Supplementary Figure 1. A HRTEM image of a segment between Si crystal dots in Fig. 1a in the main text.
Supplementary Figure 2. Geometric relationships in Si nanodots. Error bars represent standard deviation.
Supplementary Figure 3. Original image used in Figure 2a of the main text.
Supplementary Figure 4. Quantitative geometric relationships in ZnS nanocore reported in Figure 1b of reference 8 in the main paper. a) Plot of the 1/L against serial number. b) Plot of diameter of dots against Length. Error bars represent standard deviation.
Supplementary Figure 5. Quantitative geometric relationships in silica nanofibre reported in Figure 3 of reference 20 in the main paper. a) Plot of the $1/L$ against serial number. b) Plot of diameter of dots against Length. Error bars represent standard deviation.
Supplementary Figure 6. Quantitative geometric relationships in silica nanofibre reported in Figure 1g of reference 7 in the main paper. a) Plot of the $1/L$ against serial number. b) Plot of diameter of dots against Length (numbers in bracket are slopes of the segments). Error bars represent standard deviation.
Supplementary Figure 7. Bulk preparation of ultralong (>1.5 cm) single crystal Si nanowire with average diameter 240 nm. Detailed experiments will be published in future work.
Supplementary Figure 8. A composite SEM image of a single SiNW on a crystal Si wafer (the whole image is shown top left). Detailed experiments will be published in a separated paper.
Supplementary Figure 9. The growth model of VLS: a nanosized droplet sits on a solid surface surrounded by vapour. The preset $T$, $P_{out}$ and the composition of the vapour are all assumed constant, and the process is assumed to be isothermal due to the very small size of the liquid droplet.
**Supplementary Figure 10.** SCO driven VLS growth.
**Supplementary Table 1.** EDX analysis on the segments between nanodots.

<table>
<thead>
<tr>
<th></th>
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<td>location 1</td>
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</tr>
<tr>
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<td>45</td>
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<td>location 4</td>
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<tr>
<td><strong>Mean</strong></td>
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</table>

All results are in atomic %. 

**Supplementary Note 1. Statement:** When the radius of indium droplet is in micrometer, its oscillation will lead to strong oscillation in $P_{in}$ and thus the kinetic of nucleation and growth of the nanostructures. Because the pressure from the size effect could be one order of magnitude higher than the environmental pressure in the chamber ($P_{out}$).

**Justification:** The Young-Laplace equation shows:

$$P_{in} = P_{out} + \frac{2\gamma_{lv}}{R}.$$  

If the experiment pressure is 350 mbar, then the first term is:

$$P_{out} = 3.5 \times 10^4 \text{ Pa}$$

Depending on the temperature and purity, the surface tension of molten indium is the range of 500 to 530 mN/m$^2$. Using a value of 515 mN/m for the surface tension, the $(2\gamma_{lv}/R)$ term for a droplet with radius of 2.5 micrometer becomes:

$$\frac{2\gamma_{lv}}{R} = \frac{2 \times 0.515 \text{ Nm}^{-1}}{2.5 \times 10^{-6} \text{ m}} = 41.2 \times 10^4 \text{ Pa}.$$  

This term is still more than ten times larger than the $P_{out}$ term and thus should still have considerable influences on the growth dynamic. On the other hand, if the diameter reaches 100 micrometer, the $(2\gamma_{lv}/R)$ term is $2.06 \times 10^4 \text{ Pa}$ which is similar in magnitude to the $P_{out}$ term and thus would have much less influences on the growth dynamics.

**Supplementary Note 2. Statement:** The chosen $T$, $P_{out}$ and the composition of the vapor are all assumed constant.

**Justification:** The chosen $T$ and $P_{out}$ can be steadily controlled to be within 0.4% of the targeted values with our equipment. The composition of the vapor is SiO, the assumption was supported by the gravimetric analysis experiment in methods of the main paper.

**Supplementary Note 3. Statement:** $\mu_{v-\infty}$, $P^v$, $\gamma_{v-v}$, $\gamma_{v-l}$, $V^l$, $\mu^l$, and $A^{l-s}$ are assumed constant in equations (2), (3) and (4) in the main paper.

**Justification:** $\mu_{v-\infty}$ and $P^v$ can be find from handbook under determined $P_{out}$ and $T$. $V^l$ is assumed as constant because of the incompressibility of ideal liquid. $\gamma_{v-v}$ and $\gamma_{v-l}$ are constant since they are mainly functions of temperature which is set as constant in the experiment. $\mu^l$ (the chemical potential of the solid phase) and $A^{l-s}$ (the areal atom density of the liquid-solid interface) are constant in most amorphous structures considered here.

**Supplementary Note 4. Statement:** Numerical simulation plot of $\mu^l$ against $\theta$ for a nanowire of 100 nm diameter based on equations (2), (3) and (4) in the main paper with arbitrarily defined thermodynamic properties. In which $\mu_{v-l}^l = 105 + 1000 \times \frac{\sin \theta}{r}$ and $\mu_{l-s}^l = 148 - 55 \times \cos \theta$.

**Justification:** As justified in Supplementary Note 3, $\mu_{v-\infty}^l$, $P^v$, $\gamma_{v-v}$, $\gamma_{v-l}$, $V^l$, $\mu^l$, and $A^{l-s}$ are all constant. The purpose of this numerical simulation is to show that solutions
for equations (2), (3) and (4) in the main paper do exist if thermodynamic properties of the system are suitable. It implies the mathematical analysis has physical meaning.

Supplementary Note 5. Statement: Considering the supersaturation nucleation phenomenon, we assumed that the liquid in liquid droplet will only start solidification when \( \mu_{l-n}^{l} - \mu_{l-s}^{l} = \Delta \mu_{1} \). The solidification would lead to a decrease in \( R \) and increases in \( 1/R \) and \( \theta \). On the other hand, considering undersaturation nucleation, we assume that the solidification will only cease when \( \mu_{l-l}^{s} - \mu_{l-n}^{s} = \Delta \mu_{2} \).

Justification: Supersaturation and undersaturation are widely observed, the assumption that their chemical potential is quantified is consistent with the two-species model for melting-curve maxima that had been found in molten metals such as Ce, Te and intermetallic compounds BbTe3 et al.\(^5,6\).
Supplementary Discussion

Thermodynamic analysis of the SCO in VLS process. (Mathematical relations and essential concepts of physics can be found in typical text books for physical chemistry. For example “Atkins’ Physical Chemistry”, seventh edition, High education press, Beijing, 2006. Page 122 “the Maxwell relations”; page 124 “properties of the Gibbs energy”; page 142 “the response of melting to applied pressure” and page 150 “surface tension”).

Abbreviations:

∞ : Saturated vapor pressure on a flat liquid surface;
T : The preset growth temperature;
 outP : The preset growth pressure in the reaction chamber;
inP : The pressure inside the liquid droplet;
lV : The molar volume of the liquid phase;
μV, μs : Chemical potential of the vapor and solid phases, respectively;

During the growth process, the three phases (V, L, S) are dynamically changing. The main processes including condensation of the vapor phase into liquid phase and the solidification from the liquid phase into the solid phase. μV-L and μL-S are respectively the chemical potentials of the liquid phase during the condensation and solidification processes. These two values can be respectively determined from μV, μL and the processing conditions using thermal dynamic rules.

Assumptions: Based on the results from “Composition of the species evaporated from the solid SiO source” in the methods of the main paper, we assume that change in composition of the vapor is negligible.

We further assume that the preset growth pressure in the reaction chamber P_out and the preset growth temperature T have negligible changes during the growth process.

Chemical potential of the liquid catalyst droplet in Vapor-liquid phase change. We first consider the vapor-liquid phase change. The change in Gibbs energy, dG, for infinitesimal amounts of materials transferred between the vapor and the liquid phase is

\[ dG = -SdT + VdP + \gamma_{v-l} dA + \mu_{v-L} dn_{v-L} + \mu^* d\nu^* , \]  

(1)

Where \( \mu^* \) is the chemical potential of the vapor; \( dn_{v-l} \) is the amount of liquid evaporates into vapor; \( d\nu^* \) is the amount of vapor condenses into liquid. By definition, \( -d\nu^* = dn_{v-l} \), and thus,

\[ dG = -SdT + VdP + \gamma_{v-l} dA + (\mu_{v-L} - \mu^*) dn_{v-l} \]  

(2)

For complete differential,

\[ \frac{\partial (\mu_{v-L} - \mu^*)}{\partial P} = \frac{\partial V}{\partial n_{v-l}} = V^l \]  

(3)

In which \( V^l \) is the molar volume of the liquid phase. In this equation, \( \mu^* \) can be treated as a constant for an experiment carried out at relatively stable pressure, temperature and vapor composition. Then we have,
\[
\frac{\partial \mu'_{v-l}}{\partial P} = \frac{\partial V}{\partial m_{v-l}} = V' \tag{4}
\]

As the properties of liquid are \textit{weak functions} of the pressure, the chemical potential of the liquid droplet with a surface curvature \(1/R\) can be approximately written as,

\[
\mu'_{v-l} = \mu'_{v-l}^{i} + \left( P_{out} + \frac{2\gamma_{l,v}}{R} \right) \left( \frac{\partial \mu'_{v-l}}{\partial P} \right) \tag{5}
\]

in which, \(\mu'_{v-l}^{i}\) is the chemical potential of the curved liquid phase with surface curvature \(1/R\), pressure \(P_{out}\) and temperature \(T\); \(\mu'_{v-l}^{i,\infty}\) is the chemical potential of liquid phase with a flat surface under its saturated pressure \(P^{\infty}\) and temperature \(T\), respectively.

Put (4) into (5), we have,

\[
\mu'_{v-l} = \mu'_{v-l}^{i,\infty} + \left( P_{out} - P^{\infty} \right) V' + 2\gamma_{l,v} V' \frac{\theta}{r} \tag{6}
\]

As \(R = r/\sin \theta\) (Supplementary Figure 9), we can write,

\[
\mu'_{v-l} = \mu'_{v-l}^{i,\infty} + \left( P_{out} - P^{\infty} \right) V' + 2\gamma_{l,v} V' \frac{\sin \theta}{r} \tag{7}
\]

**Chemical potential of the liquid catalyst droplet in Liquid-Solid phase change.** The change in Gibbs energy for an infinitesimal amount of material transferred between the liquid and the solid phase is,

\[
dG = -SdT + VdP + \gamma_{l-s} dA + \mu^{i} dn^{i} + \mu^{i}_{l-s} dn_{l-s} \tag{8}
\]

where \(\mu^{i}\) is the chemical potential of the vapor; \(dn^{i}\) is the amount of solid dissolves into liquid; \(dn_{l-s}\) is the amount of liquid condenses into solid. By definition, \(dn^{s} = -dn_{l-s}\), and thus,

\[
\mu^{i} = \mu^{i}_{l-s} + \mu^{i}_{l-s} \frac{\gamma_{l-v} V' - \gamma_{l-v} V' \sin \theta}{A^{l-s}} \tag{9}
\]

Under equilibrium and constant \(T\) and \(P\), the equation can be rearranged to,

\[
\left( \mu^{i} - \mu^{i}_{l-s} \right) = \frac{1}{A^{l-s}} \gamma_{l-s} \tag{10}
\]

where \(A^{l-s}\) is the areal atom density at the liquid-solid interface.

When the surface tension at the liquid-solid interface is in equilibrium, combining the Young equation \(\gamma_{l-s} = \gamma_{s-v} + \gamma_{l-v} \cos \theta\) with (10), we have,

\[
\mu^{i}_{l-s} = \mu^{i} - \gamma_{l-v} \frac{A^{l-s}}{A^{l-s}} \cos \theta \tag{11}
\]

**Periodic growth.** For the \(n\)th and \(n+1\)th growth periods, the difference in \(\mu'_{v-l}\) for the two periods can be calculated from equation (7),

\[
\Delta \mu'_{v-l} = 2\gamma_{l,v} V' \left( \frac{\sin \theta_{n}}{r_{n}} - \frac{\sin \theta_{n+1}}{r_{n+1}} \right) \tag{12}
\]

Considering \(\gamma_{l-s} = \gamma_{s-v} + \gamma_{l-v} \cos \theta\), then

\[
\sin \theta = \frac{\sqrt{(\gamma_{l-v} - \gamma_{l-s} + \gamma_{l-v})(\gamma_{l-v} + \gamma_{l-s} - \gamma_{s-v})}}{\gamma_{l-v}} \tag{13}
\]
Defining \[ W_{\text{VLS}}^2 = (\gamma_{f-v} - \gamma_{s-v}) (\gamma_{f-v} + \gamma_{s-v}) \] (14).
Then
\[ \Delta \mu_{l} = 2 \mu (\frac{W_{\text{VLS},n}}{r_n} - \frac{W_{\text{VLS},n+1}}{r_{n+1}}) \] (15).

**Geometric relationships along the periodic growth.** We first consider the process when the liquid droplet increases in size (the red process as shown in Supplementary Figure 10), in which pressure in the liquid decreases. Here we use the subscripts \( h \) and \( l \) to denote these high and low pressure states. As \( \theta \) changes from \( \theta_h \) to \( \theta_l \), the axial growth would hibernate since \( dV/dR < 0 \) as stated in the equation 4 of the main text.

Let \( V \) be the volume change of the liquid droplet, \( r_i \) and \( r_h \) are respectively the radii of the nanostructures when liquid droplet is in the low- and the high-pressure states. Then, the change in radius will be \( \Delta r_{h\rightarrow l} = r_i - r_h \); and the change in length will be very small, \( \Delta L_{h\rightarrow l} \rightarrow 0 \) as described in the equation 4 of the main text.

We now consider the second half of the growth period in which the liquid droplet decreases in size (the blue process in Supplementary Figure 10). In this process, \( \theta \) changes back from \( \theta_l \) to \( \theta_h \), and the change in length will be \( \Delta L_{l\rightarrow h} = \Delta V / S \).

The volume of the spherical cap is
\[ V = \frac{1}{6} \pi h (3r^2 + h^2) \] (16);
in which \( V \) and \( h \) are the volume and height of the liquid droplet, respectively; and \( h \) (see Supplementary Figure 9) can be determined from the geometry as \( h = R + R \cos \theta = r \cotg \left( \frac{\theta}{2} \right) \).

Then we rewrite the volume of the liquid droplet as
\[ V = \frac{1}{6} \pi r \cotg \left( \frac{\theta}{2} \right) \left[ 3r^2 + r^2 \cotg^2 \left( \frac{\theta}{2} \right) \right] = \pi r \cotg \left( \frac{\theta}{2} \right) \left[ \frac{1}{2} \cotg \left( \frac{\theta}{2} \right) + \frac{1}{6} \cotg^3 \left( \frac{\theta}{2} \right) \right] \] (17).

then
\[ \Delta L_{l\rightarrow h} = \Delta V_{l\rightarrow h} / S \]
\[ = \left[ \frac{1}{6} \pi \cotg \left( \frac{\theta}{2} \right) \left[ 3 \cotg \left( \frac{\theta}{2} \right) - \cotg \left( \frac{\theta}{2} \right) \right] + \left[ \cotg^3 \left( \frac{\theta}{2} \right) - \cotg^3 \left( \frac{\theta}{2} \right) \right] \right] \]
\[ = \frac{1}{6} r_i \left[ 3 \cotg \left( \frac{\theta}{2} \right) - \cotg \left( \frac{\theta}{2} \right) \right] + \left[ \cotg^3 \left( \frac{\theta}{2} \right) - \cotg^3 \left( \frac{\theta}{2} \right) \right] \] (18).

In the whole SCO cycle, the axial growth length \( L \) is:
\[ L = \Delta L_{l\rightarrow h} + \Delta L_{h\rightarrow l} \]
\[ = \frac{1}{6} r_i \left[ 3 \cotg \left( \frac{\theta}{2} \right) - \cotg \left( \frac{\theta}{2} \right) \right] + \left[ \cotg^3 \left( \frac{\theta}{2} \right) - \cotg^3 \left( \frac{\theta}{2} \right) \right] + \Delta L_{h\rightarrow l} \] (19).
Let $\alpha = \frac{1}{6} \left[ 3 \left( \ctg \left( \frac{\theta_1}{2} \right) - \ctg \left( \frac{\theta_2}{2} \right) \right) + \left( \ctg^3 \left( \frac{\theta_1}{2} \right) - \ctg^3 \left( \frac{\theta_2}{2} \right) \right) \right]$ (20).

and $\beta = \Delta L_{n-1}$, $\beta$ will be a small value compared to $L$, then we take $\beta$ as a constant and (19) can be rewritten as,

$L = \alpha \tau_i + \beta$ (21).

Supplementary References