Supporting Information

Modeling of Solution Growth of ZnO Hexagonal Nanorod Arrays in Batch Reactors

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SUPP 1. Schematic drawing of trenches milled by FIB.

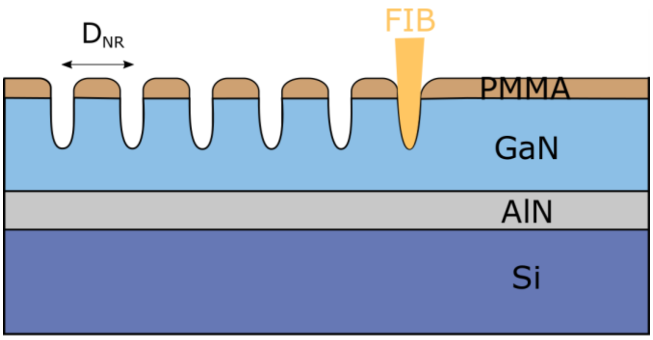


Figure SUPP 1.1. Schematic drawing of the trenches fabricated by FIB.

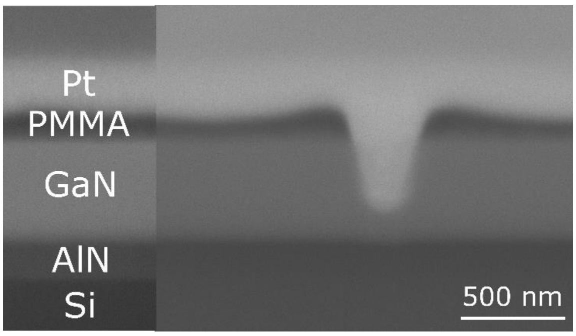
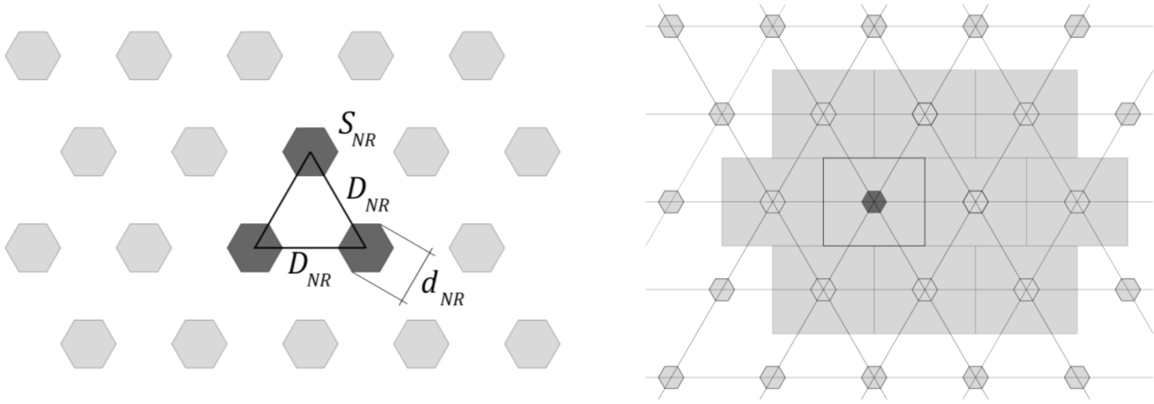


Figure SUPP 1.2. SE and BSE SEM cross-section images of a trench fabricated by FIB lithography.

SUPP 2. Estimation of the surface coverage ratio of hexagonal nanorod arrays.



(a) (b)

Figure SUPP 2. (a) Schematic top view of a hexagonal nanorod array for the calculation of the surface coverage ratio. The nanorods have the diameter d_{NR}, the top face area S_{NR}, and the distance between the nanorods is D_{NR}. (b) Schematic view of a rectangular area surrounding a single nanorod, which was used for the calculation of the nanorod density.

Let us assume a periodic hexagonal array of vertically grown ZnO nanorods with internanod distances D_{NR} and uniform nanorod diameters d_{NR} (**Figure SUPP 2a**). The surface coverage ratio S of this ZnO nanorod array is given by the total area of top faces of ZnO nanorods divided by the total area covered by these nanorods. S can be generally calculated by the following equation

$$S = n_{NR} S_{1NR} \tag{S2.1}$$

where $n_{NR} = N_{NR}/S_{TOT}$ is the number density of the nanorods within a total area covered by the nanorod pattern S_{TOT}, where N_{NR} is the number of nanorods within this area. S_{1NR} is the average surface area of a single nanorod. If we assume that the nanorods have a regular hexagonal shape, S_{1NR} can be calculated

$$S_{1NR} = \frac{3\sqrt{3}}{8} d_{NR}^2 \tag{S2.2}$$

To estimate the nanorod number density n_{NR}, let us assume that every nanorod is surrounded by a rectangle with sides of D_{NR} and $\left(\sqrt{3}/2\right) D_{NR}$. The area of the rectangle is

$$\tilde{S}_{1NR} = \frac{\sqrt{3}}{2} D_{NR}^2 \tag{S2.3}$$

Clearly, the rectangles can completely fill the total area S_{TOT} (**Figure SUPP 2b**). Then the number of nanorods within S_{TOT} is

$$N_{NR} = \frac{S_{TOT}}{\tilde{S}_{1NR}} \tag{S2.4}$$

Combining **eq S2.3** and **eq S2.4**, we obtain the relation for the number density of nanorods

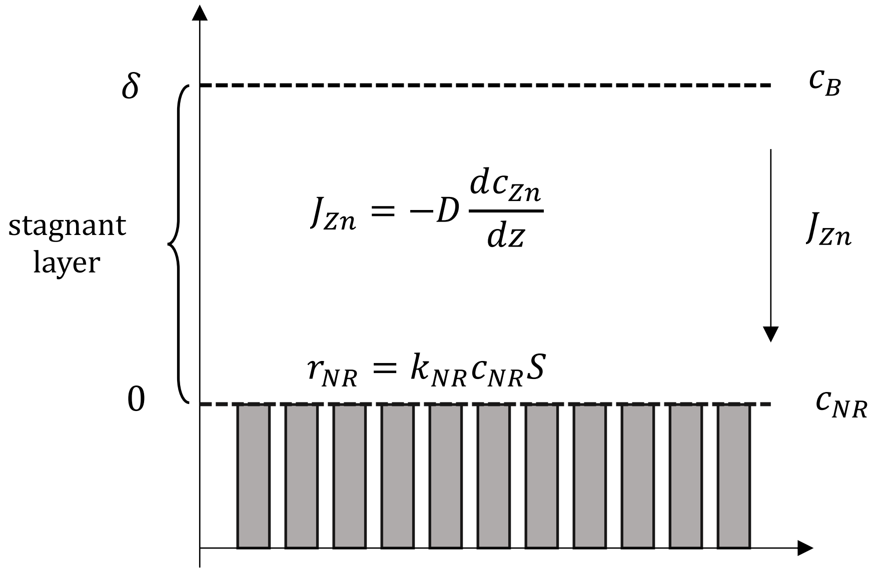
$$n_{NR} = \frac{N_{NR}}{S_{TOT}} = \frac{1}{\tilde{S}_{1NR}} = \frac{2\sqrt{3}}{3}\frac{1}{D_{NR}^2} \approx 1.1547\frac{1}{D_{NR}^2} \qquad \text{(S2.5)}$$

Using **eq S2.1**, **S2.2**, and **S2.5**, we can find the relation of the surface coverage ratio

$$S = \frac{2\sqrt{3}}{3}\frac{S_{1NR}}{D_{NR}^2} = \frac{3}{4}\frac{d_{NR}^2}{D_{NR}^2} \qquad \text{(S2.6)}$$

This simple equation (**eq S2.6**) was then used as an estimation for the surface coverage ratios of all the arrays.

SUPP 3. Reaction/Diffusion limited growth model.



The reaction/diffusion limited growth model assumes that there is a nanorod array with infinite lateral dimensions with the surface coverage ratio S, which is the ratio of the area of all c-plane faces to the total area (see **SUPP 2**). These nanorods are immersed in a solution with the reactants. As a first approximation, we consider that only the concentration of Zn^{2+} ions c_{Zn} is responsible for the growth kinetics of the nanorods. As the nanorods grow, they consume the growth units from the solution and a stagnant layer is formed between the top nanorod faces (with the interface Zn^{2+} ion concentration c_{NR}) and the area with the bulk concentration c_B at the distance δ. Within this stagnant layer, a concentration gradient is formed. According to the first Fick's law, the diffusion flux of Zn^{2+} ions J_{Zn} is governed by the concentration gradient (here in z axis)

$$J_{Zn} = -D\frac{dc_{Zn}}{dz} \tag{S3.1}$$

where D is the diffusion coefficient of Zn^{2+} ions in water. During the growth of nanorods, the rate of consumption of Zn^{2+} ions by the nanorod array is proportional to the interface concentration c_{NR} and to the surface coverage ratio S

$$r_{NR} = k_{NR}c_{NR}S \tag{S3.2}$$

where k_{NR} is the first-order reaction rate constant, which characterizes the rate of incorporation of the growth unit into the nanorod. In equilibrium, the diffusion flux J_{Zn} has to be equal to the rate of incorporation Zn^{2+} ions to the nanorods r_{NR}

$$J_{Zn} = r_{NR} \tag{S3.3}$$

In steady state, the diffusion flux is constant, and therefore the concentration gradient is linear. We can then write

$$-D\frac{c_B - c_{NR}}{\delta} = k_{NR}c_{NR}S \tag{S3.4}$$

After rewriting, we obtain the relation for the interface ion concentration c_{NR}

$$c_{NR} = \frac{c_B}{\phi + 1} \tag{S3.5}$$

where ϕ is the Thiele modulus

$$\phi = \frac{k_{NR} S \delta}{D} \tag{S3.6}$$

Note that the Thiele modulus is a measure whether the reaction rate or the diffusion rate dominates the growth process.

Let us now assume, that the nanorods grow in c direction only. The volume increment of total ZnO nanorod array dV/dt can be expressed as

$$\frac{dV_{TOT}}{dt} = \frac{dh}{dt} S_{TOT} S \tag{S3.7}$$

where $R_h = \frac{dh}{dt}$ is the growth velocity in c direction, S_{TOT} is the total area covered by nanorods and $S_{TOT}S$ is the total area of nanorod top faces. If we consider that $V_{TOT} = n_{TOT}V_M$, where $V_M = 1.45 \times 10^{-5}\ \mathrm{m^3 mol^{-1}}$ is the molar volume of ZnO and n is the number of moles corresponding to the ZnO volume V, we can then write

$$R_h = \frac{dh}{dt} = \frac{V_M}{S} \frac{dn_{TOT}}{S_{TOT} dt} = \frac{V_M}{S} r_{NR} \tag{S3.8}$$

Using **eq S3.2**, we can rewrite equation **eq S3.8**

$$\frac{1}{R_h} = \frac{1}{k_{NR} V_M c_B} + \frac{\delta}{D V_M c_B} S \tag{S3.9}$$

which is the equation used for the fitting of the measured data. From the linear fit of the dependence of the inverse growth velocity $1/R_h$ on the surface coverage ratio S, we can extract the reaction constant k_{NR} and the stagnant layer thickness δ.

$$\frac{1}{R_h} = A + BS \tag{S3.10}$$

where A is the intercept and B is the slope of the linear fit. Then

$$k_{NR} = (A V_M c_B)^{-1}, \delta = B V_M D c_B \tag{3.11}$$

<u>Assumptions:</u>

1. The nanorod array has infinite lateral dimensions and the height of the nanorods is uniform. Effects at the borders of the arrays are neglected.
2. Only the concentration of Zn^{2+} ions is responsible for the growth kinetics of ZnO nanorods.
3. The nanorods grow only in the direction of c-axis. Radial growth is neglected.
4. The growth of the nanorods is driven by first-order kinetics.
5. The system is in equilibrium.
6. The system is in a steady state, which is not valid for batch reactors, where the total concentration of reactants decreases with time.

SUPP 4. Experimental determination of the surface coverage ratio.

The diameter of the nanorod d_{1NR} was calculated from the measured area of the top nanorod face using SEM images. From this value, the nanorod diameter was calculated using **eq S2.2**. Since the shape of the nanorods is usually not a regular hexagon, the value of d_{1NR} is only an approximation, i.e. it is a diameter of a regular hexagon with the same area as is the measured area.

Since the height and diameter of the ZnO nanorods depends on the position within the nanorod array, only the nanorods around the middle of the array were considered for further analysis. The heights and diameters were calculated as the average of the nanorod dimensions in the center and of the six nanorods surrounding the one in the center.

SUPP 5. Finite element method implementation in COMSOL.

COMSOL Multiphysics software package was used to solve the diffusion equation by finite element method (FEM) to obtain the concentration c of the growth units (here Zn^{2+} ions) in the vicinity of the nanorod array. We solved the diffusion equation on the domain illustrated in **Figure SUPP 5.1**

$$\frac{\partial c}{\partial t} + D\Delta c = R$$

where D is the diffusion coefficient of Zn^{2+} in aqueous media, and $R = -k_{tit}c$ is the rate of homogeneous reaction. Here, k_{tit} is the rate constant of homogeneous reactions which was measured by titration of the growth solution at different growth times.

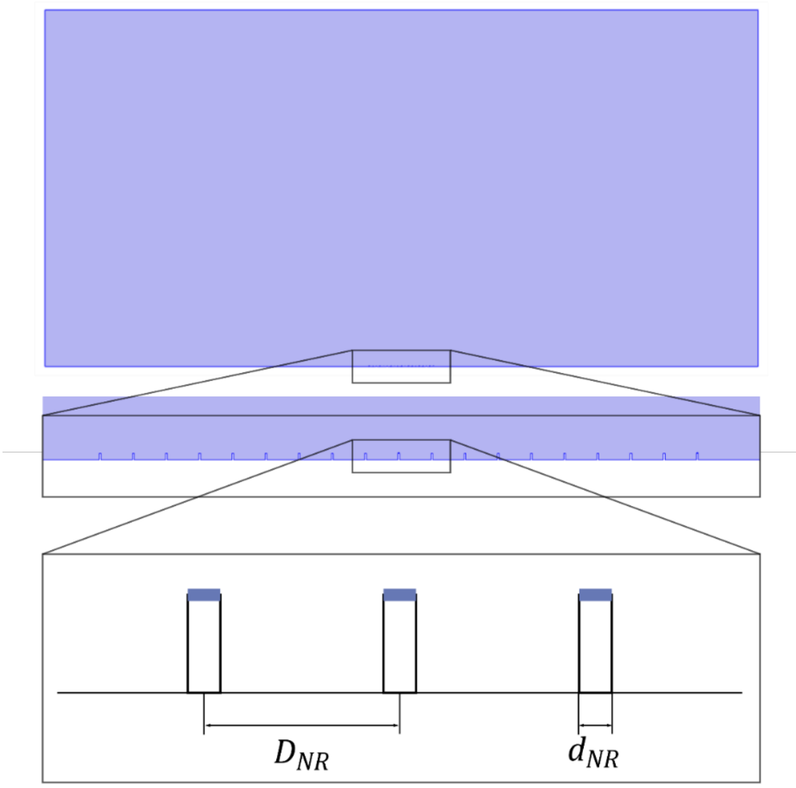


Figure SUPP 5.1. The 2D domain shape used in FEM calculations. 19 rectangles at the bottom part of the domain represent 19 nanorods within a pattern.

The diffusion equation was solved in 2D on the domain shown in **Figure SUPP 5.1**. The domain had a rectangular shape with 19 smaller rectangles at the bottom part of this domain representing 19 nanorods within the nanorod array. The top nanorod faces (see the bottom part of **Figure SUPP 5.1** – blue lines) acted as sinks and the rate of consumption of the growth units by these top nanorod faces was represented by a flux through them:

$$J = -k_{NR}c$$

where k_{NR} is the reaction constant determined by the diffusion/reaction model and c is the local concentration at the nanorod top surface. The size of the computation domain was selected to be 100 times larger than the size of the 19 nanorod pattern (at minimum). This domain was found to be sufficiently large, so that further increase of its size had no impact on the results. The simulation mesh was composed of free triangular elements with the density of 100 elements at the nanorod top faces and 50 elements at the walls. Further increase of the density of the mesh elements did not lead to any significant change of the results. From the calculated solution of the diffusion equation, the diffusive fluxes of Zn^{2+} ions through each of the nanorod top face J_{top_face} were computed and integrated over the length of the nanorod top face (represented by blue lines in **Figure SUPP 5.1**) and over the whole time period of nanorod growth T, giving the total amount of moles of Zn^{2+} ions consumed by the particular nanorod n_{TOT}

$$n_{TOT} = \int_0^T \int J_{top\_face} dl\, dt$$

The calculated n_{TOT} was used for the calculation of the nanorod height h_{NR} taking the nanorod as a rectangle with both the top and bottom side of the same length d_{NR}

$$h_{NR} = \frac{V_M n_{TOT}}{d_{NR}}$$

where V_M is the molar volume of ZnO. The ratio of the nanorod height at the boundary and in the center of the array is plotted in **Figure 7**.

SUPP 6. SEM images of the time evolution of the growth of ZnO nanorods.

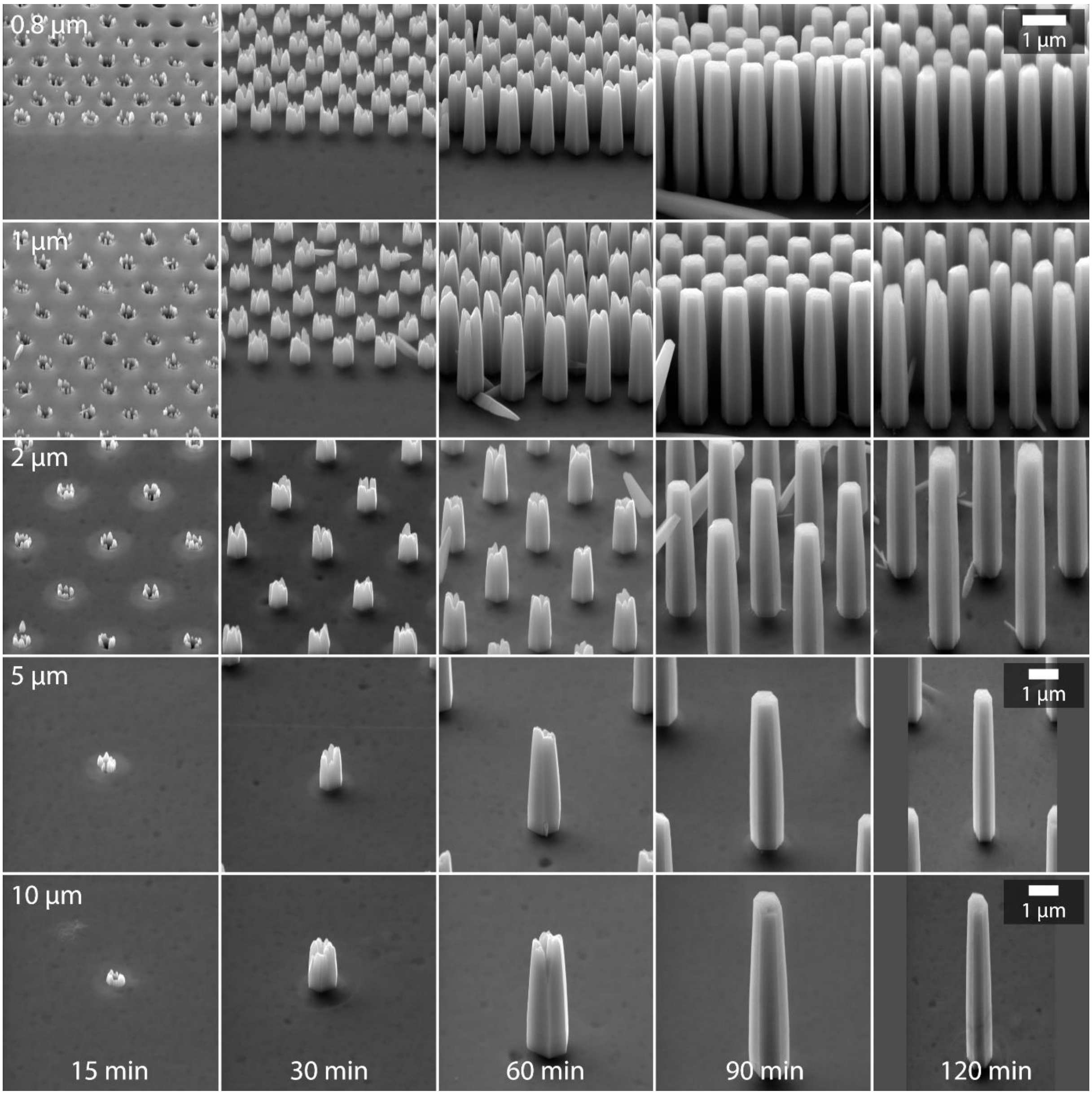


Figure SUPP 6.1. Tilted-view SEM images of hexagonal ZnO nanorod arrays with different internanorod distances (0.8 µm, 1 µm, 2 µm, 5 µm, and 10 µm). The growth time was varied from 15 min to 120 min. Other parameters of the growth were fixed (concentration of the reactants 2.5 mM, growth time 2 h, temperature 95°C).

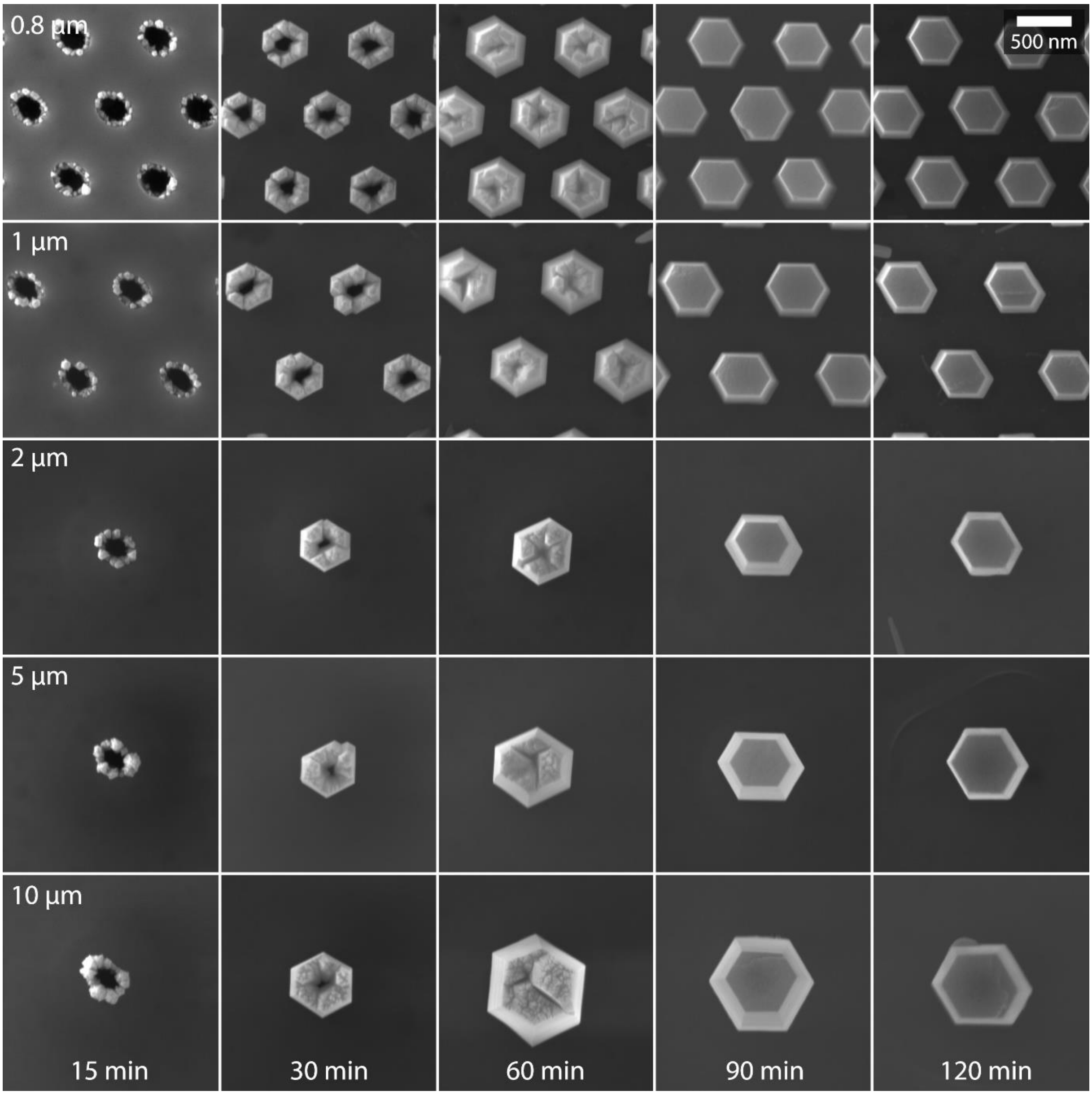


Figure SUPP 6.2. Top-view SEM images of hexagonal ZnO nanorod arrays with different internanorod distances (0.8 µm, 1 µm, 2 µm, 5 µm, and 10 µm). The growth time was varied from 15 min to 120 min. Other parameters of the growth were fixed (concentration of the reactants 2.5 mM, growth time 2 h, temperature 95°C).

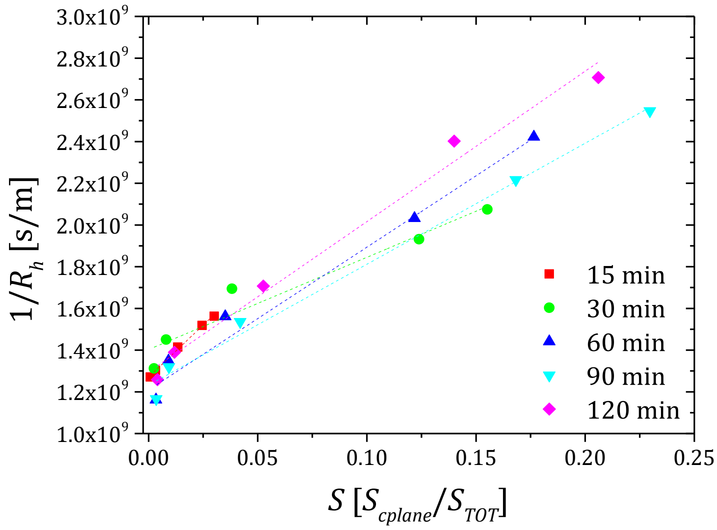


Figure SUPP 6.3. Dependence of the inverse growth velocity $1/R_h$ on the surface coverage ratio S for hexagonal ZnO nanorod arrays with different internanorod distances (0.8 µm, 1 µm, 2 µm, 5 µm, and 10 µm) grown at different growth times (15, 30, 60, 90, 120 min) shown in **Figures SUPP 6.1** and **SUPP 6.2**.

SUPP 7. TEM measurements.

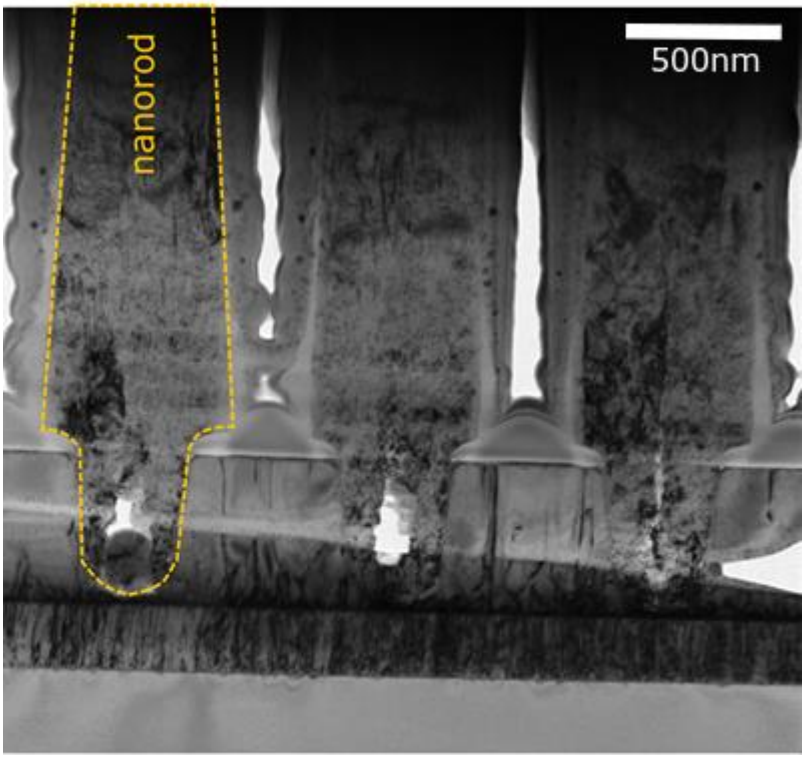


Figure SUPP 7. Bright field TEM image showing the nanorods growing from the trenches fabricated by FIB. The first crystallites appear around the upper part of the trench, which further develop and merge into a nanotube with a facetted outer and rough inner surface. By lateral growth the nanotubes are gradually filled and transform into nanorods. There is a hollow left in the trench, as the growth units have a spatial a temporal limitation to diffuse through the upper part of the nanotube. The growth time was 120 min, and the growth temperature 95°C. The measured upper diameter of the FIB trench was 360 nm and the measured depth of the trench was 490 nm.

SUPP 8. Used Constants and Symbols

Table of constants:

$\boldsymbol{D}$	diffusion coefficient	2.91×10^{-9} m^2/s
$\boldsymbol{\rho_M}$	ZnO molar density	6.8×10^{4} mol/m^3
$\boldsymbol{V_M}$	molar volume of ZnO	1.452×10^{-5} m^3/mol
$\boldsymbol{k_{tit}}$	reaction constant from titrations	0.026 min^{-1}

Table of symbols:

$\boldsymbol{c_0}$	initial concentration	mol/m^3
$\boldsymbol{c_\infty}$	concentration at $t \to \infty$ from titration	mol/m^3
$\boldsymbol{c_{NR}}$	interface concentration between nanorods and solution	m^3/mol
$\boldsymbol{c_B}$	bulk concentration	m^3/mol
$\boldsymbol{c_{eq}}$	equilibrium concentration from MINTEQ calculations	m^3/mol
$\boldsymbol{D_{NR}}$	distance between nanorods	m
$\boldsymbol{h_{NR}}$	height of nanorod	m
$\boldsymbol{R_h}$	c-plane growth velocity	m/s
$\boldsymbol{\delta}$	stagnant layer thickness (**SUPP 3**)	m
$\boldsymbol{k_{NR}}$	first-order surface reaction rate constant	m/s