(r_{u}\) and \(\alpha_{u}\) are given as follows when \(i\) is even or odd.

When \(i\) is even,

\[
\alpha_{u} = 2 \times \sin^{-1} \frac{a_{u}}{r_{u}} \quad \text{Eq. S38}
\]

\[
r_{u} = \frac{(a_{u}^2 + H_{u}^2)}{2H_{u}} \quad \text{Eq. S39}
\]

where \(a_{u} = \sqrt{a_{1}^2 - \kappa_{d} \cdot (u \cdot l)^2}\); and \(H_{u} = \sqrt{r_{1}^2 - \kappa_{d} \cdot (u \cdot l)^2} - r_{1} + H\)

When \(i\) is odd,

\[
\alpha_{u} = 2 \times \sin^{-1} \frac{a_{u}}{r_{u}} \quad \text{Eq. S40}
\]

\[
r_{u} = \frac{(a_{u}^2 + H_{u}^2)}{2H_{u}} \quad \text{Eq. S41}
\]

where \(a_{u} = \sqrt{a_{1}^2 - \kappa_{d} \cdot ((u - 0.5) \cdot l)^2}\);

and \(H_{u} = \sqrt{r_{1}^2 - \kappa_{d} \cdot ((u - 0.5) \cdot l)^2} - r_{1} + H_{u-1}\)

(2) Calculation of \(V_{ds}\) and \(S_{ds}\). A side domain consists of multiple stacked partial arches made of hexagonally packed nanorods. To simplify the calculation, we combine the two side domains together and divide it into two zones perpendicular to the radial direction of the partial arches (Fig. S16). The two side domains occupy a relatively smaller percentage of the dome volume as compared to the middle domain, thus we assume that the relative curvatures are 1 in the directions parallel and perpendicular to the radial direction of these partial arches. Therefore, the volume and surface area of the two side domains are given by:
\[ V_{dm} = \sum_{w}^{w} V_{w}' \]  
\[ S_{dm} = \sum_{w}^{w} S_{w}' + 0.5 \]

\[
\times \left[ \frac{r_{1}^2}{2} \left( \alpha_1 - \sin \alpha_1 - 2 \cdot \sin^{-1} \frac{uf \cdot l}{r_{1}} + \sin \left( 2 \times \sin^{-1} \frac{uf \cdot l}{r_{1}} \right) \right) \right.
\]

\[
- \tan \left( \sin^{-1} \frac{uf \cdot l}{r_{1}} \right) \times \left( \sqrt{r_{1}^2 - (uf \cdot l)^2} - r_1 - H \right)^2 \]

\[ \text{Eq. S43} \]

where \( uf = \text{int}\left[ \frac{f}{2} \right] \):

\[
V_{w}' = \frac{1}{2} \times l \times r_{sw} \left( \beta_w - \eta_w - \sin \beta_w + \sin \eta_w \right) - l
\]

\[
\times \tan \frac{\eta_w}{2} \times \left( \sqrt{r_{sw}^2 - (u \cdot \delta)^2} - r + H \right)^2
\]

\[ \text{Eq. S44} \]

\[
S_{w}' = (\beta_w - \eta_w) \cdot r_{sw} \cdot l
\]

\[ \text{Eq. S45} \]

\[ w = 1, 2, 3 \cdots \text{int}\left[ \frac{f}{2} \right] \]  
\[ \text{Eq. S46} \]

\[ u = \text{int}\left[ \frac{i}{2} \right] \]  
\[ \text{Eq. S47} \]

\[ r_{1} = \frac{R^2 + H^2}{2H} \]  
\[ \text{Eq. S48} \]

\[ \alpha_1 = 2 \times \sin^{-1} \left( \frac{2 \times R \cdot H}{R^2 + H^2} \right) \]  
\[ \text{Eq. S49} \]

When \( j \) is even, \( r_{sw}, \beta_w, \) and \( \eta_w \) are given by

\[ r_{sw} = \frac{(b_w^2 + K_w^2)}{2K_w} \]  
\[ \text{Eq. S50} \]

\[ \beta_w = 2 \times \sin^{-1} \left( \frac{b_w}{r_{sw}} \right) \]  
\[ \text{Eq. S51} \]
Figure S16. (A) Proposed model of the two side domains in a dome, consisting of multiple pairs of stacked partial arches and defined with $j$, $H$, and $\kappa_{dsr} = 1$. (B) Right-angle side view showing that the partial arches have different heights labeled with $H_{dsr}$, where $w$ is 1, 2, ..., int[$\frac{j}{2}$]. Two identical zones were separated to assist the calculation. (C) Proposed model of the partial arches. To assist the calculation, the radius ($r_{sw}$) and angle ($\beta_w$) of the partial arches and the angle ($\eta_w$) and height ($K_w$) that are associated with the void space in each pair of partial arches are defined in the panel. (D) Side view of the partial arch pair with largest height: $H_{ds1} = \left(\frac{R^2 + H^2}{2 \cdot H}\right) \times \left[\cos \left(\frac{\eta_1}{2}\right) - \cos \left(\frac{\beta_1}{2}\right)\right]$. The pair of partial arches and the void space together form a new arch with a base radius ($b_1 = R$) and arch radius of $r_{ds1}$ as labeled in the panel.
$\eta_w = 2 \times \sin^{-1} \left( \frac{u \cdot L}{2r_{sw}} \right) \quad \text{Eq. S52}$

where $H_{dsw}$ and $b_w$ are given by

$K_w = \sqrt{r^2_{s1} - (w \cdot l)^2 - r_{s1} + K_1} \quad \text{Eq. S53}$

$b_w = \sqrt{b_{1}^2 - (w \cdot l)^2} \quad \text{Eq. S54}$

When $j$ is odd, $q_w$, $\beta_w$, and $\eta_w$ are given by

$q_w = \frac{(b_w^2 + K_w^2)}{2K_w} \quad \text{Eq. S55}$

$\beta_w = 2 \times \sin^{-1} \frac{b_w}{r_{sw}} \quad \text{Eq. S56}$

$\eta_w = 2 \times \sin^{-1} \frac{u \cdot L}{2r_{sw}} \quad \text{Eq. S57}$

where $K_w$ and $b_w$ are given by

$K_w = \sqrt{r^2_{s1} - ((w - 0.5) \cdot l)^2 - r_{s1} + K_1} \quad \text{Eq. S58}$

$b_w = \sqrt{b_{1}^2 - ((w - 0.5) \cdot l)^2} \quad \text{Eq. S59}$

2.2.3.3. Numerical simulations. To determine the structure of a superparticle with a given $N$, we first calculate its total volume according to Eq. S10. Under the restriction of $V(N) = V_c + 2 \times V_d$, we use mixed integer linear regression to find the values of $R$, $H$, $n$, $i$, $j$, $\kappa_d$, and $\kappa_c$ that result in the global minimum of superparticle surface area. The mixed integer linear regression was programmed using MATLAB® 7.0.1. Our simulations show that for a given $N$, the superparticle structure with the minimal surface area is determined by a unique set of variables: $R$, $H$, $n$, $i$, $j$, $\kappa_d$, and $\kappa_c$ (Figs. S17 to S19).
Figure S17. Results from numerical simulations for the formation of double-domed cylinders which are presented by the plots of $n$, $R$, $H$ and $2V_d/V_c$ as a function of $N$, where $n$ is the number of lamellar layers in the cylinder, $R$ is the radius of the cylinder, $H$ is dome height, and $2V_d/V_c$ is the volume ratio of the two domes and the cylinder. The results show these are the significant fluctuations of $n$ as a function of $N$. The zoomed-in image of the boxed area (in red) is shown in Fig. S18.
Figure S18. The zoomed-in image of the boxed area in Fig. S17. The results show that the significant fluctuations of $n$ as a function of $N$ can be attributed to the strong intercorrelations among $R$, $H$, and $n$ during the minimization of superparticle surface area through the distribution of constituent nanorods into the cylindrical domain and domes. With an increase in $N$, the corresponding decrease of $n$ (labeled in blue) is associated with an increase in $R$ and/or $H$, and a substantial increase in $2V_d/V_c$ (labeled in orange). The zoomed-in image of the boxed area (in black) is shown in Fig. S19.
Figure S19. The zoomed-in image of the boxed area in Fig. S18. The results show that a 0.05% increase in N leads to a significant change in H and in turn the ratio of $2V_d/V_c$, while R and $n$ are unchanged. When N reaches certain local thresholds, the values of R and n change dramatically in opposite directions.
Figure S20. (A) Schematic illustration of the difference in specific bulk free energy ($G^b_{b,d}$) between a dome and cylindrical domain. Because of the strong anisotropic interactions between neighboring rods aligned side-by-side, the stacked arches in the domes of a superparticle can have a specific bulk free energy ($G^b_{b,d}$) substantially higher than that of stacked disks in the cylindrical domain ($G^b_{b,c}$). (B) Scheme of the formation mechanism of the double-domed cylinder and irregular-multidomain particle structures for a given N: a double-domed cylinder forms when $2V_d$ is smaller than $V_c$, whereas an irregular-multidomain particle forms when $2V_d$ is larger than $V_c$.

Figure S21. TEM images of superparticles made from nanorods of $l = 45.0\pm1.8$ nm and $d = 7.1\pm0.2$ nm (A and B), and made from nanorods of $l = 78.0\pm2.1$ nm and $d = 5.4\pm0.3$ nm (C-E).
**Figure S22.** Schemes of the atomic packing structures of a CdS crystal at (A) the (10\bar{1}0), (B) (11\bar{2}0), and (C) (0001) faces, where Cd atoms are labeled as red balls and S atoms are labeled as indigo balls. Characteristic interatomic distances are labeled in each image.

**Figure S23.** Intraparticle ripening of needle-like superparticles in ethylene glycol (EG). (A) Scanning electron microscope image of typical needle-like superparticles dispersed in water, (B) TEM image of typical needle-like superparticles after aging in EG for three days. (C) TEM image of typical needle typical needle-like superparticles dispersed in water. The results show that a significant morphological change occurred after the aging treatment, while the average volume of the superparticles nearly remained unchanged (10±7 μm³).
Figure S24. Scheme of the preparation of freestanding PDMS thin films embedded with unidirectionally aligned needle-like CdSe/CdS superparticles. **Step 1** and **2**: unidirectional alignment of needle-line CdSe/CdS superparticles. **Step 3**: Incubation of superparticle-containing template with a PDMS-forming solution in glass petri dish. **Step 4**: PDMS film formation through polymerization at 100 °C. **Step 5**: Detachment of PDMS film from a template.

2.3. Template-assisted assembly of needle-like superparticles

2.3.1 Preparation of freestanding polymer thin films with unidirectionally aligned needle-like superparticles (**Fig. S24**). As a template, a line-patterned Si$_3$N$_4$ substrate of 1.0 cm × 2.0 cm (groove width = 2 μm, depth = 1.2 μm, gap = 2 μm) or an optical grating of 5.0 cm × 5.0 cm (groove width = 3 μm, depth = 1.2 μm, gap = 0.5 μm) were cleaned under sonication for 15 min in each of the following solvents: hexane, chloroform, and acetone, and then were rinsed with ethanol and dried under Ar flow. Next, an ethanol solution containing tetraethoxysilane (TEOS, 40 % in volume) and needle-like superparticles (100 μL, 2 mg/mL) was dropped onto the surface of a template with 45°
tilting. The droplet was forced to spread back and forth on the template using an Ar flow of ~60 cm/min until the solution was totally dried (Fig. S24). The superparticle-containing template was washed using ethanol three times to remove free superparticles that were not inside the template channels, and then was dried using Ar. SEM shows that nearly all needle-like superparticles were assembled and unidirectionally aligned inside template channels (Fig. 4E in the main text). In the next step, the template was immersed with a solution contain polydimethylsiloxane (PDMS) elastomer and curing agent (with a 10:1 volume ratio) in a 20-mL glass petri dish, and then was annealed in an oven at 100 °C for 1 h. After cooling to room temperature, a uniform, free-standing PDMS film was peeled off the template, the PDMS film was characterized using SEM (Fig. S25A) and fluorescence microscopy (a TE-2000 Nikon EZ-C1 confocal microscope).

2.3.2 Photoluminescence (PL) polarization measurements. The polarized PL emission from a needle-like superparticle embedded PDMS thin film was recorded with a fluorometer (Fluorolog-3, Horiba Jobin-Yvon, Irvine, CA). The samples were excited with a circularly polarized light at 380 nm generated via a linear polarizer and a quarter wave plate (Fig. S26). The linearly polarized PL emission from the film was measured through a linear polarizer and a quarter wave plate mounted on a rotation stage for polarization rotation, and the resulting circularly polarized light was measured by a fluorometer detector (32).

Figure S25. (A) Scheme of a superparticle-embedded PDMS thin film transferred from a Si$_3$N$_4$ substrate. (B) SEM image and (C) optical fluorescence image of a freestanding superparticle-embedded PDMS thin film
Figure S26. Scheme of the PL measurement setup. Inset: linearly polarized PL emission spectra measured from a typical freestanding PDMS film embedded with unidirectionally aligned CdSe/CdS nanorods at varying polarization angles.

2.3.3. Energy down-conversion LED panel. A light panel consisting of 10 LEDs (\(\lambda = 380\) nm, \(P = 20\) mW, Super Bright LEDs, Inc., St. Louis, Missouri, USA) was built and covered with two pieces of superparticle-embedded PDMS thin films with nanorod-alignment directions at a 90° angle (Fig. S27A). Under the excitation of LED lights, orange emission lights can been seen through a 500-nm cutoff filter. Optical images were taken using a Nikon D3000 camera with or without a polarizer (Fig. S27B), and the optical images are shown in Fig. 4, G to J in the main text.
Figure S27. (A) Photo image of a light panel consisting of ten LEDs, covered with two pieces of freestanding PDMS films, and (B) scheme for the measurements of polarized lights from the LED panel.

References and Notes

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17. See supplementary materials on Science Online.


