

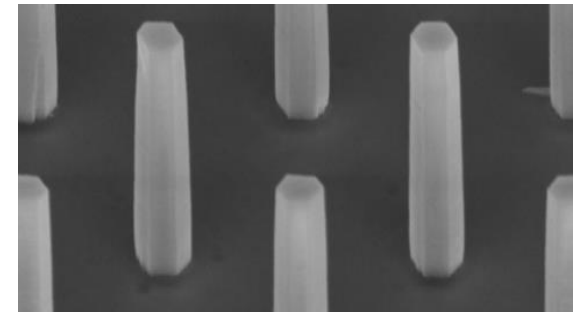
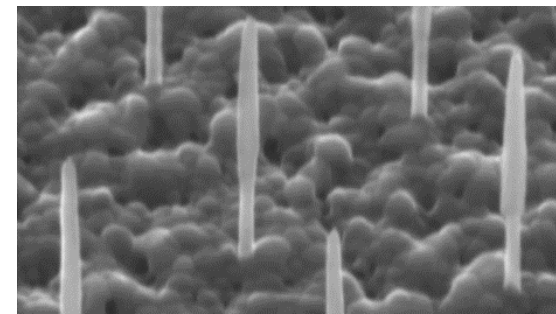
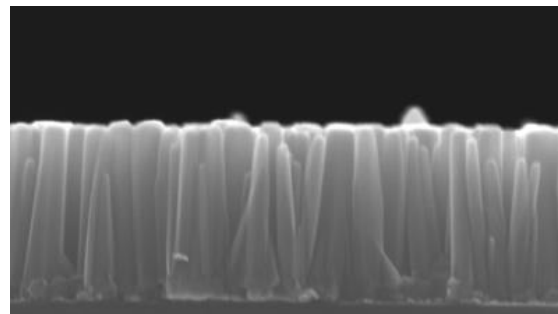
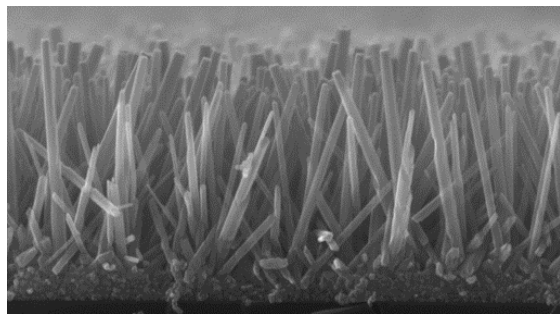
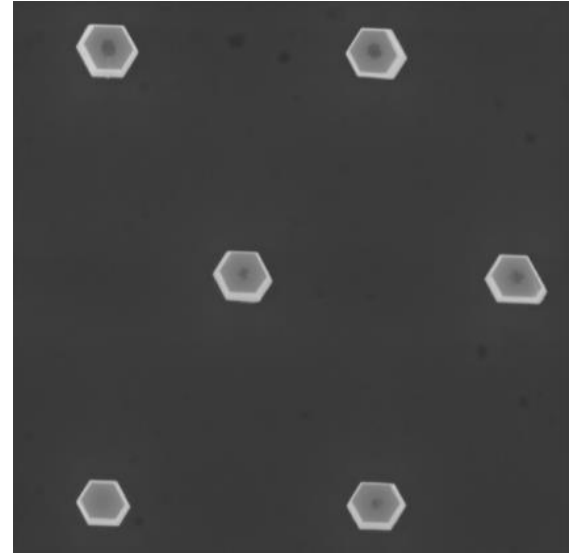
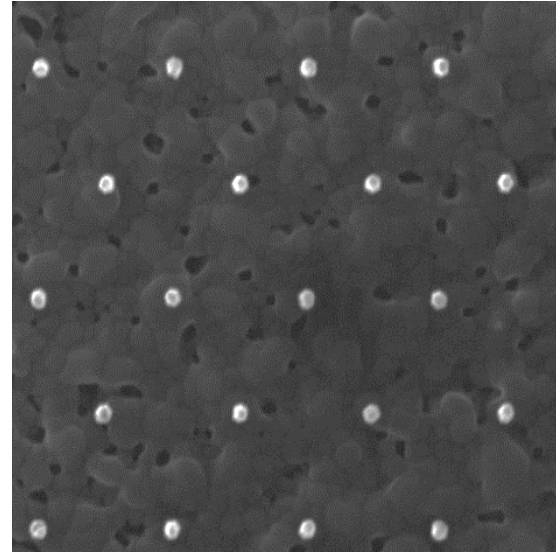
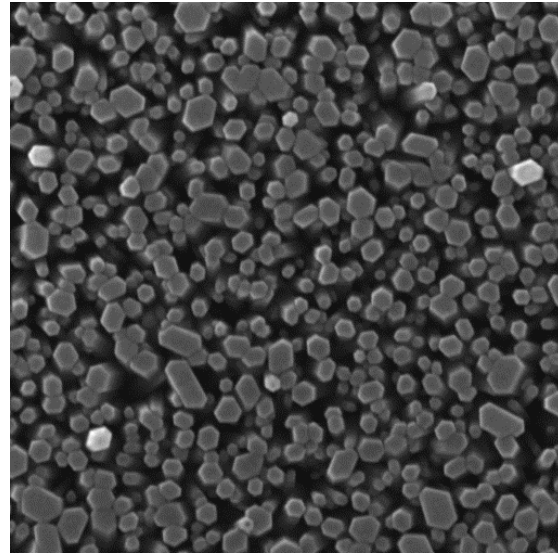
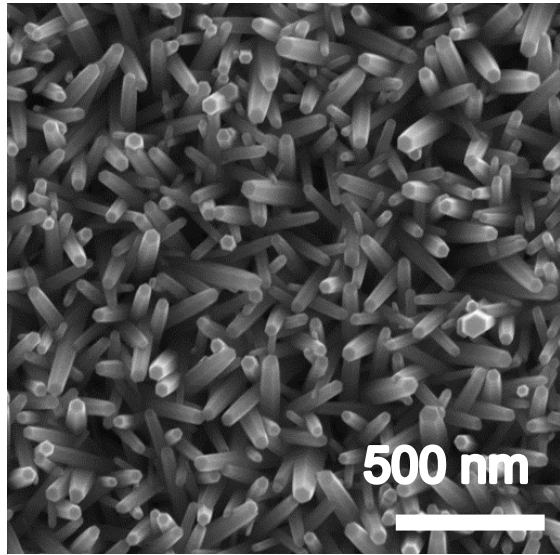
# Modelování růstu nanostruktur z kapaln<sup>é</sup> fáze v COMSOL Multiphysics

*Ondřej Černohorský, Šárka Kučerová, Nikola Bašinová, Hana Faitová,  
Roman Jackiv, Stanislav Tiagulskyi, Jan Vaniš and Jan Grym*

Ústav fotoniky a elektroniky AV ČR, v.v.i.

COMSOL MULTIPHYSICS 2021, Zaječí, 2021

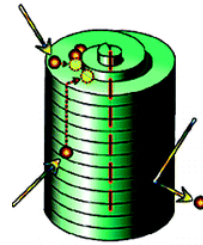
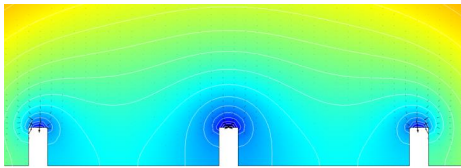
# Úvod



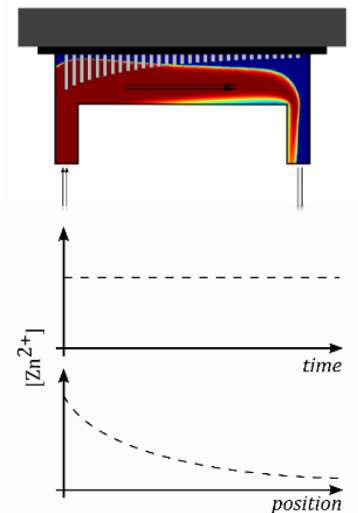
# Úvod

## Růst nanostruktur

### Modelování růstových mechanismů

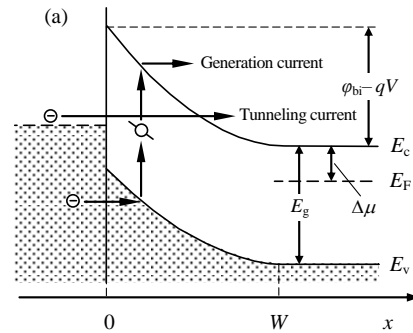


### Návrh reaktorů pro růst

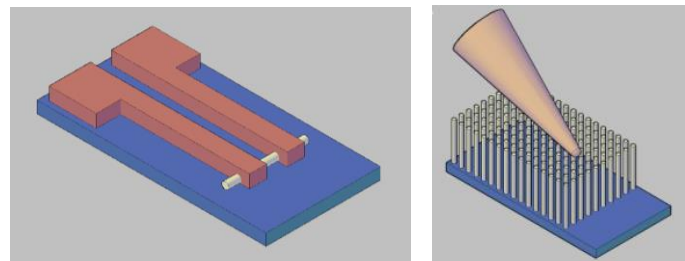


## Charakterizace

### Mechanismy přenosu náboje



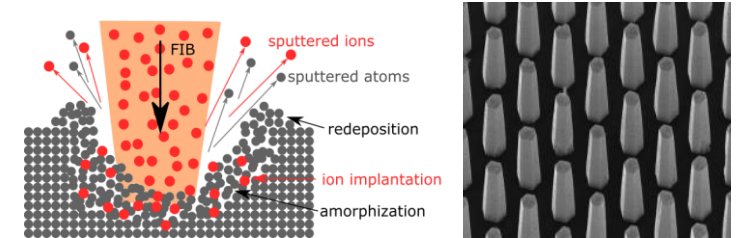
### Charakterizace jednotlivých nanostruktur



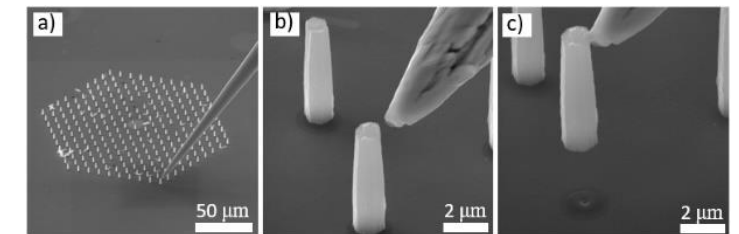
### Optická charakterizace

## Nanofabrikace

### Elektronová a iontová litografie



### Nanomanipulace



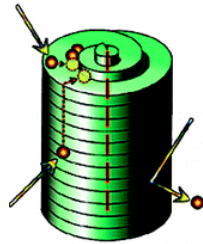
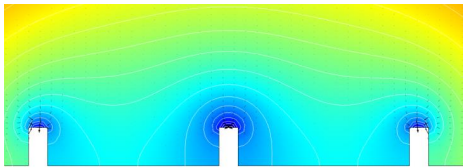
### Příprava lamel do TEMu



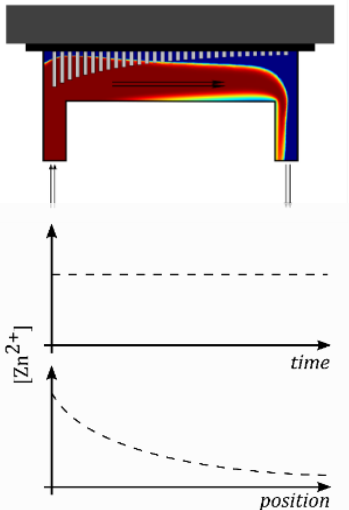
# Úvod

## Růst nanostruktur

### Modelování růstových mechanismů

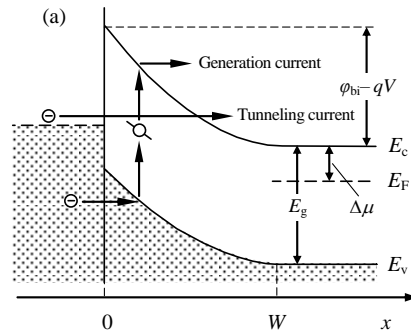


### Návrh reaktorů pro růst

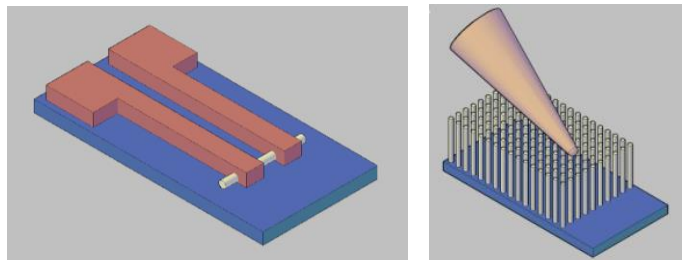


## Charakterizace

### Mechanismy přenosu náboje



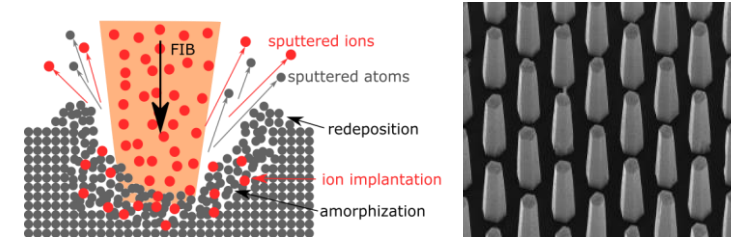
### Charakterizace jednotlivých nanostruktur



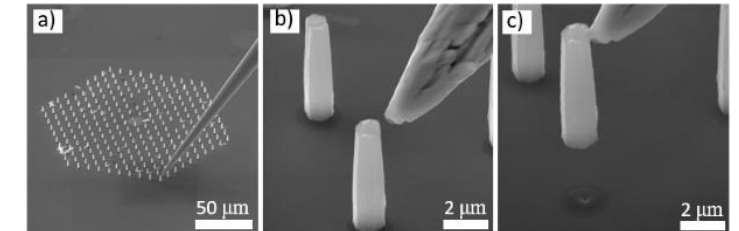
### Optická charakterizace

## Nanofabrikace

### Elektronová a iontová litografie



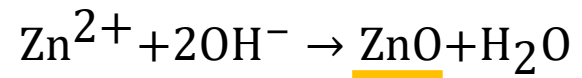
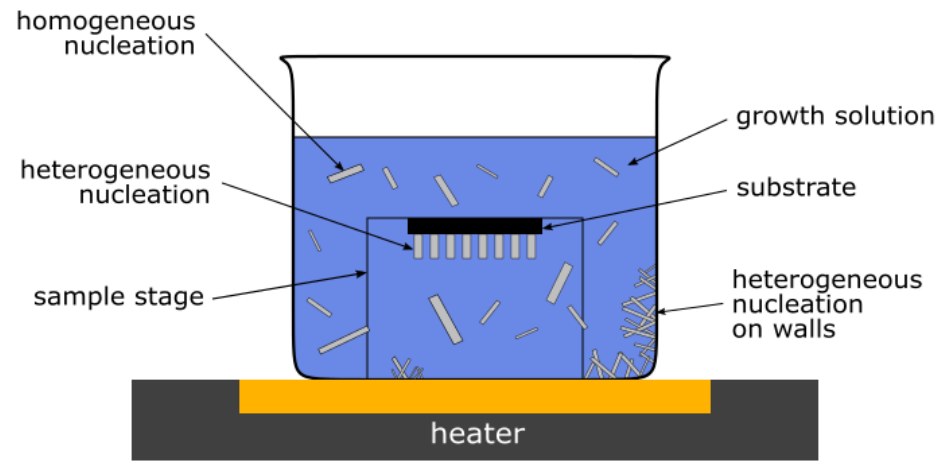
### Nanomanipulace



### Příprava lamel do TEMu

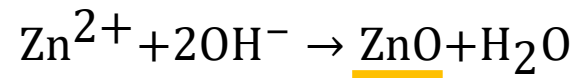
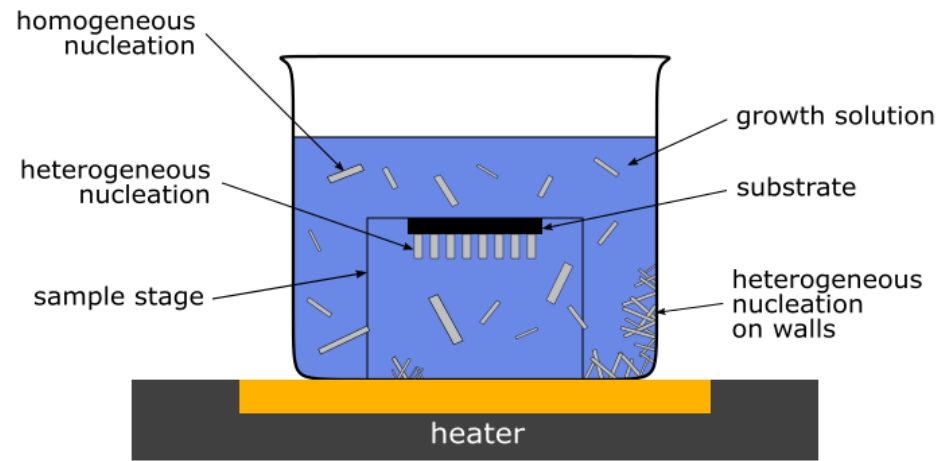


# Úvod

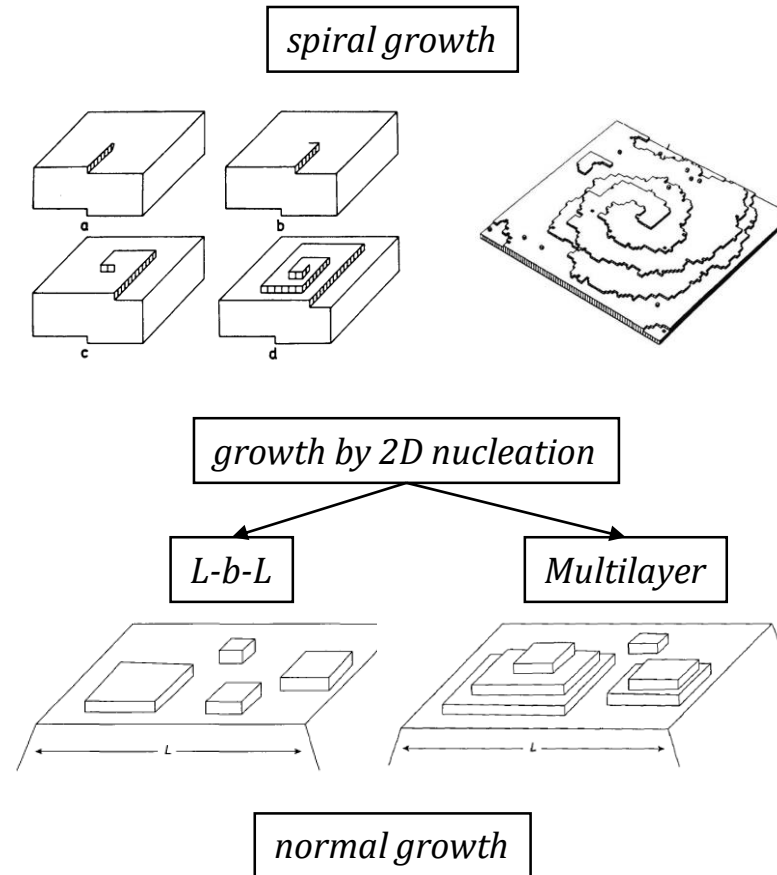


$$\sigma = [\text{Zn}^{2+}]_{akt} - [\text{Zn}^{2+}]_{eq}$$

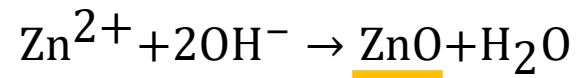
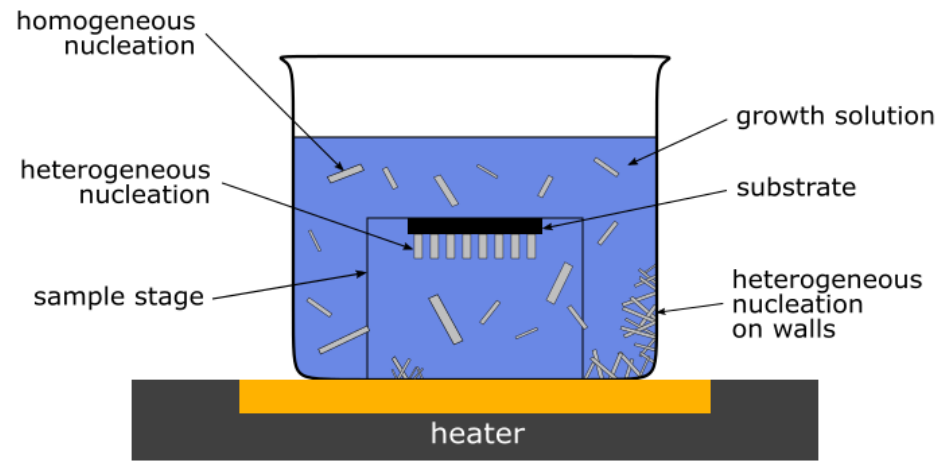
# Úvod



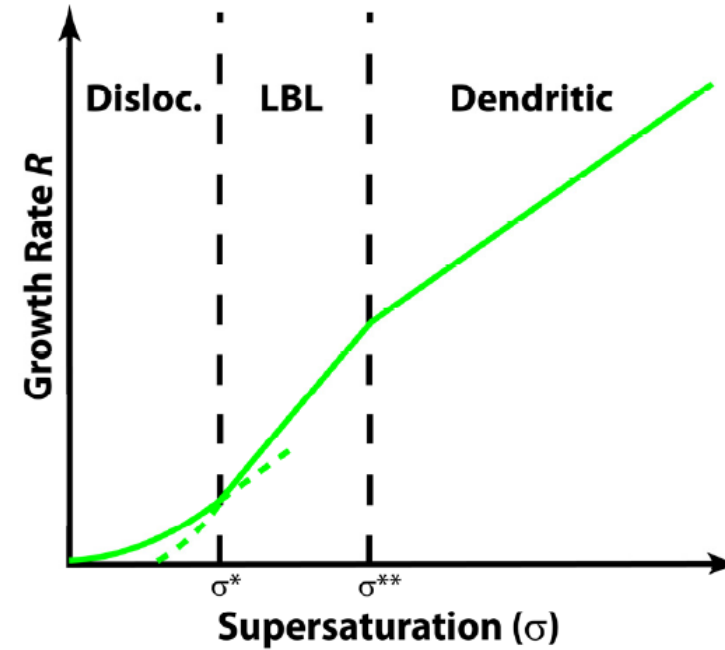
$$\sigma = [\text{Zn}^{2+}]_{akt} - [\text{Zn}^{2+}]_{eq}$$



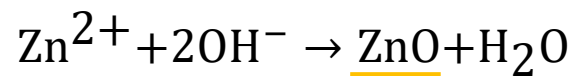
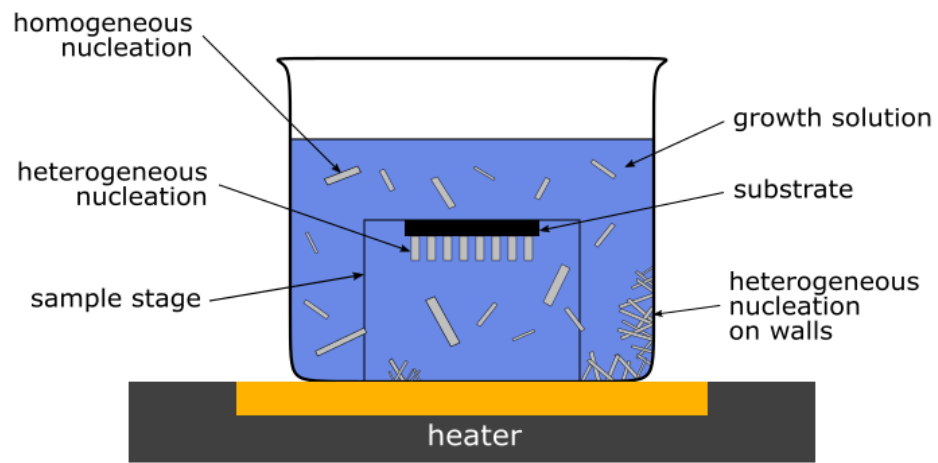
# Úvod



$$\sigma = [\text{Zn}^{2+}]_{akt} - [\text{Zn}^{2+}]_{eq}$$



# Úvod



$$\sigma = [\text{Zn}^{2+}]_{akt} - [\text{Zn}^{2+}]_{eq}$$

## Chemismus

reakční kinetika – rychlostní konstanty  
chemické složení  
(pH, teplota, ...)

## Transportní jevy

difuze, tok reaktantů (flow reaktor),  
geometrické podmínky

## Závislost na teplotě

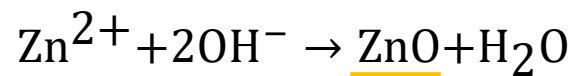
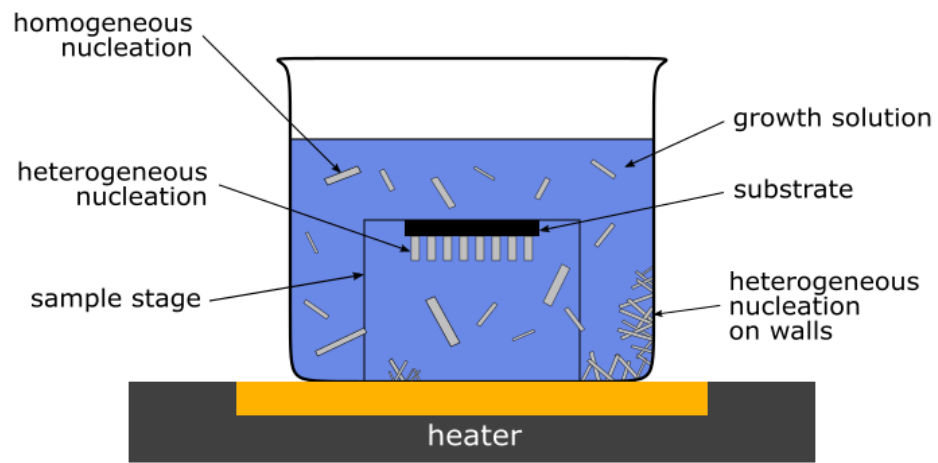
rychlostní konstanty, difúzní  
koeficient

## Závislost na čase

úbytek reaktantů  
náběh teploty



# Úvod



$$\sigma = [\text{Zn}^{2+}]_{akt} - [\text{Zn}^{2+}]_{eq}$$

## Chemismus

reakční kinetika – rychlostní konstanty  
chemické složení  
(pH, teplota, ...)

## Transportní jevy

difuze, tok reaktantů (flow reaktor),  
geometrické podmínky

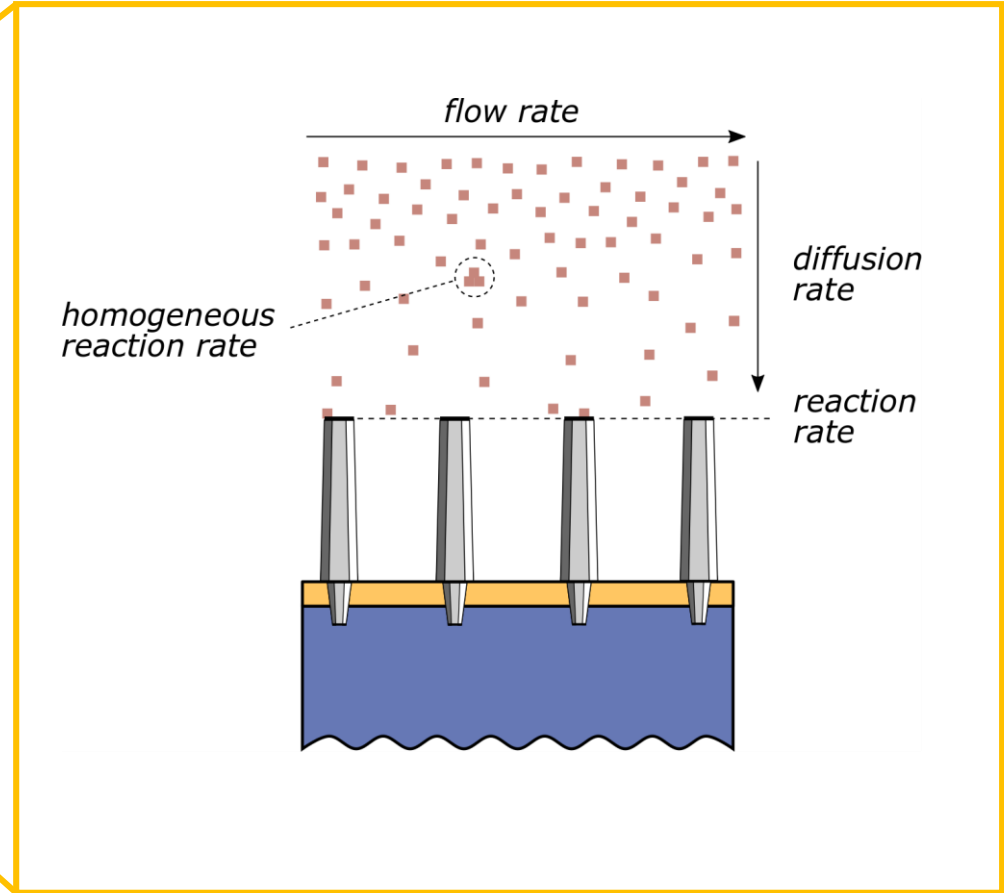
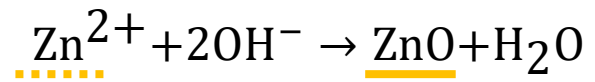
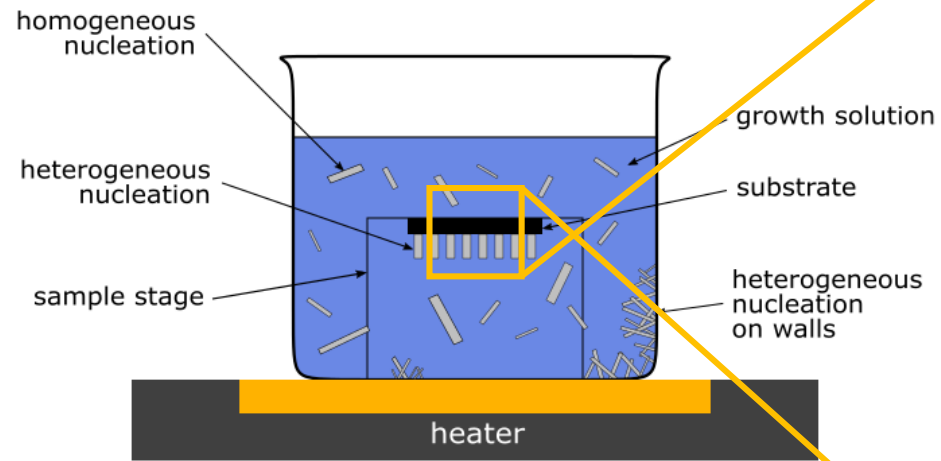
## Závislost na teplotě

rychlostní konstanty, difúzní  
koeficient

## Závislost na čase

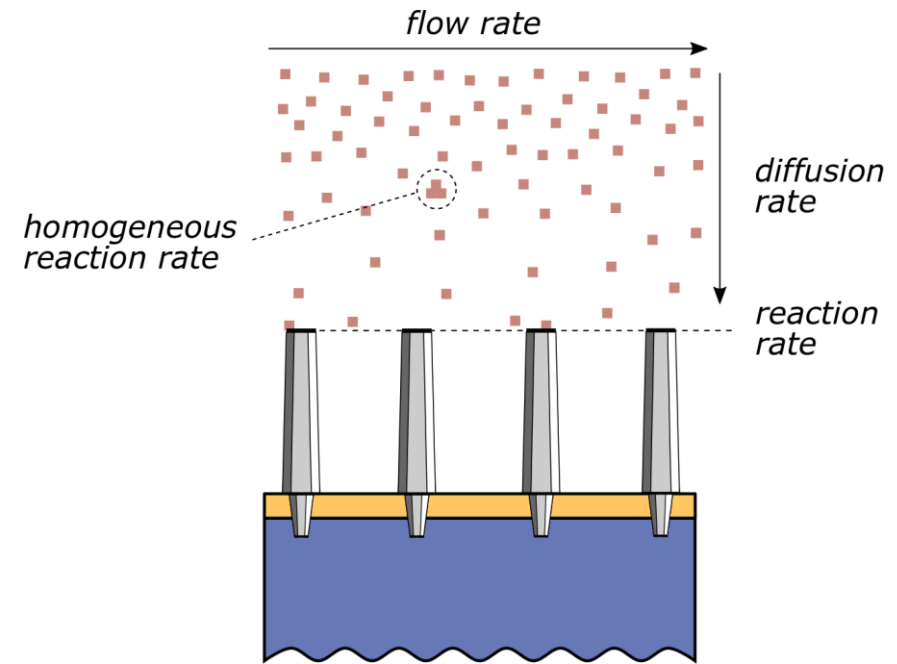
úbytek reaktantů  
náběh teploty

# Úvod



# Implementace v COMSOLu

- Laminar Flow (*spf*)
      - Fluid Properties 1
      - Initial Values 1
      - Wall 1
      - Gravity 1
      - Inlet 1
      - Outlet 1
      - Pressure Point Constraint 1
    - Transport of Diluted Species (*tds*)
      - Transport Properties 1
      - No Flux 1
      - Initial Values 1
      - Reactions 1
      - NR Growth
      - Inflow 1
      - Outflow 1
    - Heat Transfer in Fluids (*ht*)
      - Fluid 1
      - Initial Values 1
      - Thermal Insulation 1
      - Temperature Up
      - Temperature Down
      - Inflow 1
      - Outflow 1
      - Solid 1
      - Radiace ze strany substratu
    - Multiphysics
      - Reacting Flow, Diluted Species 1 (*rfd1*)
      - Nonisothermal Flow 1 (*nitf1*)



$$\frac{dc}{dt} = -k_{HOMO}(c - c_{eq})$$

$$k_{HOMO}(T), k_{NR}(T), D(T), T(t)$$

$$\frac{dc}{dt} = \frac{k_{NR}}{D}(c - c_{eq})$$

postupné zvyšování teploty

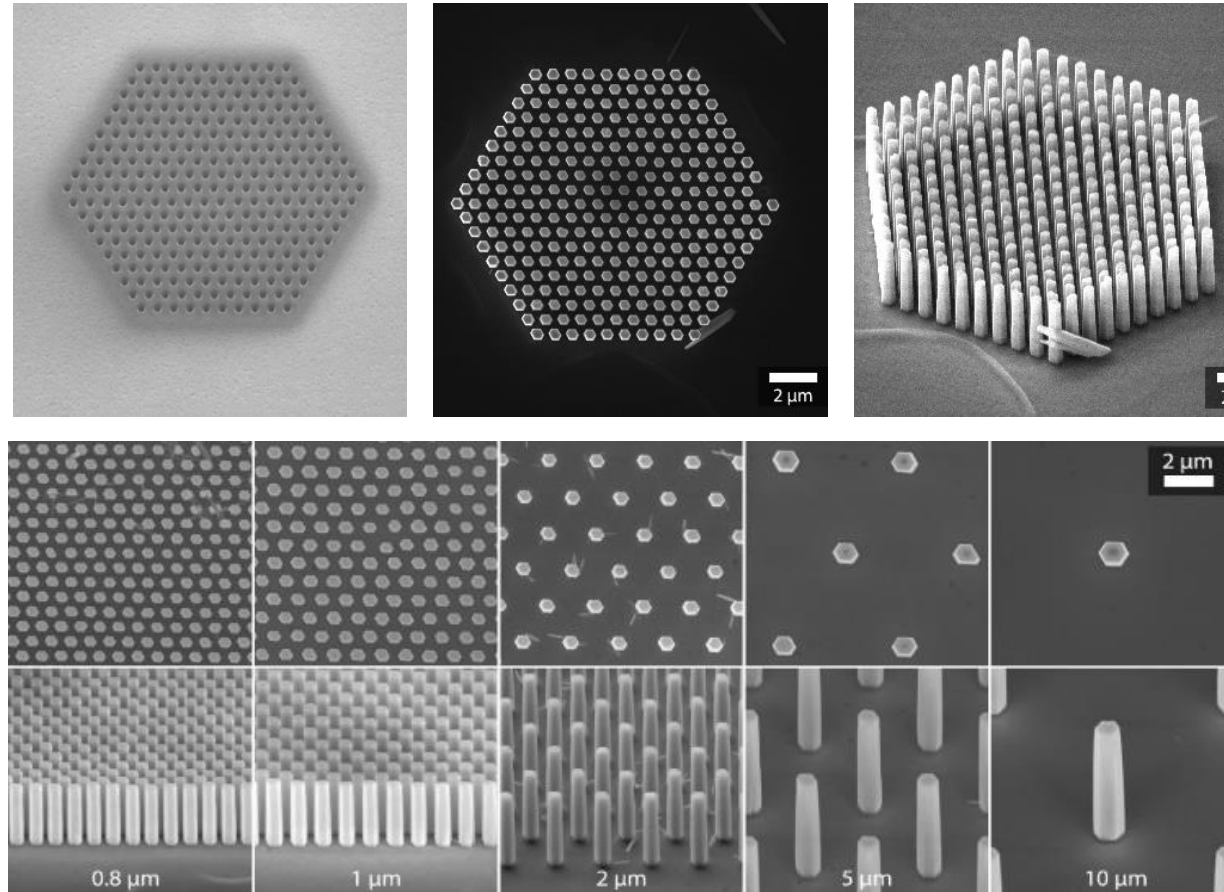
# Dva příběhy

- 1 Závislost rychlostí růstu na geometrické poloze v poli nanotyček**
- 2 Závislost výšky tyček a jejich tvaru na vzdálenosti od vstupu průtočného reaktoru**

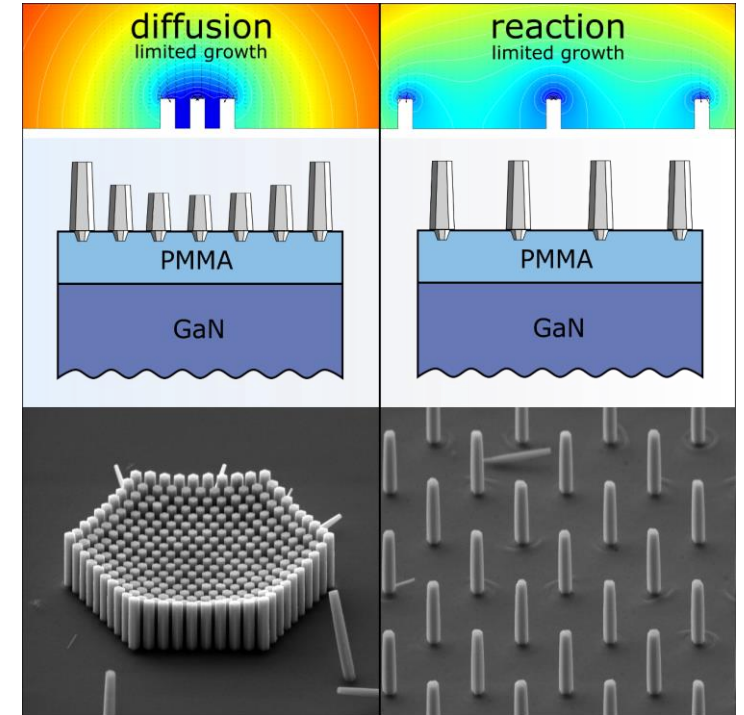
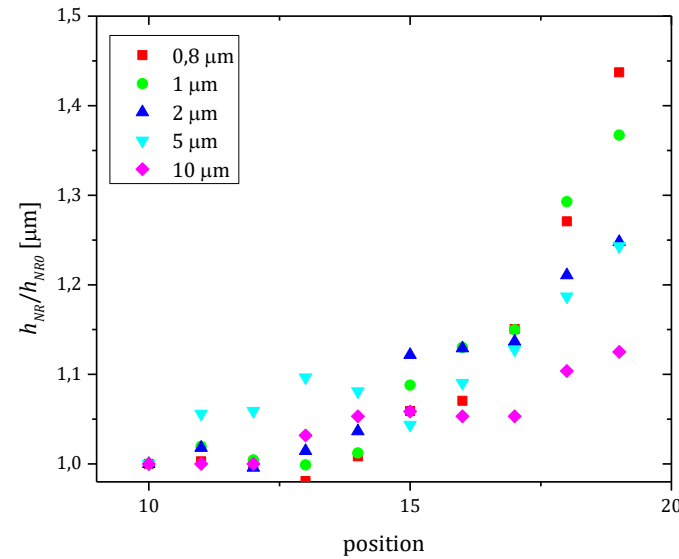
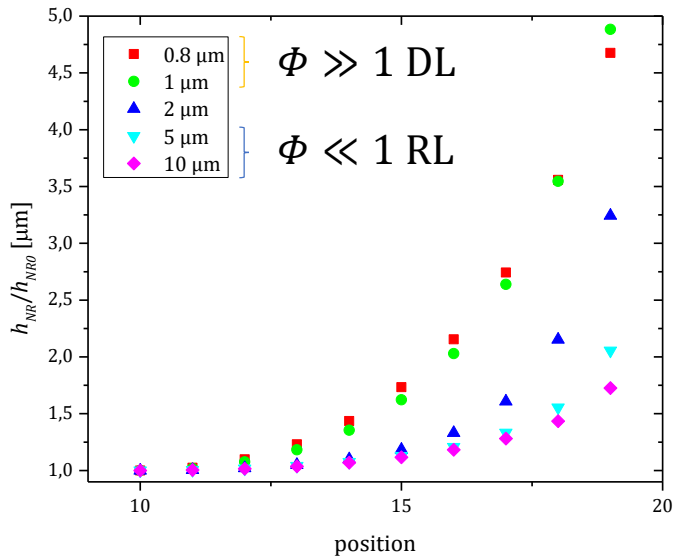
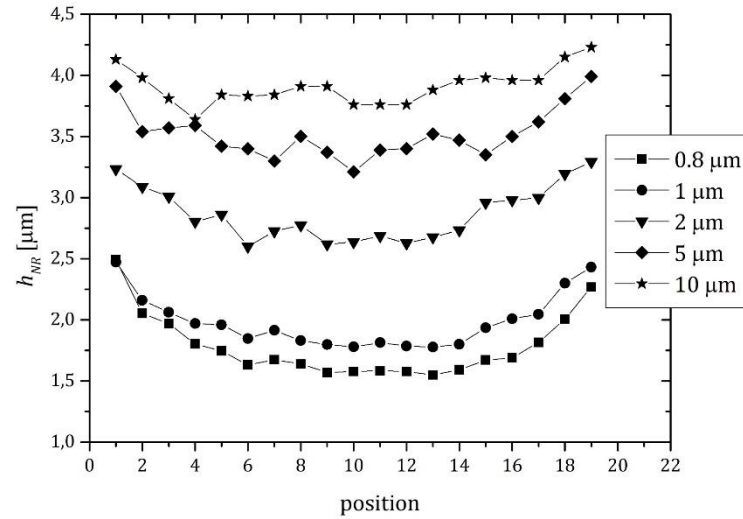
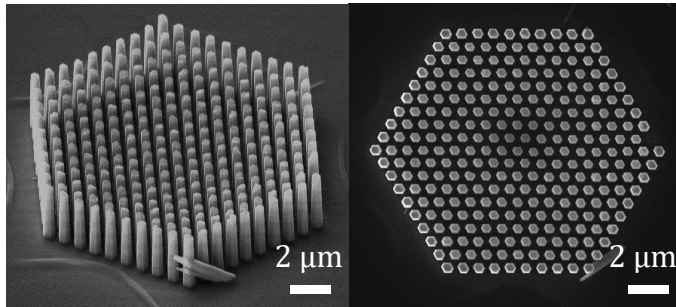
# Dva příběhy

- 1 Závislost rychlostí růstu na geometrické poloze v poli nanotyček**
- 2 Závislost výšky tyček a jejich tvaru na vzdálenosti od vstupu průtočného reaktoru**

# #1



# #1



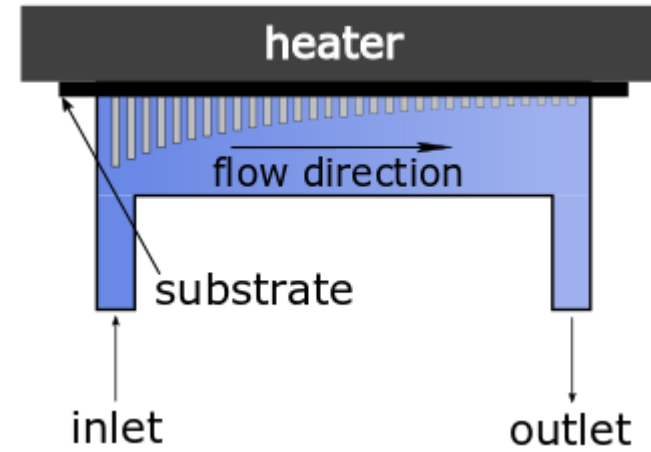
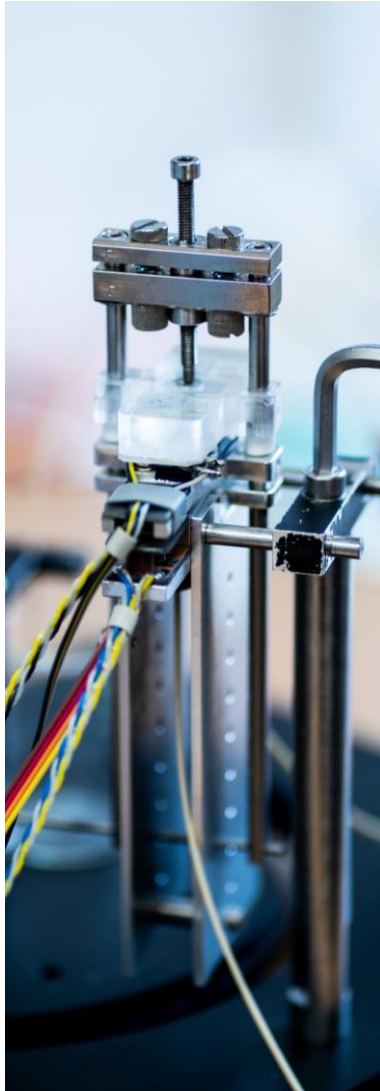
O. Černohorský, J. Grym, H. Faitová, N. Bašinová, Š. Kučerová, R. Yatskiv, J. Veselý; *Modeling of Solution Growth of ZnO Hexagonal Nanorod Arrays in Batch Reactors*, Cryst. Growth Des., 2020.

# Dva příběhy

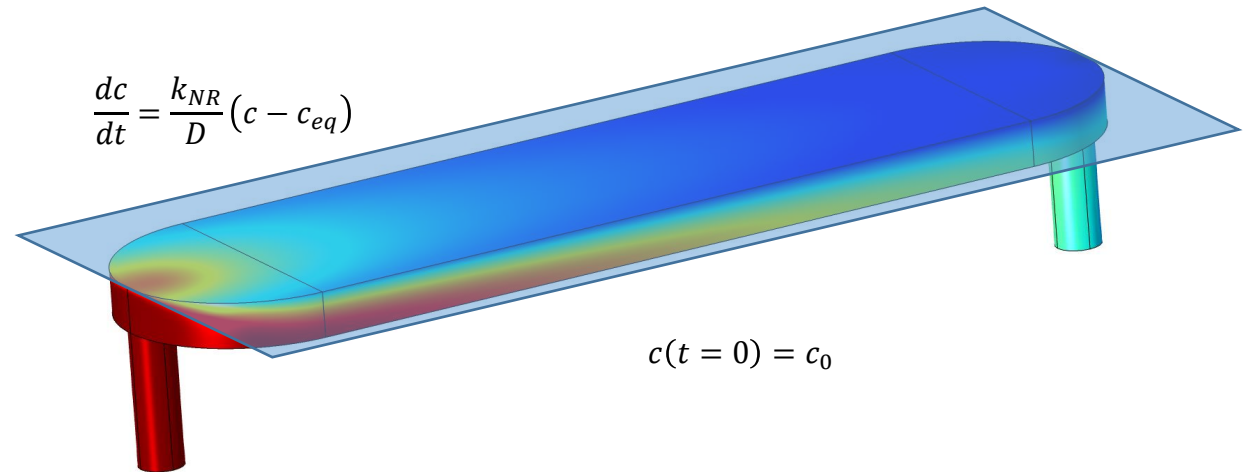
- 1 **Závislost rychlostí růstu na geometrické poloze v poli nanotyček**
- 2 **Závislost výšky tyček a jejich tvaru na vzdálenosti od vstupu průtočného reaktoru**



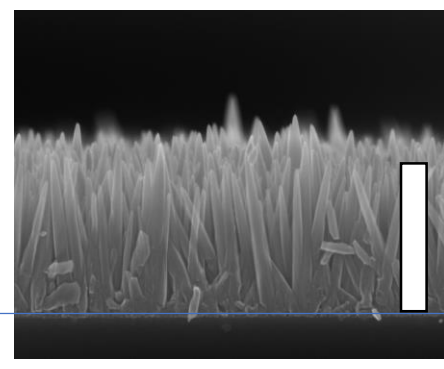
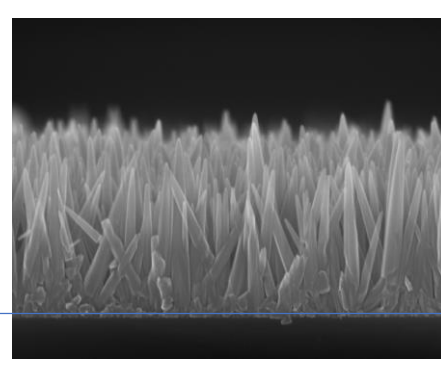
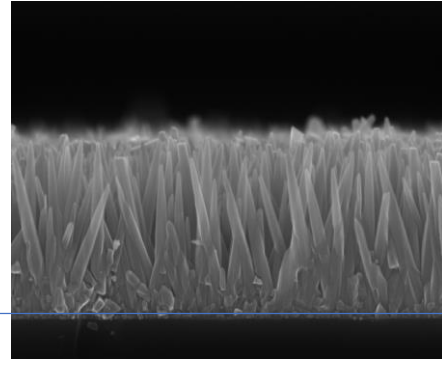
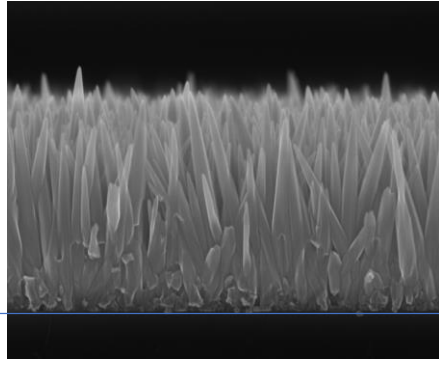
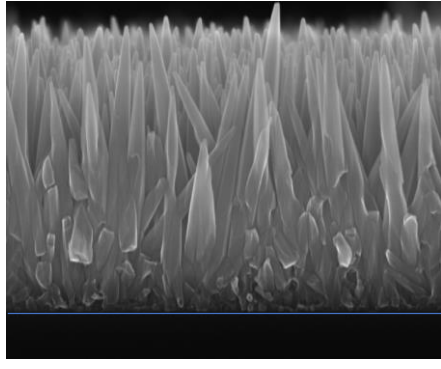
# #2



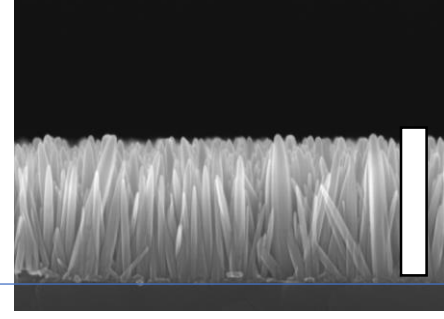
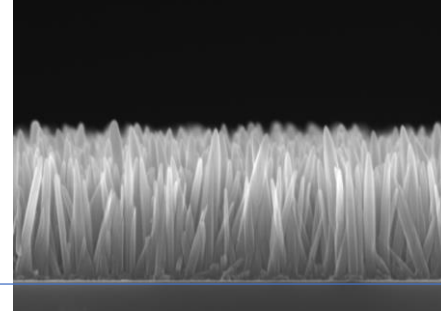
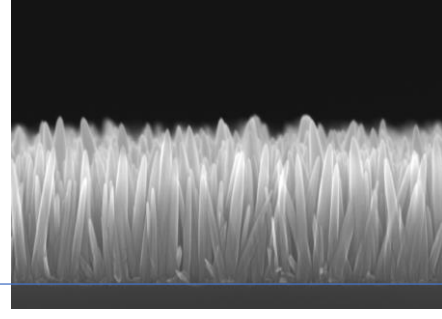
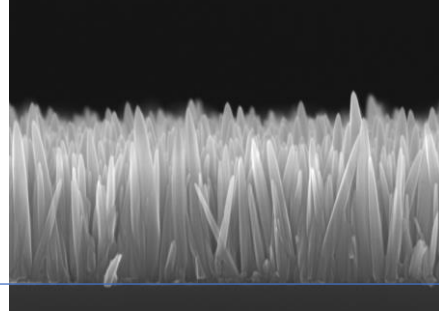
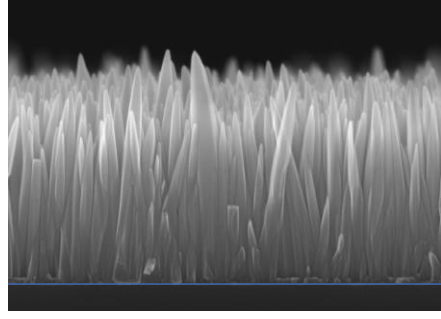
$$\frac{dc}{dt} = \frac{k_{NR}}{D} (c - c_{eq})$$



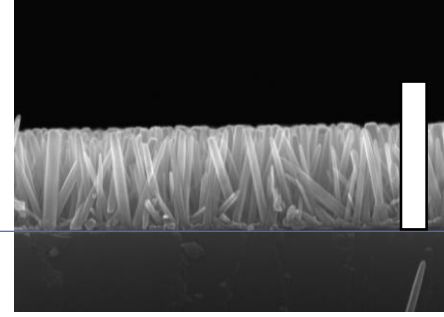
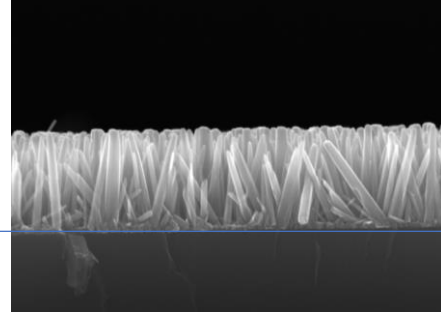
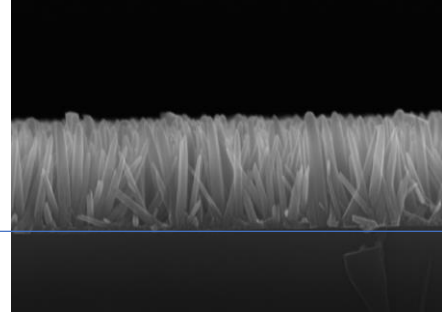
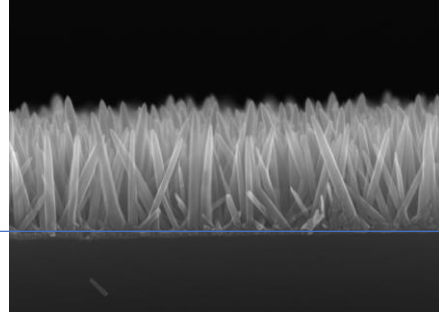
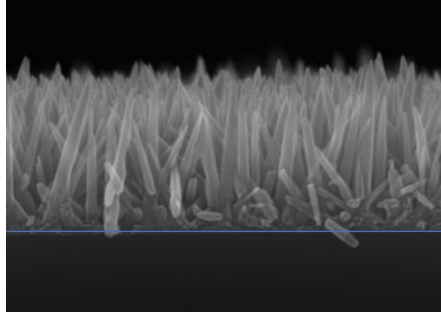
20  $\mu\text{l}/\text{min}$



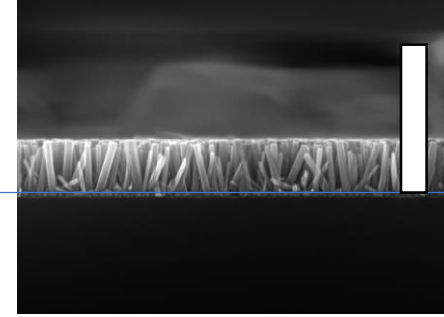
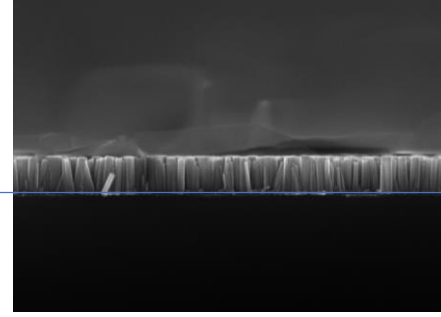
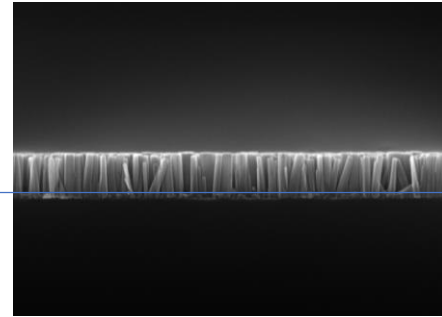
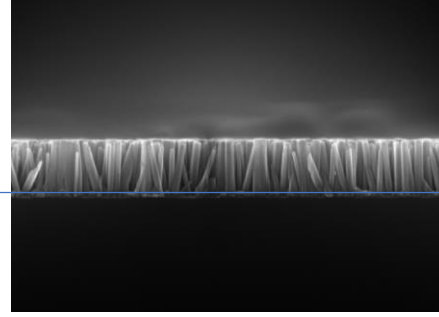
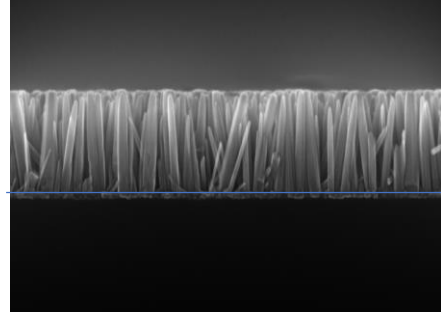
10  $\mu\text{l}/\text{min}$



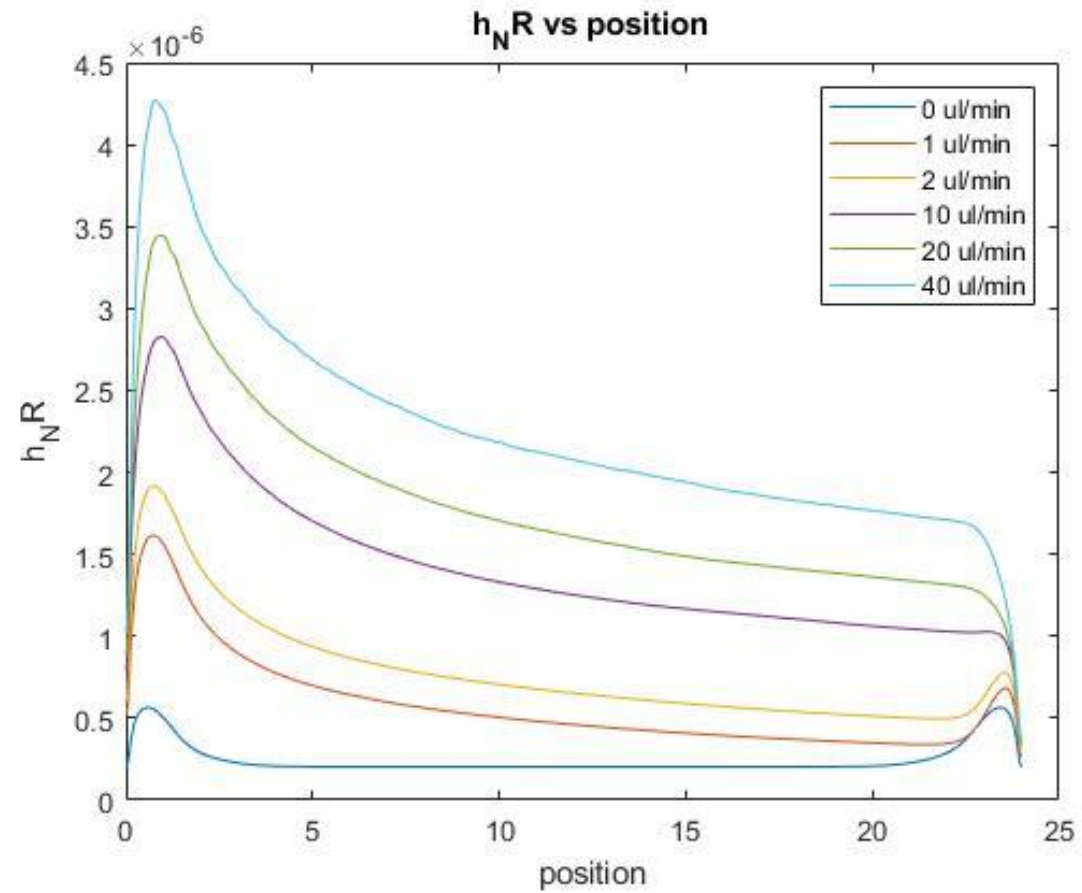
2  $\mu\text{l}/\text{min}$



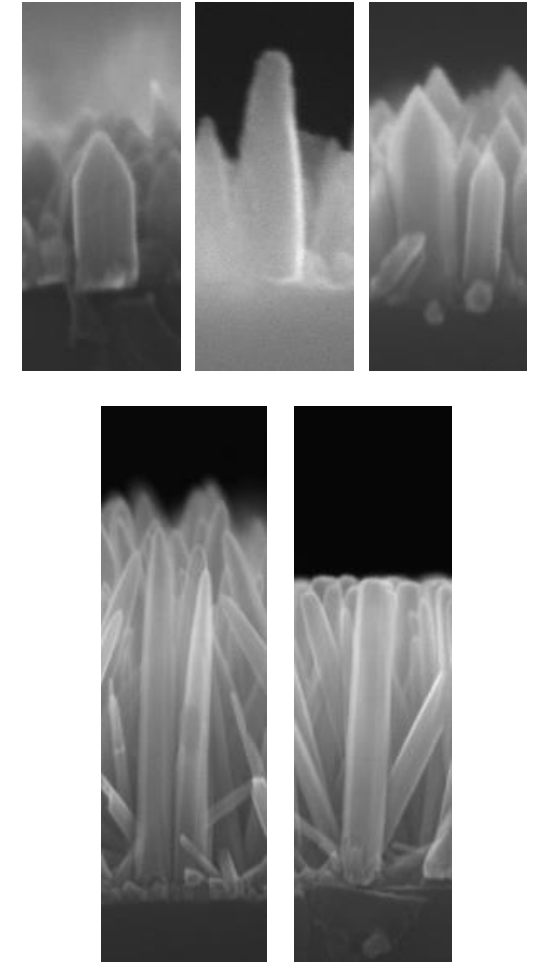
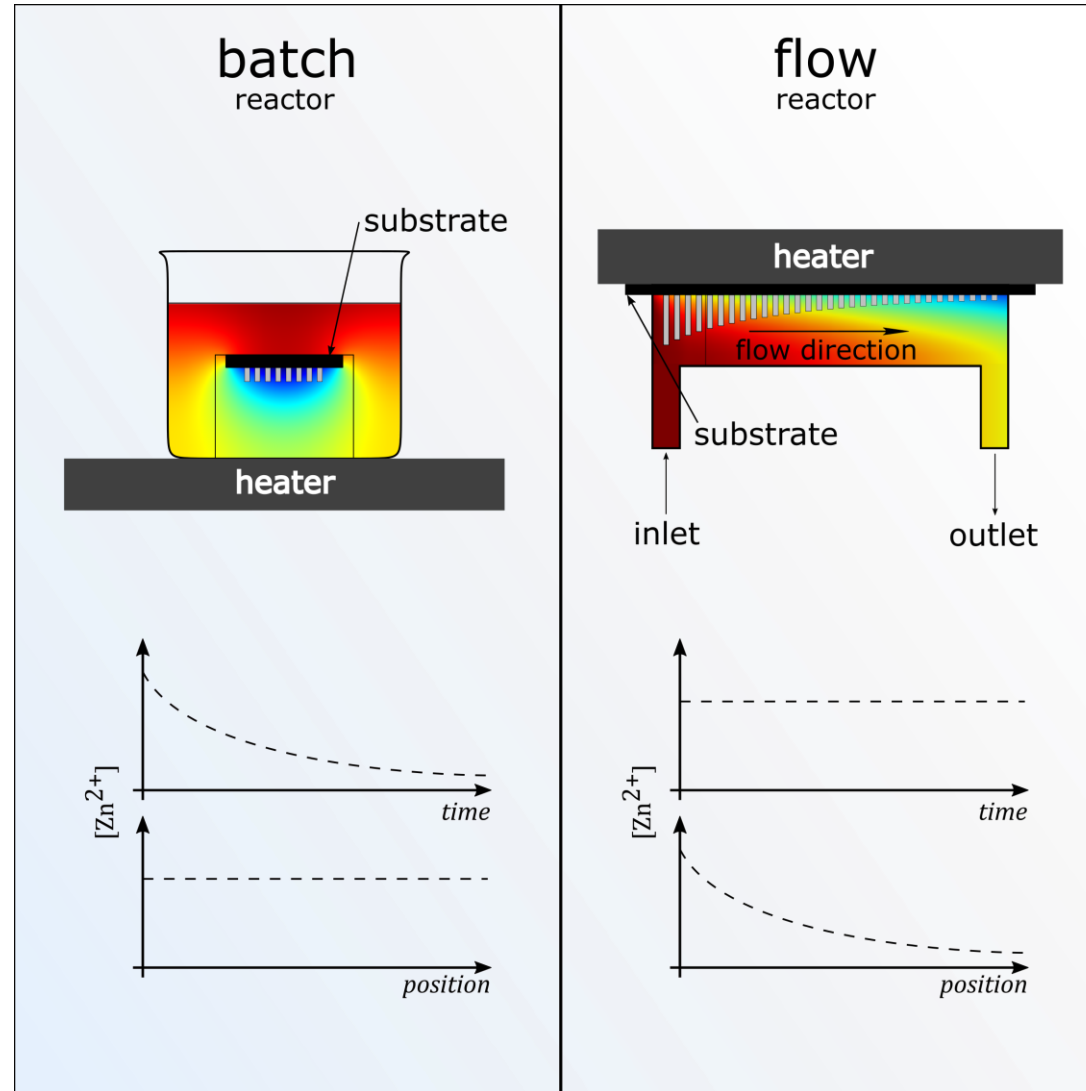
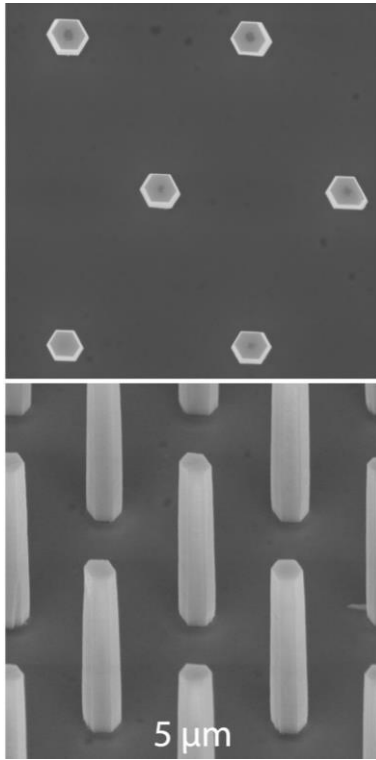
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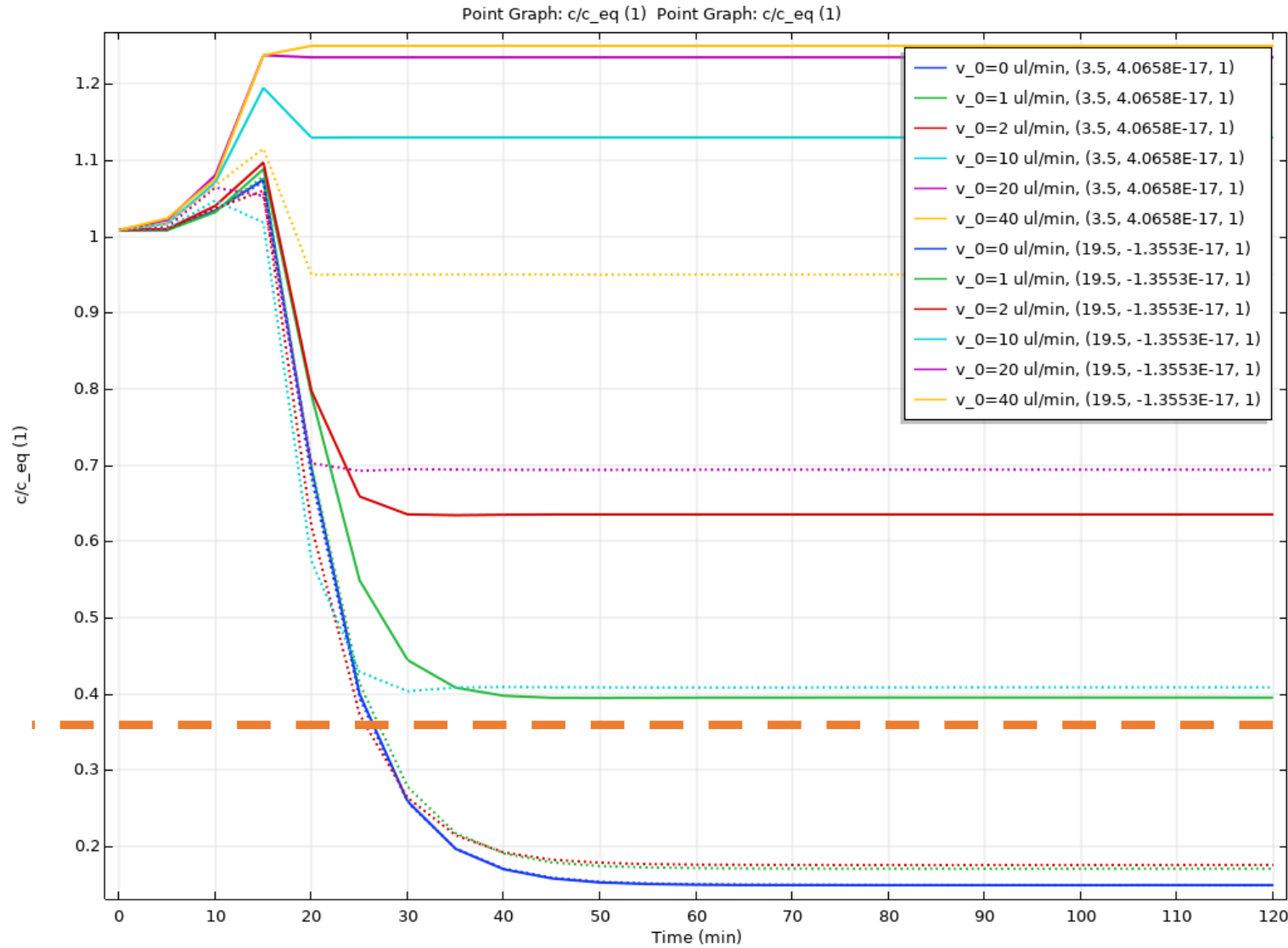
# #2



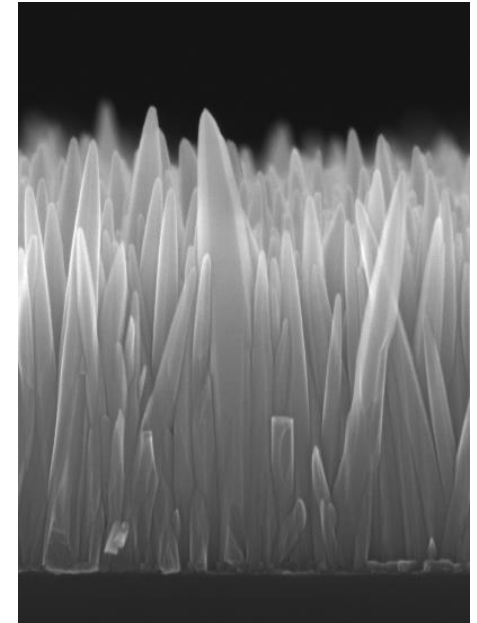
# #2



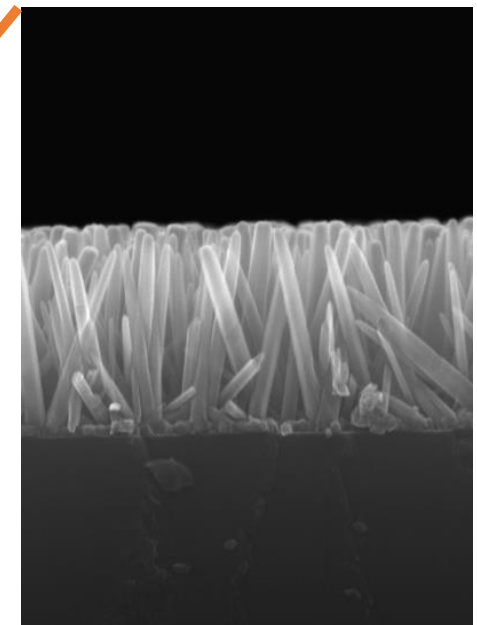
# #2



Needles



Flat tops



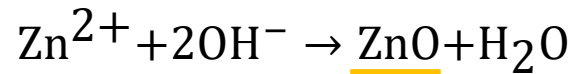
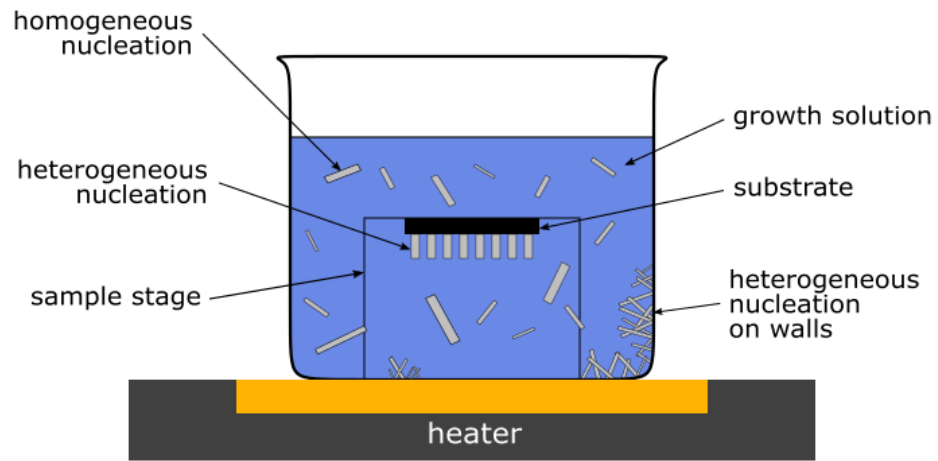
# Děkuji za pozornost

[www.ufe.cz](http://www.ufe.cz)

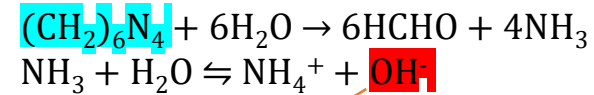
UFE



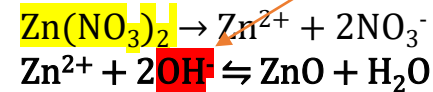
[www.ufe.cz](http://www.ufe.cz)



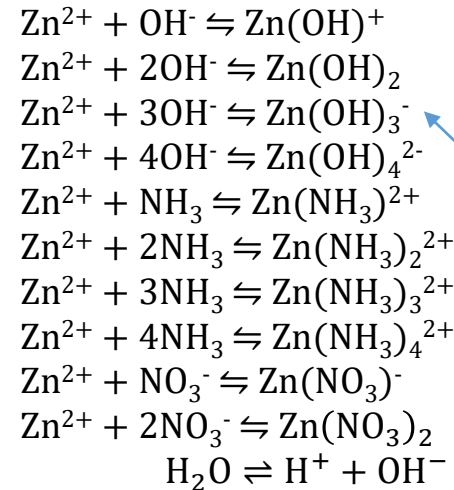
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , HMTA ( $=(\text{CH}_2)_6\text{N}_4$ ), water



HMTA dissociation,  $\text{OH}^-$  release:  
slow, dependent on heat and pH



ZnO crystallization



Other possible Zn species  
Dependent on pH

$$\text{pH} = -\log[\text{H}^+]$$

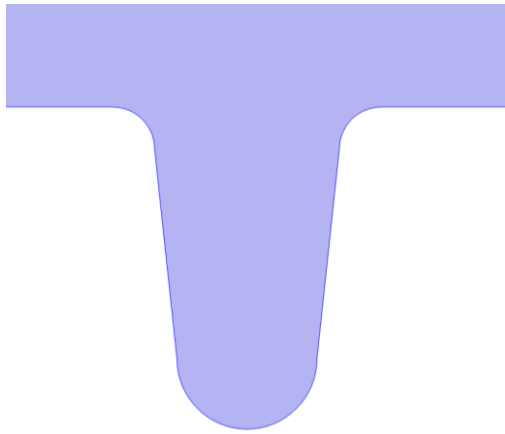
$$[\text{H}^+][\text{OH}^-] = 10^{-14}$$

Rovnovážná konstanta:

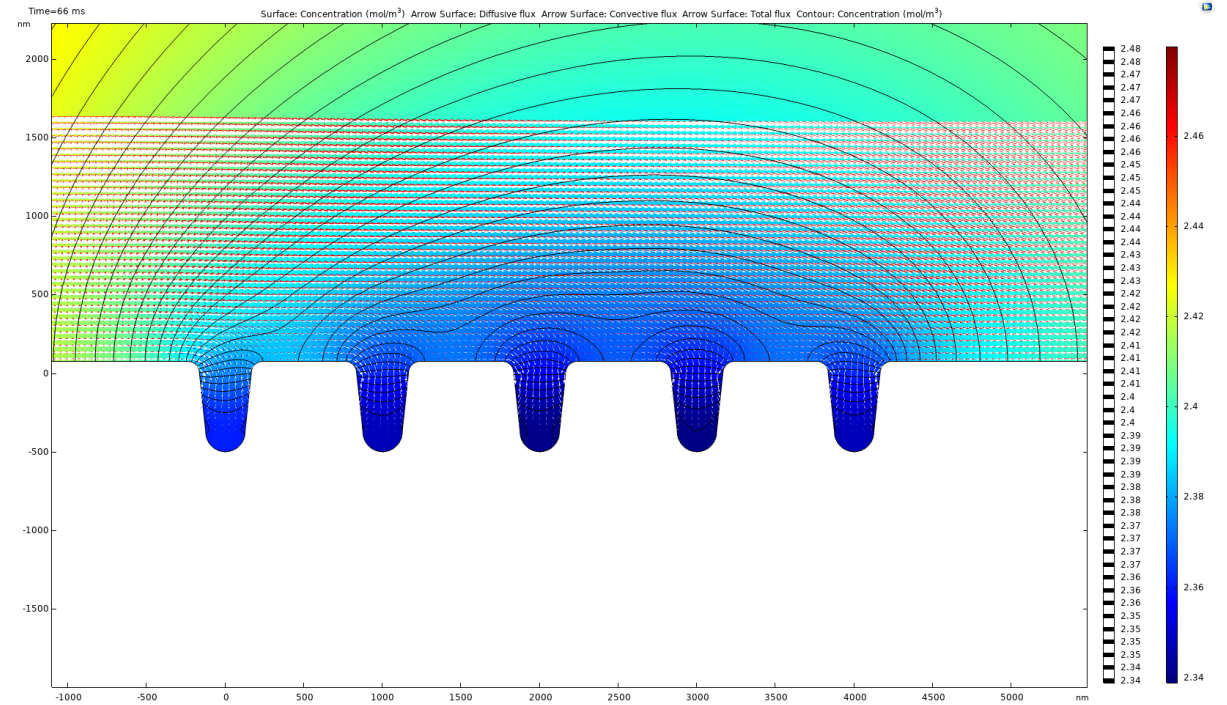
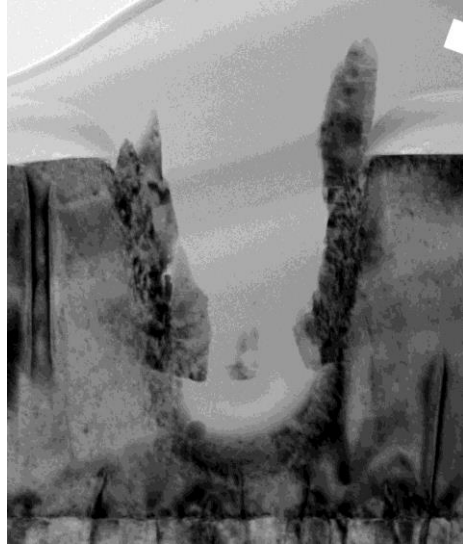
$$K = \frac{[\text{Zn}(\text{OH})_3^-]}{[\text{Zn}^{2+}][\text{OH}^-]^3}$$

# #4 – FIB hole modeling

$t = 165 \text{ ms}$



V NR za 15 min cca 10x vic material nez je rustovych jednotech v dire





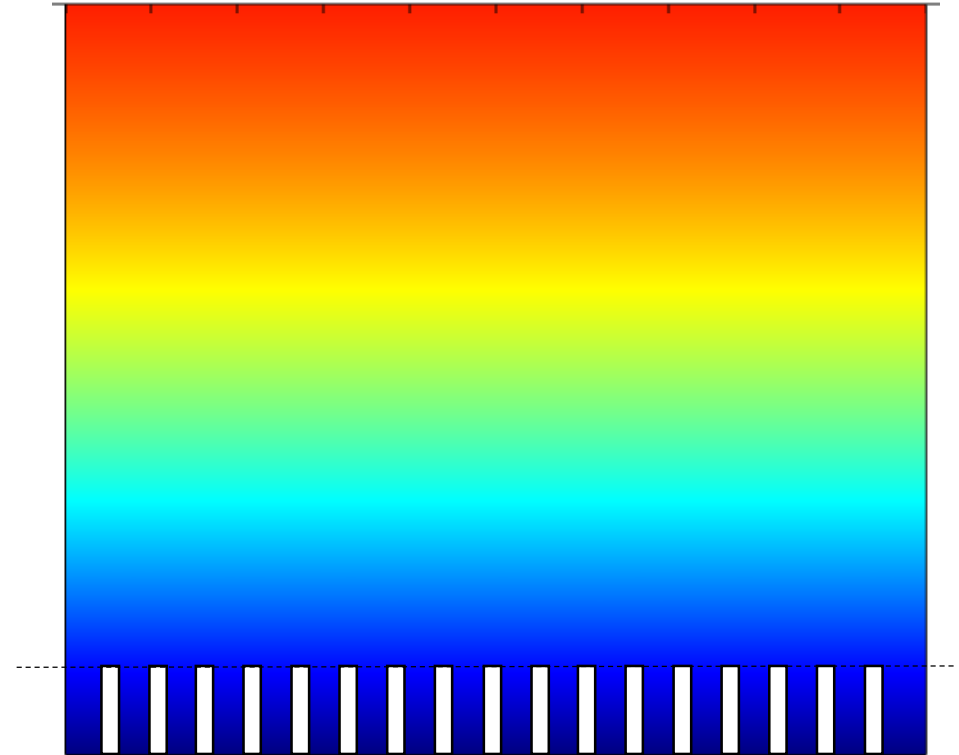
# #1

Reakčně difuzní rovnice

$$\frac{dc}{dt} - D \frac{d^2c}{dz^2} = -k_{HOMO}(c - c_{eq})$$

$$c(t = 0) = c_0$$

$$\frac{dc}{dt} = \frac{k_{NR}}{D}(c - c_{eq})$$



experimentálně zjištěné hodnoty  $k_{HOMO}$ ,  $k_{NR}$ ,  $c_{eq}$

teplotně závislý difúzní koeficient pro  $Zn^{2+}$  ve vodném prostředí:

$$D_{Zn} = 2.74 \times 10^{-11} + 1.39 \times 10^{-12}T + 1.29 \times 10^{-14}T^2 \quad m^2s^{-1}$$

# #2

Reakčně difuzní rovnice

$$\frac{dc}{dt} - D \frac{d^2c}{dz^2} = -k_{HOMO}(c - c_{eq})$$

Navier-Stokes pro laminární proudění – nízké Re ( $Re < 1$ )

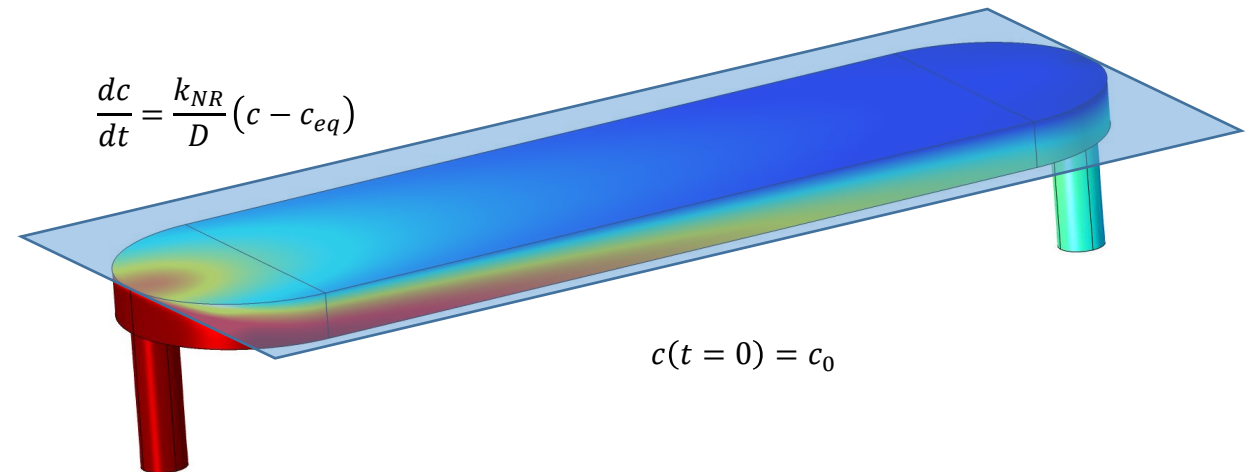
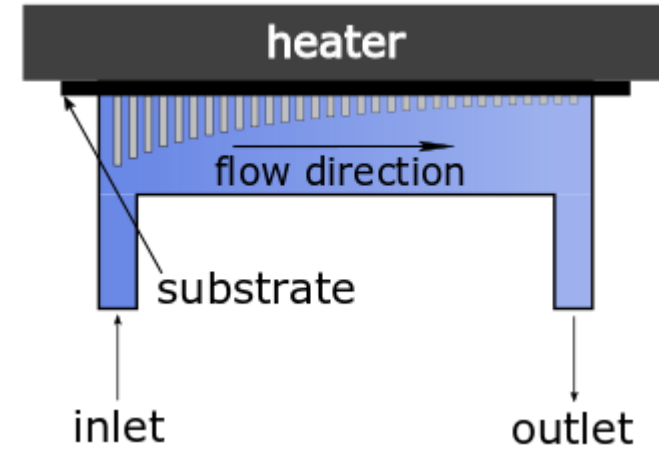
Rovnice šíření tepla

$$\frac{dc}{dt} = \frac{k_{NR}}{D}(c - c_{eq})$$

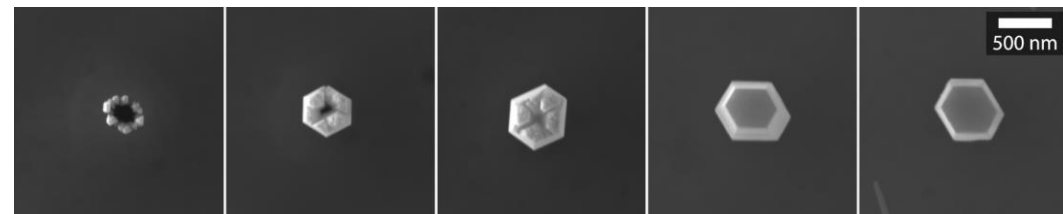
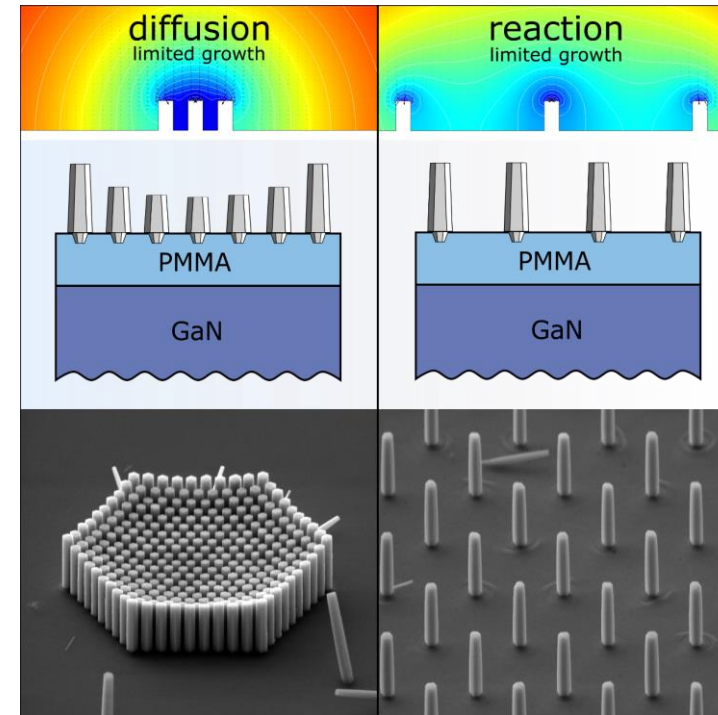
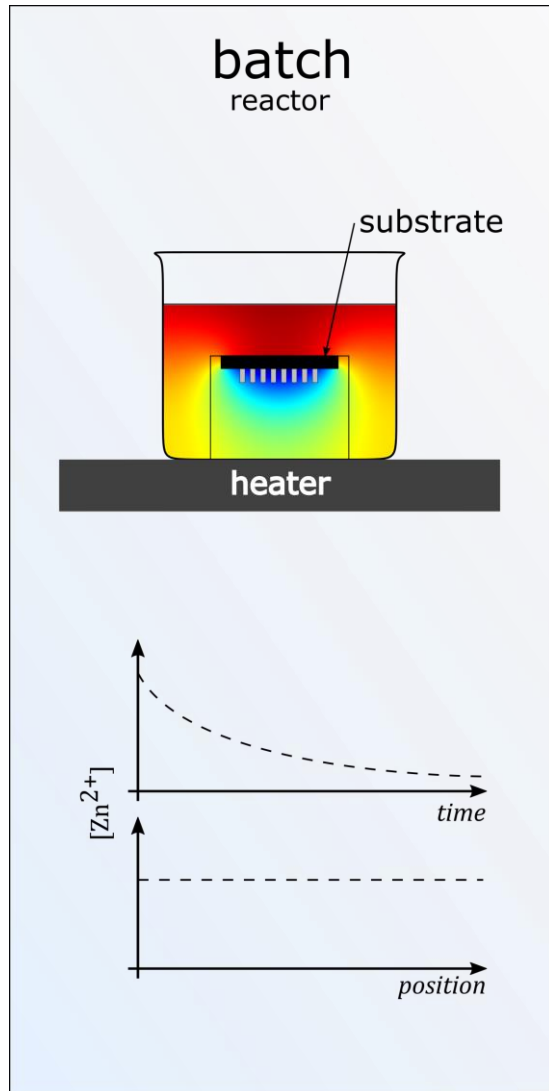
experimentálně zjištěné hodnoty  $k_{HOMO}$ ,  $k_{NR}$ ,  $c_{eq}$

teplotně závislý difúzní koeficient pro  $Zn^{2+}$  ve vodném prostředí:

$$D_{Zn} = 2.74 \times 10^{-11} + 1.39 \times 10^{-12}T + 1.29 \times 10^{-14}T^2 \quad m^2s^{-1}$$

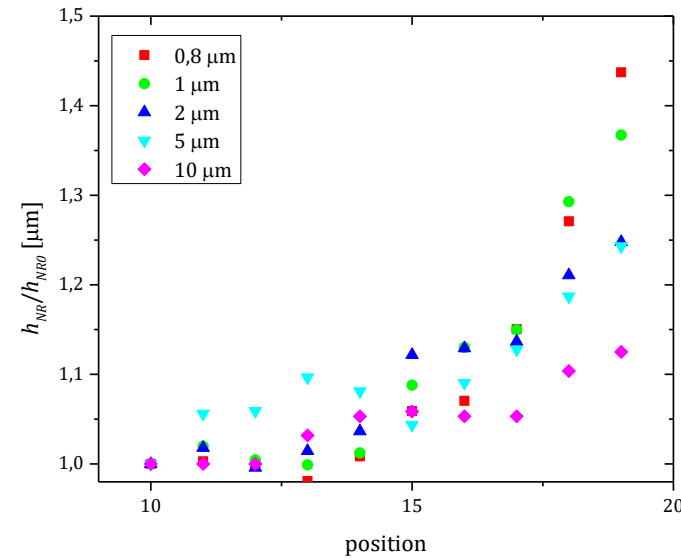
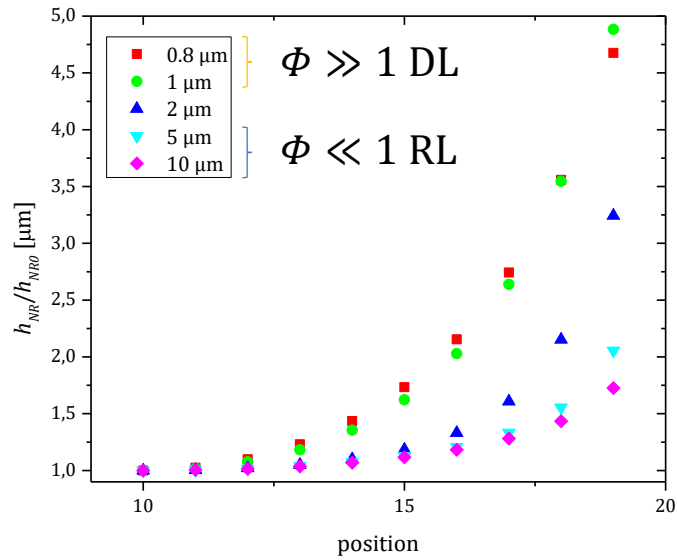
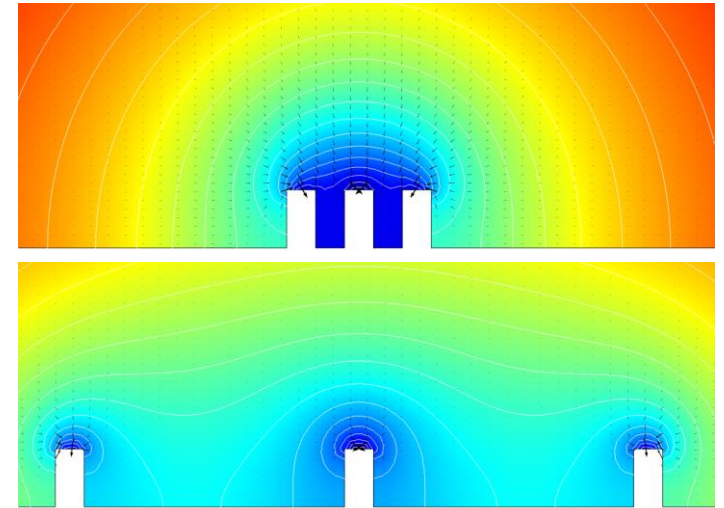
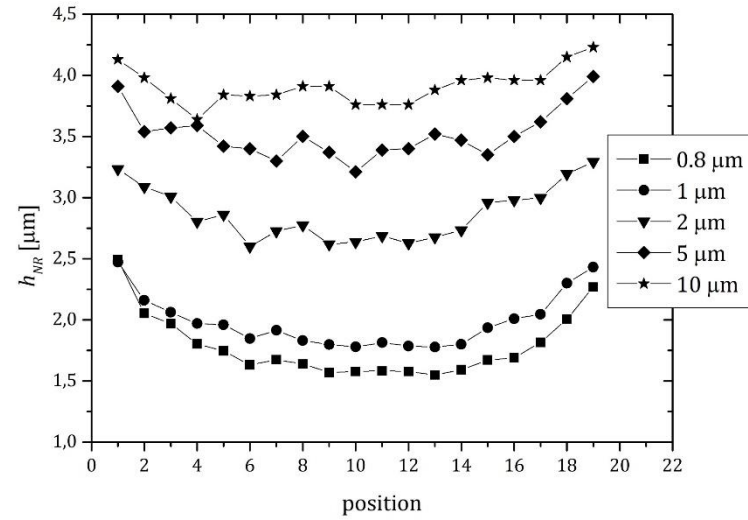
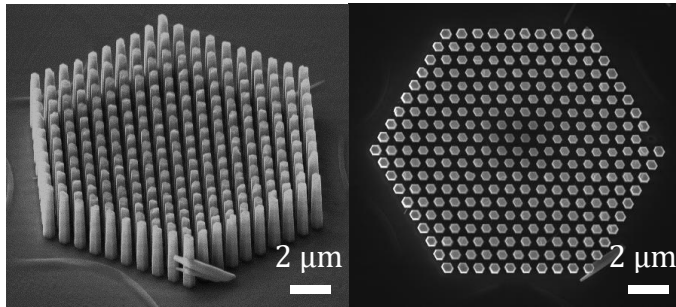


# #1

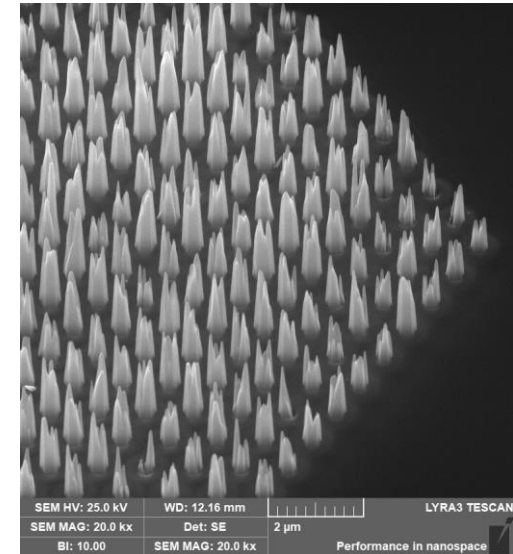
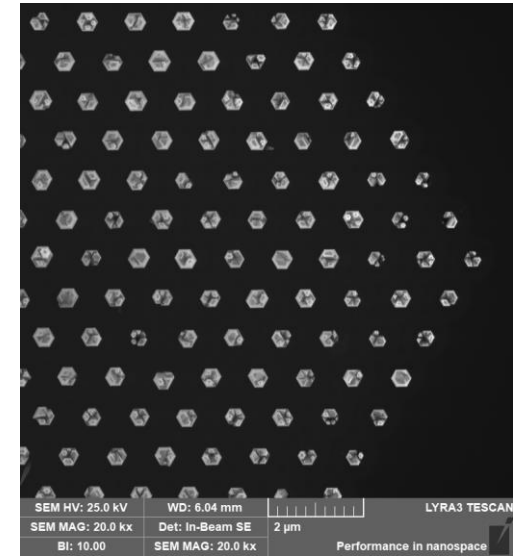
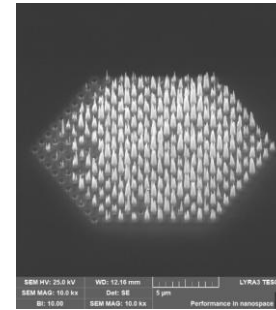
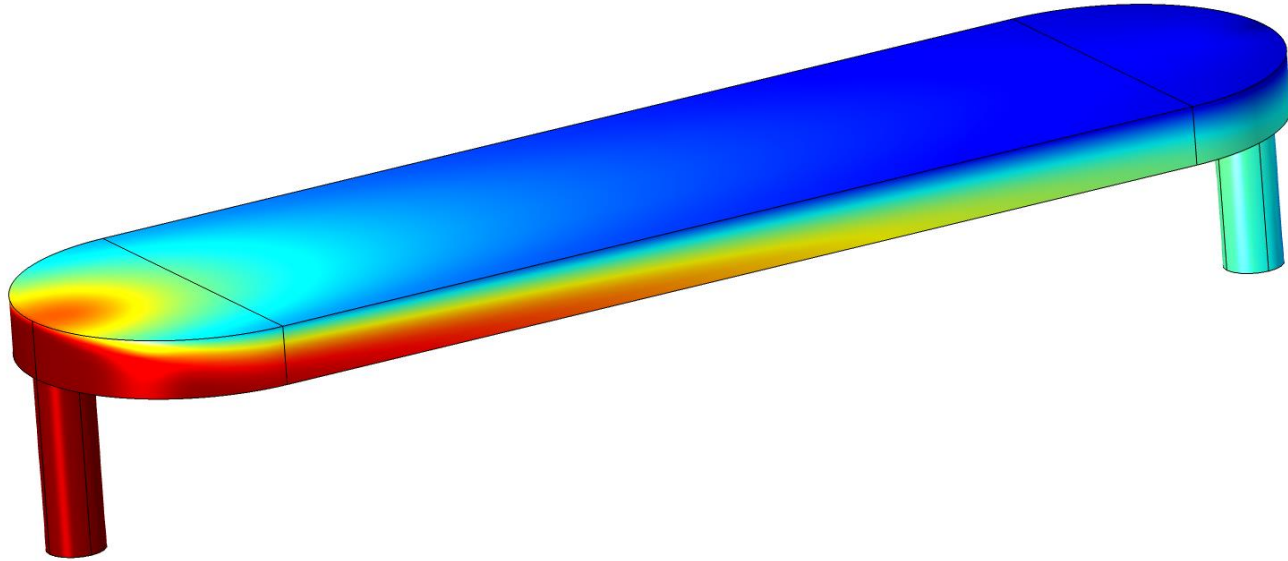


O. Černohorský, J. Grym, H. Faitová, N. Bašínová, Š. Kučerová, R. Yatskiv, J. Veselý; *Modeling of Solution Growth of ZnO Hexagonal Nanorod Arrays in Batch Reactors*, Cryst. Growth Des., 2020.

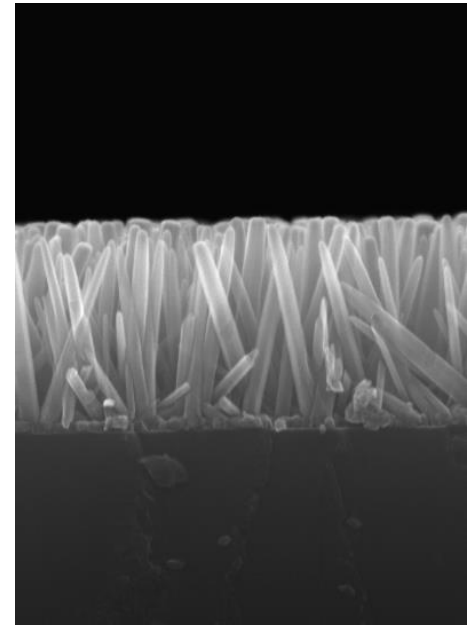
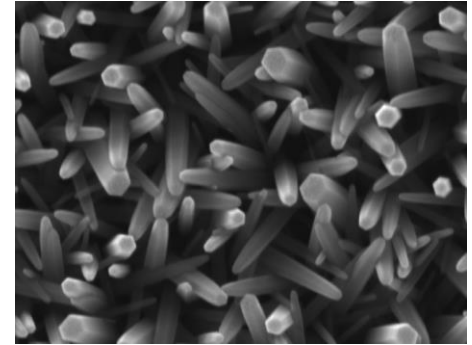
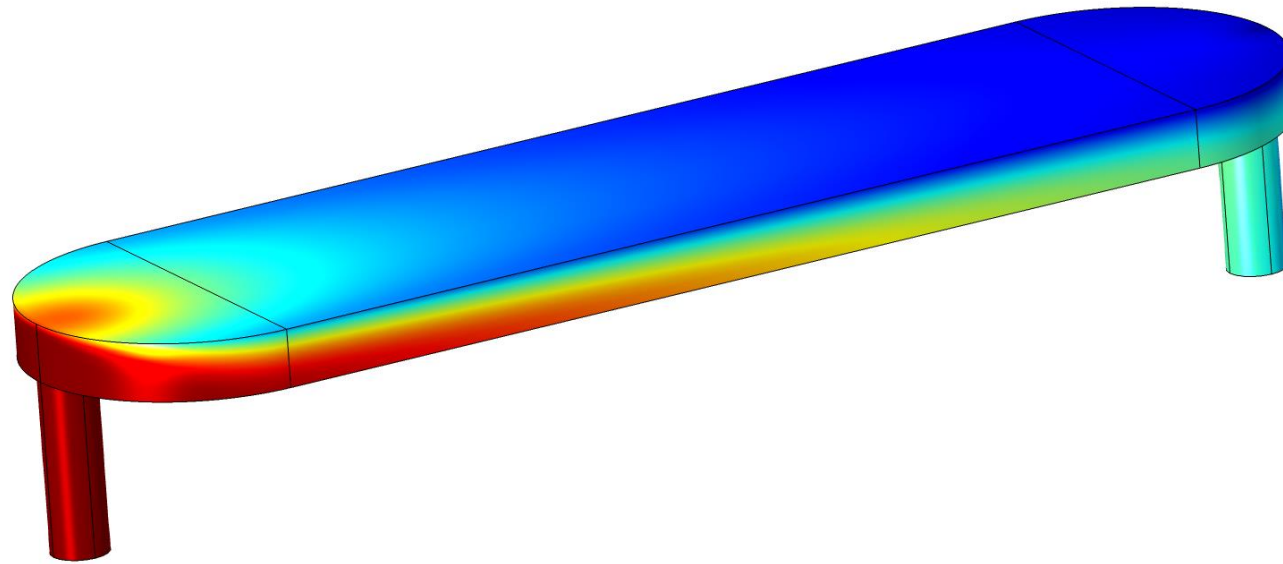
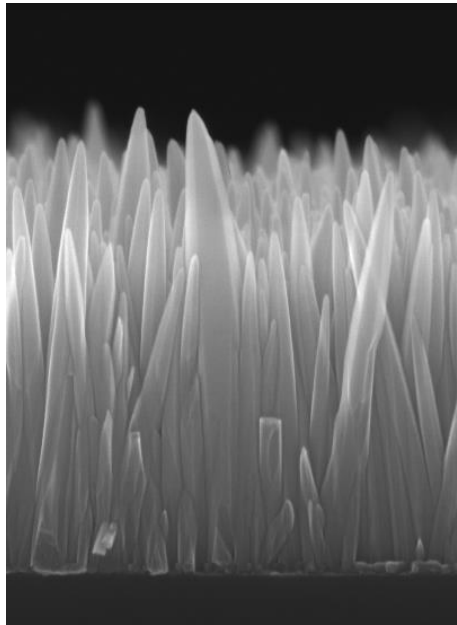
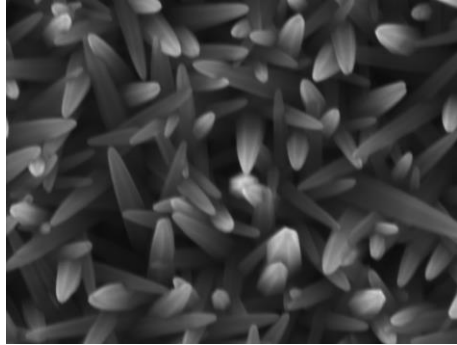
# #1



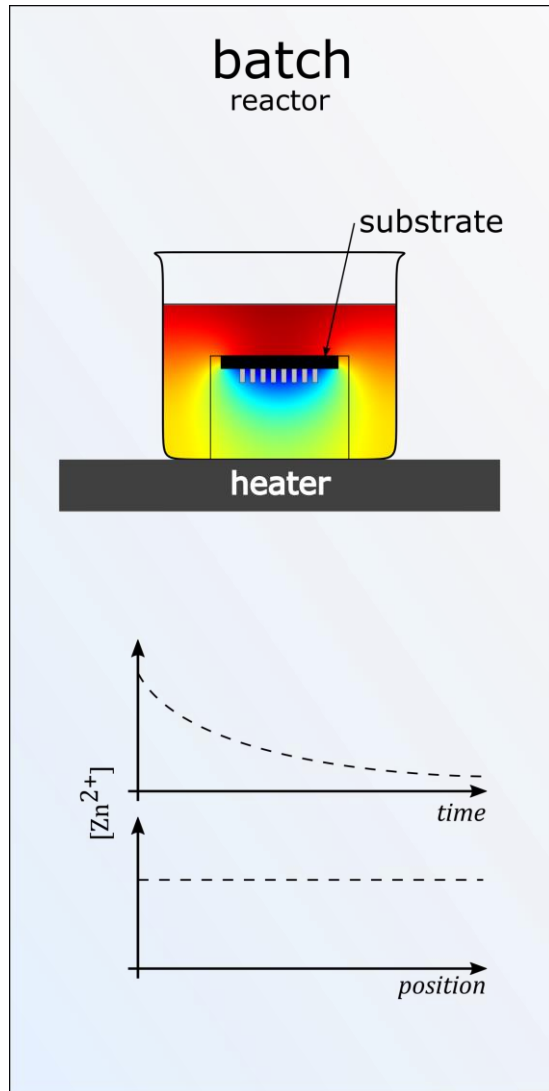
# #3.4 – Flow reactor modeling – experiments



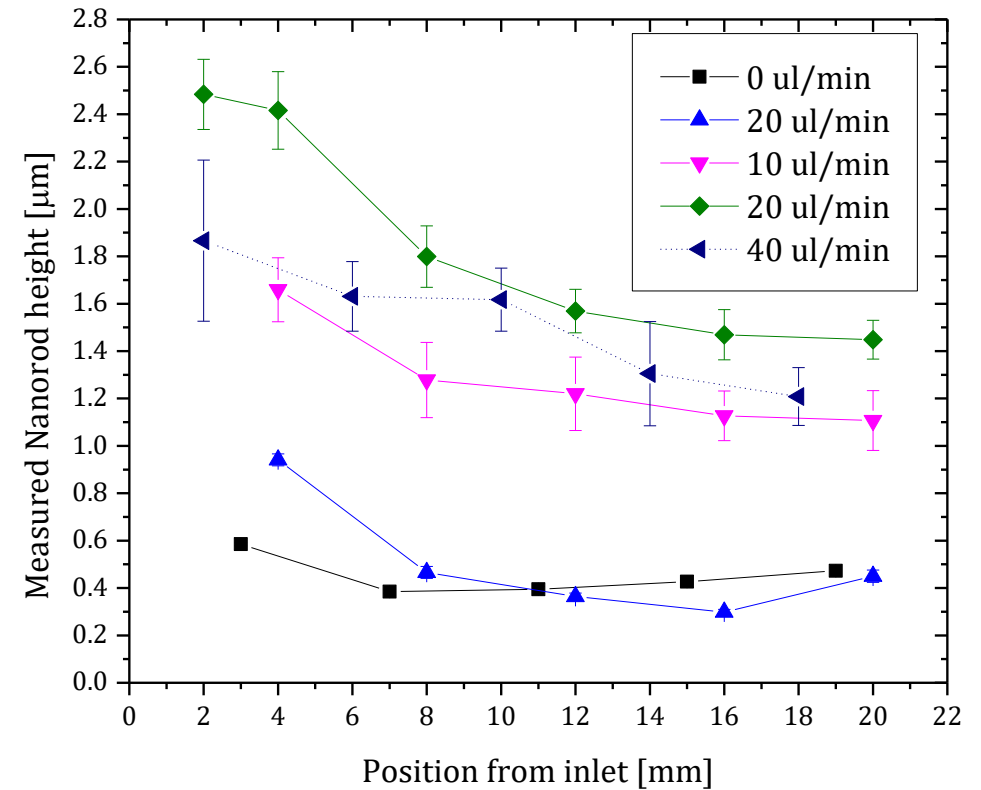
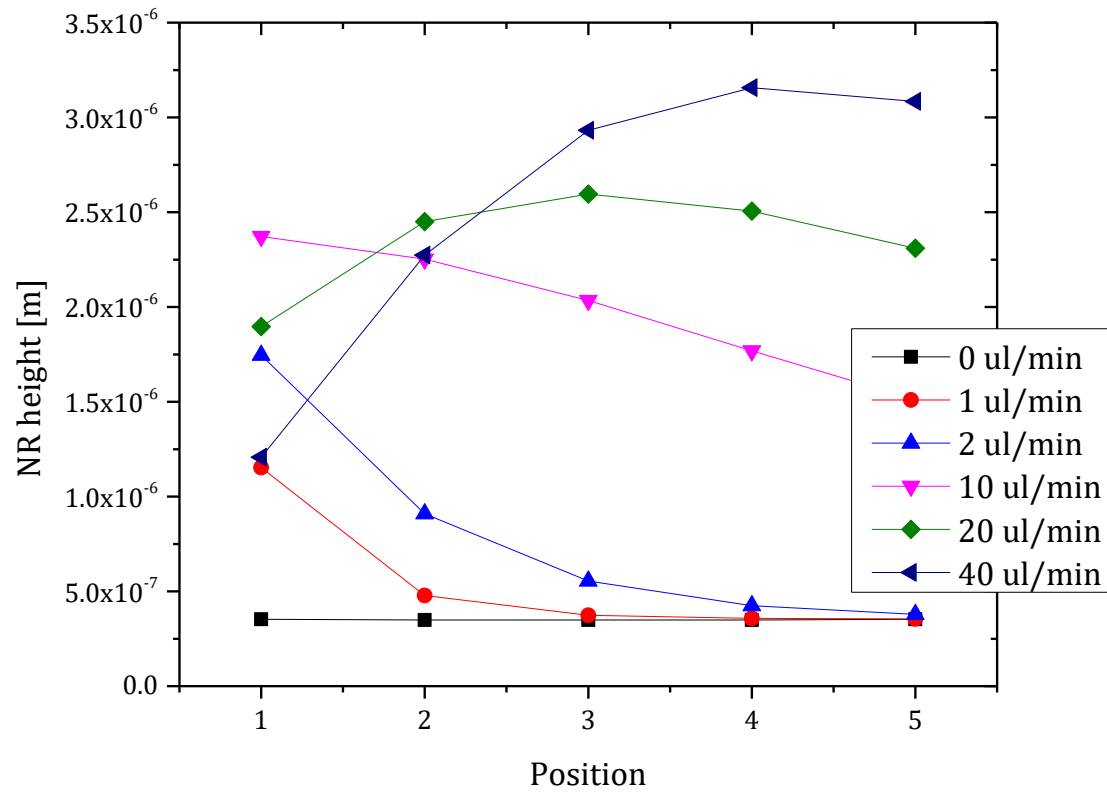
# #3.4 – Flow reactor modeling – experiments



# Batch and Flow reactors



# Flow reactor modeling - Results





# Flow reactor modeling - Results

