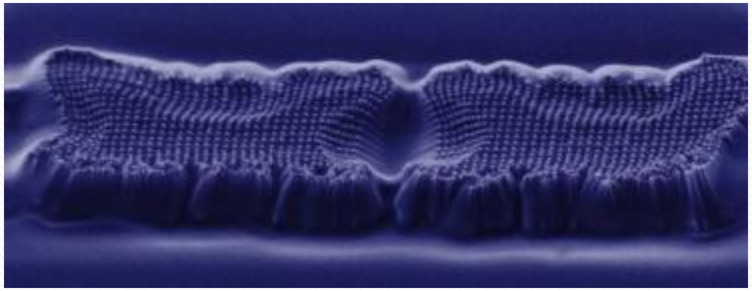
Multifunctional ZnO Nanowires

János Volk, Zoltán Szabó, Nguyen Q. Khanh, Róbert Erdélyi



NiPS Workshop, Aug. 4th, 2011

Introduction

Research Institute for Technical Physics and Materials Science (MFA)

of the Hungarian Academy of Sciences (HAS)

Mission of the Institute

Interdisciplinary research on complex functional materials and nanometer-scale structures, exploration of physical, chemical and biological principles, their exploitation in integrated micro- and nanosystems, and in the development of characterization techniques.

Departments

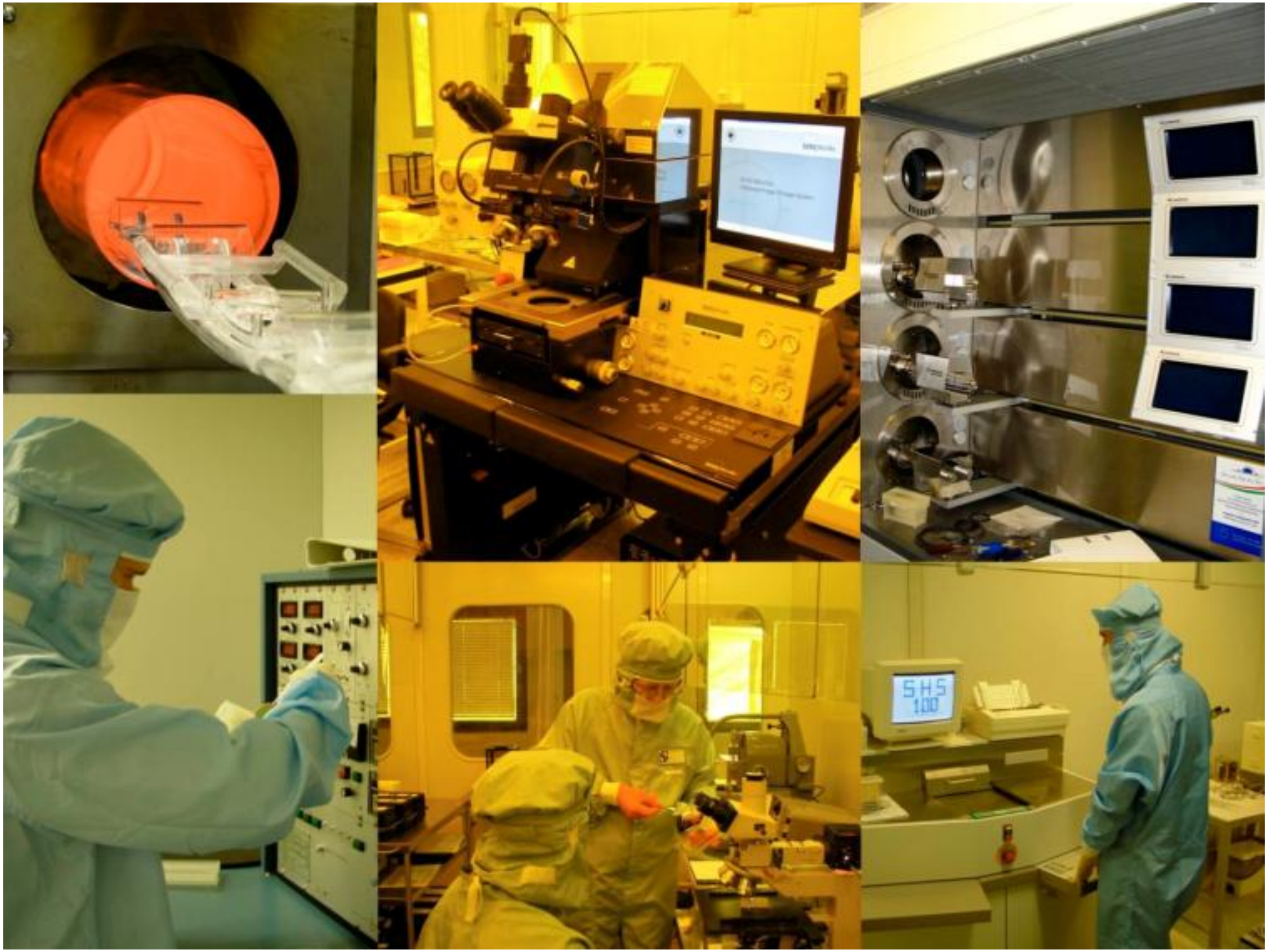
Microtechnology, Photonics, Thin Films, Complex Systems, Nanostructures, Ceramics and Nanocomposites

From 2012: New multidisciplinary institution: Material Science + Chemistry + Ensimology

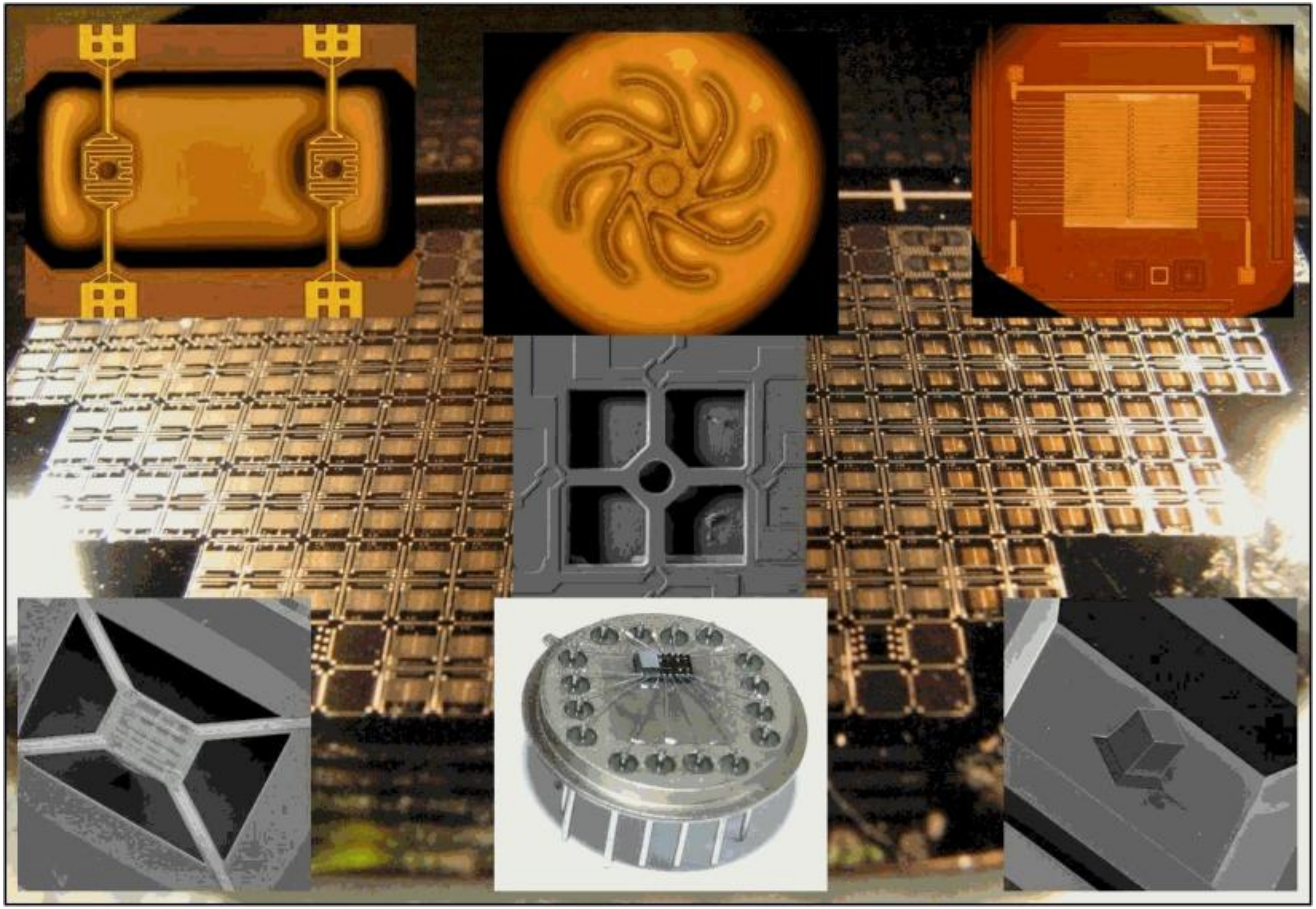
Semiconductor Nanowire and Colloid Group

@ Ceramics and Nanocomposite Department (http://www.mfa.kfki.hu/)
2 senior researcher, 1 postdoc, 2 PhD student, 2 undergraduate students + 2 persons at nano-beam lab (SEM, FIB, e-beam lithography)

MEMS laboratory



MEMS laboratory

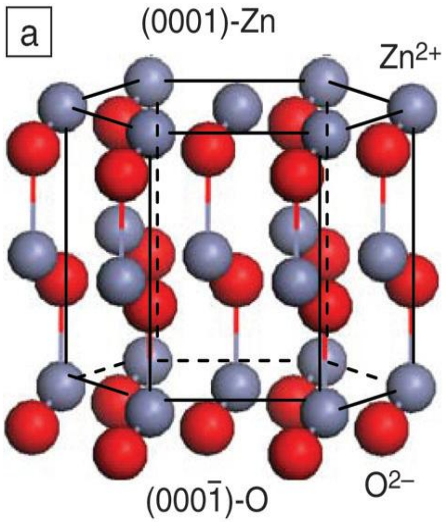


ZnO: the rediscovered material

Unique combination of bulk properties

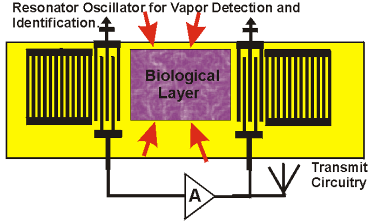
- Wide band-gap semiconductor (3.37 eV)
- N-type easy, p-type difficult
- Large exciton binding energy (60 meV)
- Tunable band-gap with Mg and Cd (3-4 eV)
- Piezoelectric and pyroelectric properties (e_{33}=1.22 Cm^{-2}, e_{31}=-0.51 Cm^{-2})
- Versatile nanostructures

Wurtzite crystal

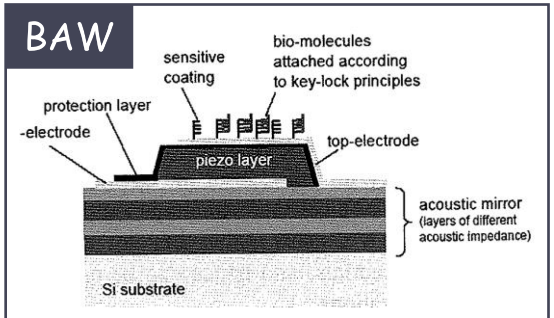


SAW

Figure 27: Example of a Biocoated Two-Port SAW Resonator Oscillator for Vapor Detection and Identification.



BAW



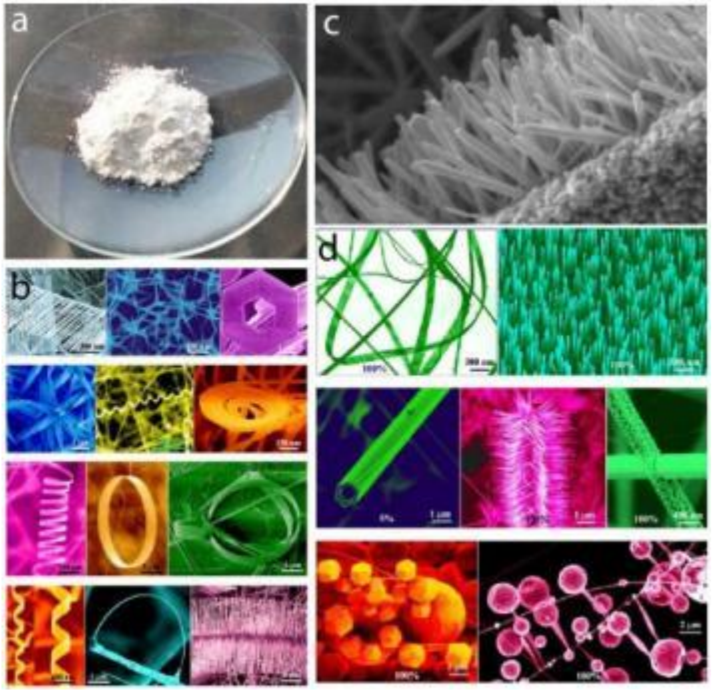
Transparent electrode

Pharmacology

Versatile nanostructures

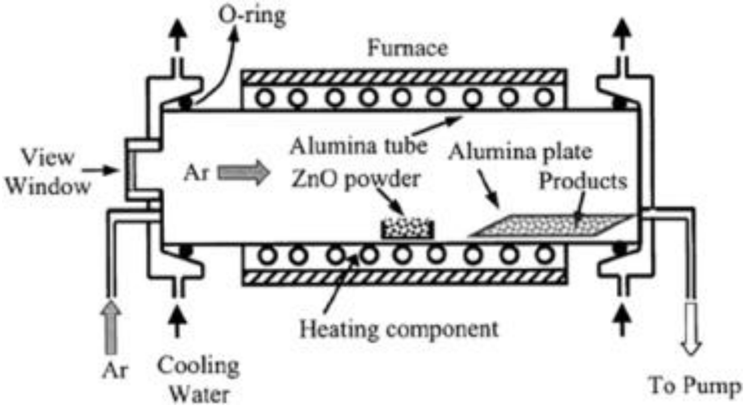
ZnO nano-

wire (NW), rod (NR), pillar, helix, belt, tetrapod, ring, tube



Synthesis processes

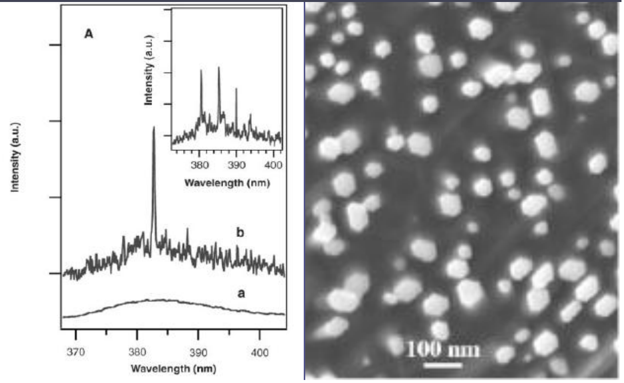
- high temperature dry: VS, VLS, PLD, MOCVD
- **low temperature wet chemical methods**



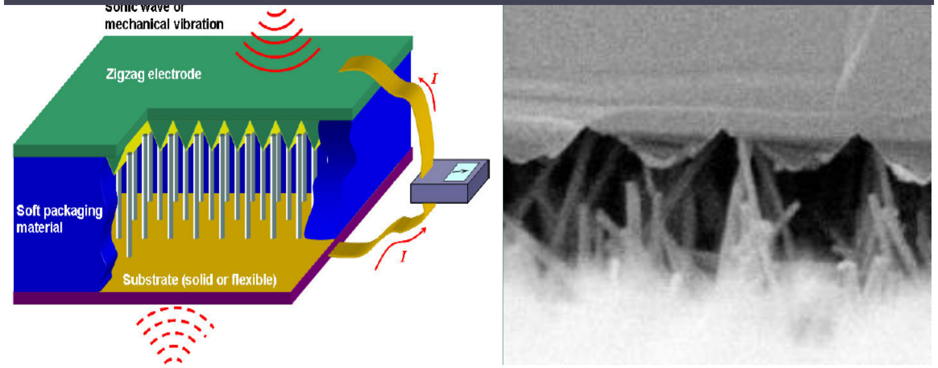
Potential applications

- Nanoelectronics,
- Nanophotonics
- **Energy harvesting**
- **Sensorics:** chemical, biological, mechanical
- **Photovoltaics**

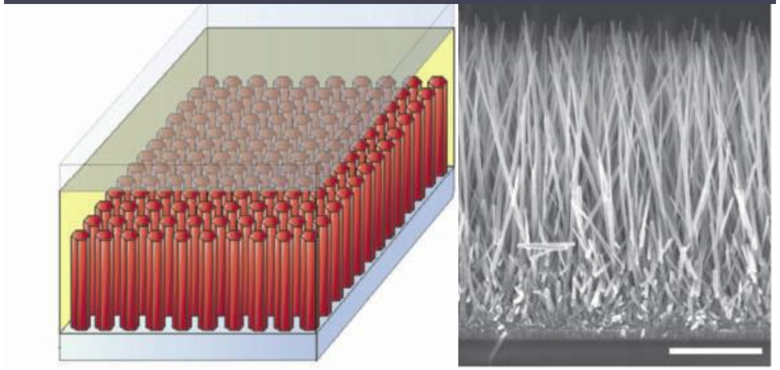
M. H. Huang et al.: RT lasing; nanocavity
Science 292, 1897 (2001)



Z. L. Wang et al., Nanogenerator Science, 316 102 (2007)



M. Law et al.: Nanowire dye-sensitized solar cells,
Nature Materials 4, 455 (2005)



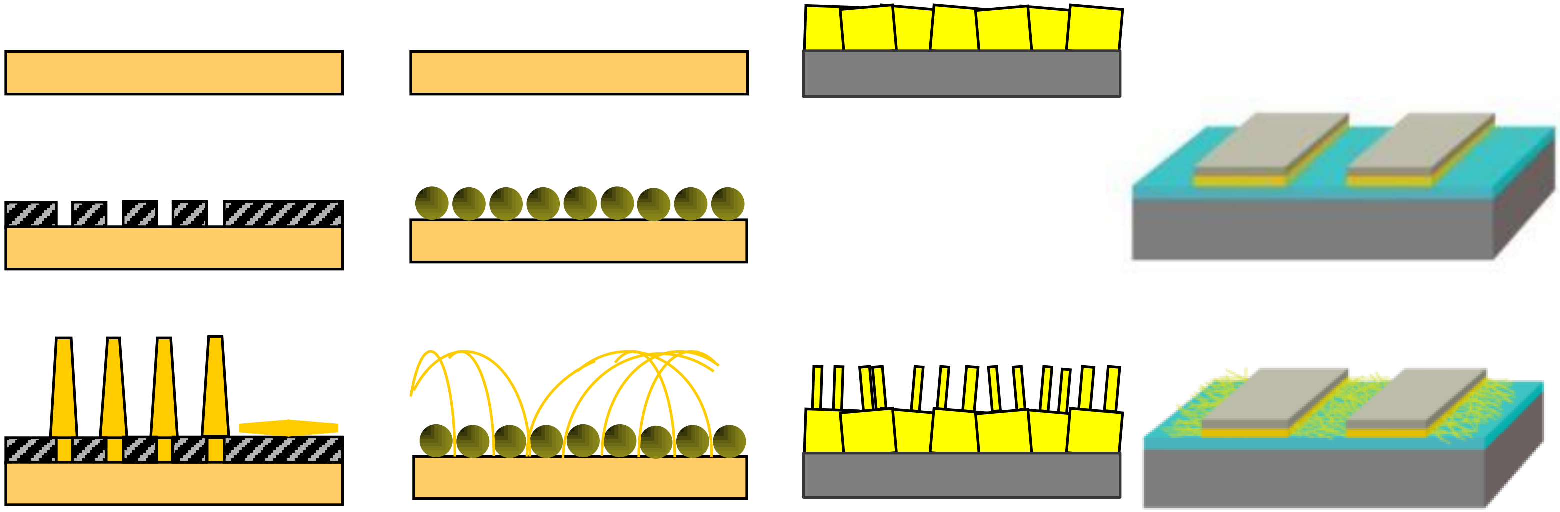
More precise control of NW and array geometry is required for device integration!

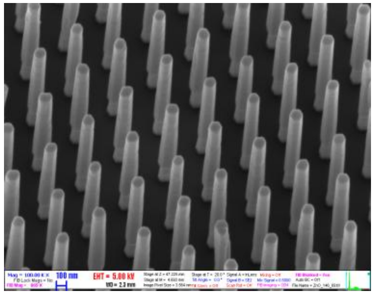
Nanowire engineering

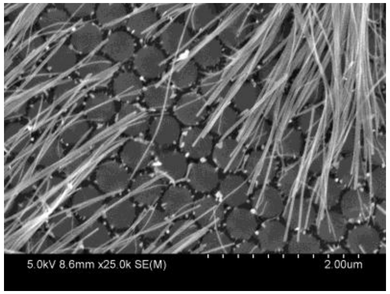
Seed surface

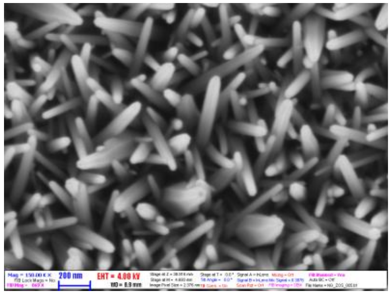
Nucleation window

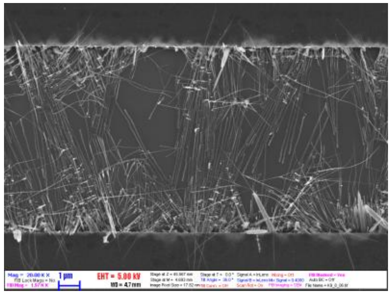
Hydrothermal growth



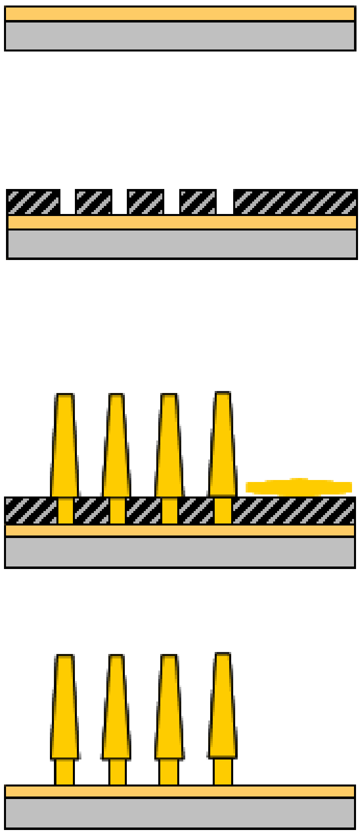








by e-beam lithography…

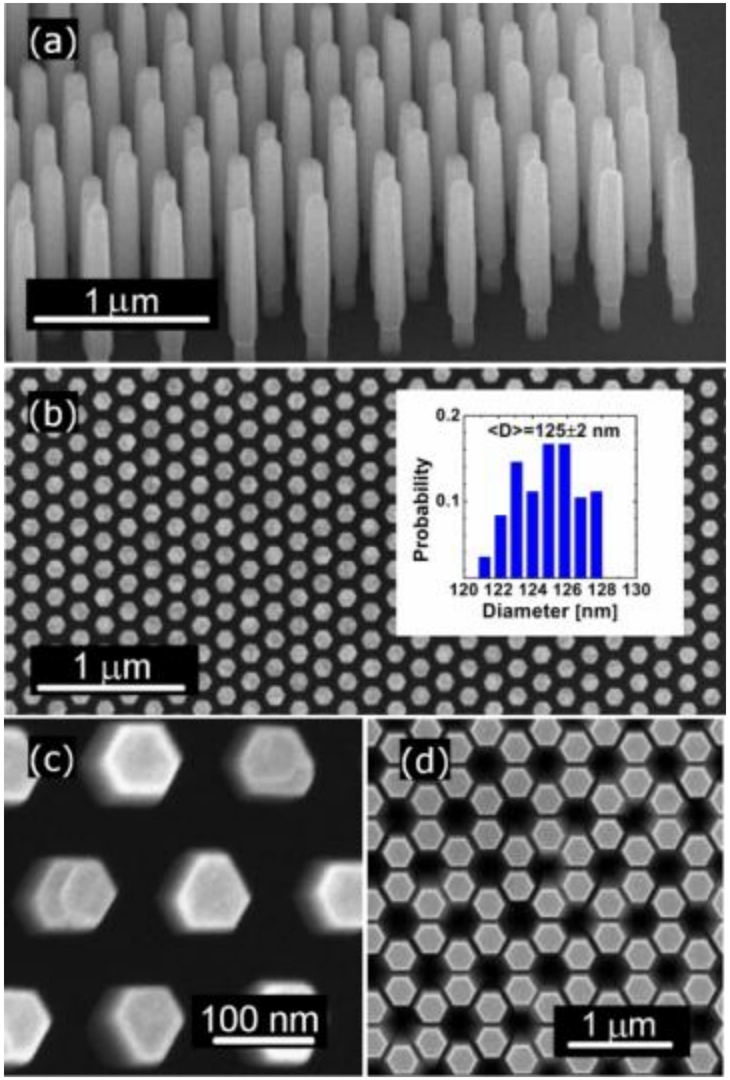


Seed layer

E-beam pattern
in PMMA

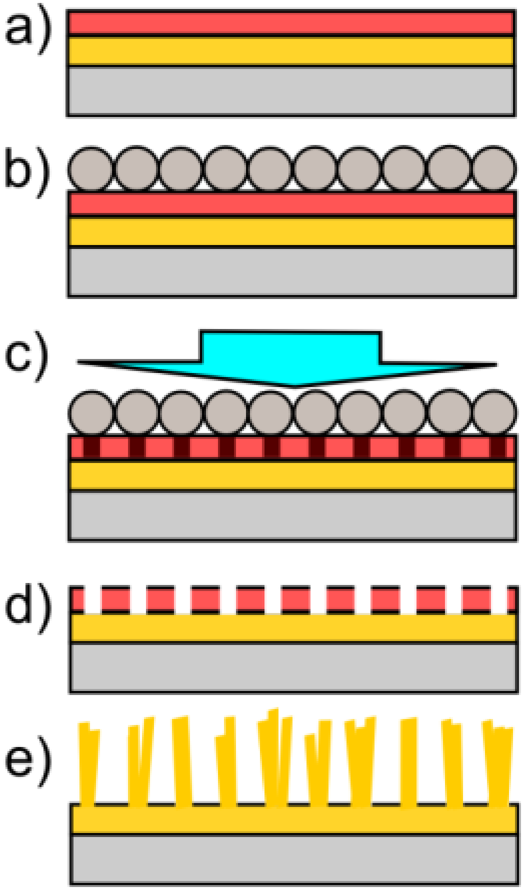
Hydrothermal
growth

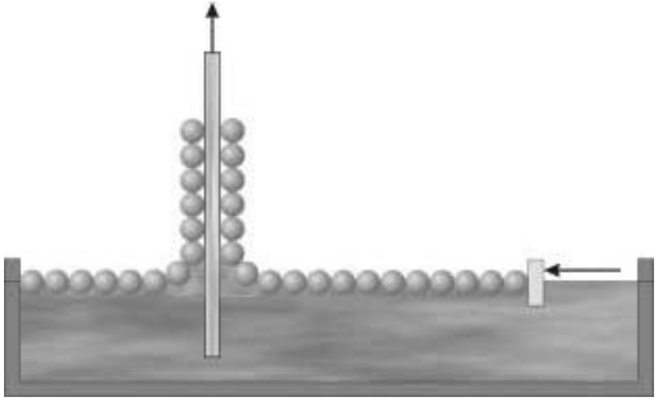
Lift-off

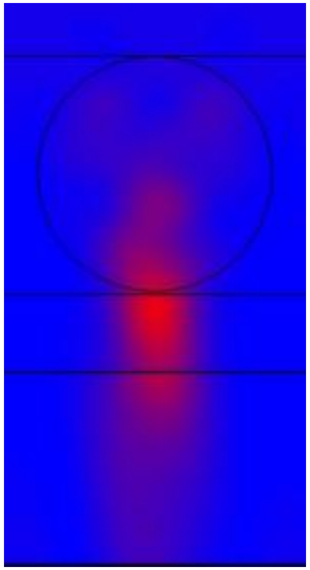


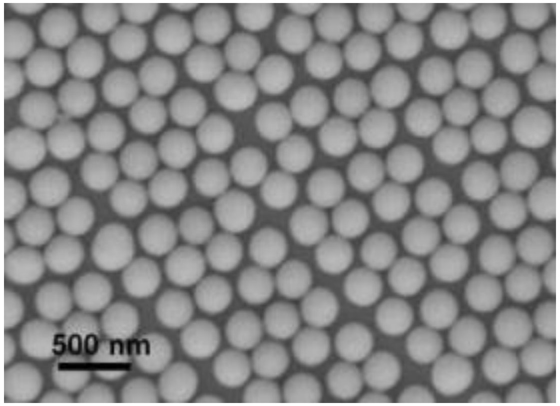
J. Volk et al., Nanoscale Res. Lett. 4, 699 (2009)

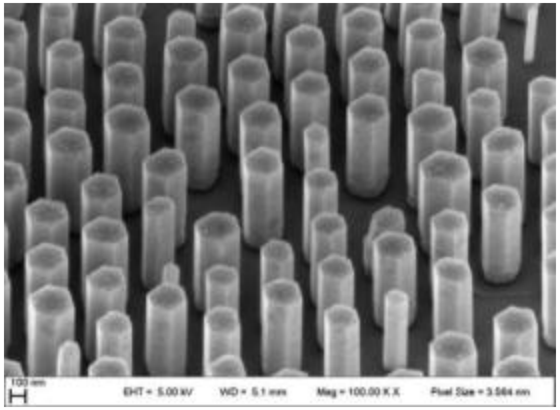
by nanosphere photolithography (NSP)...



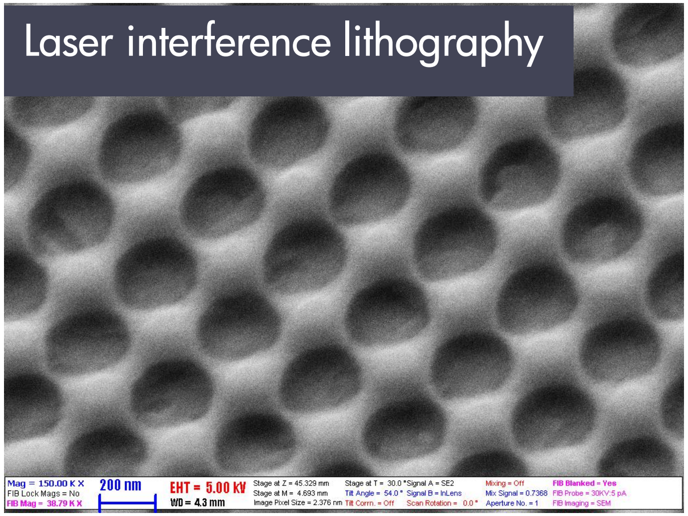


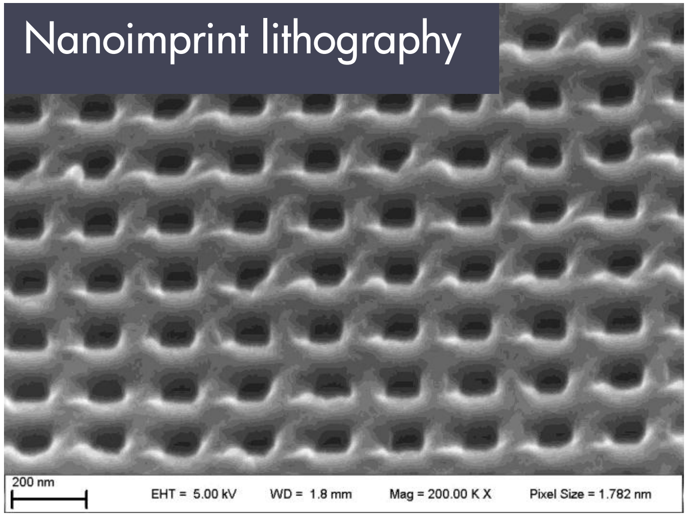


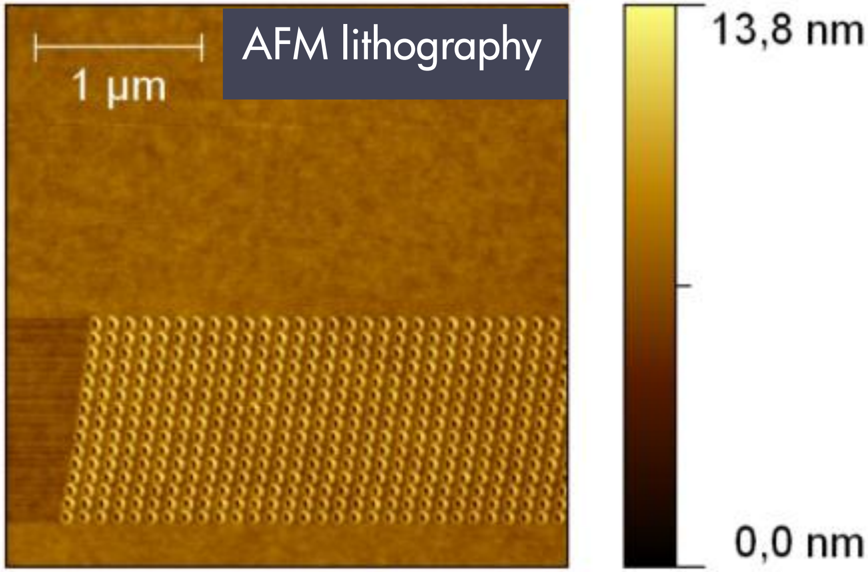




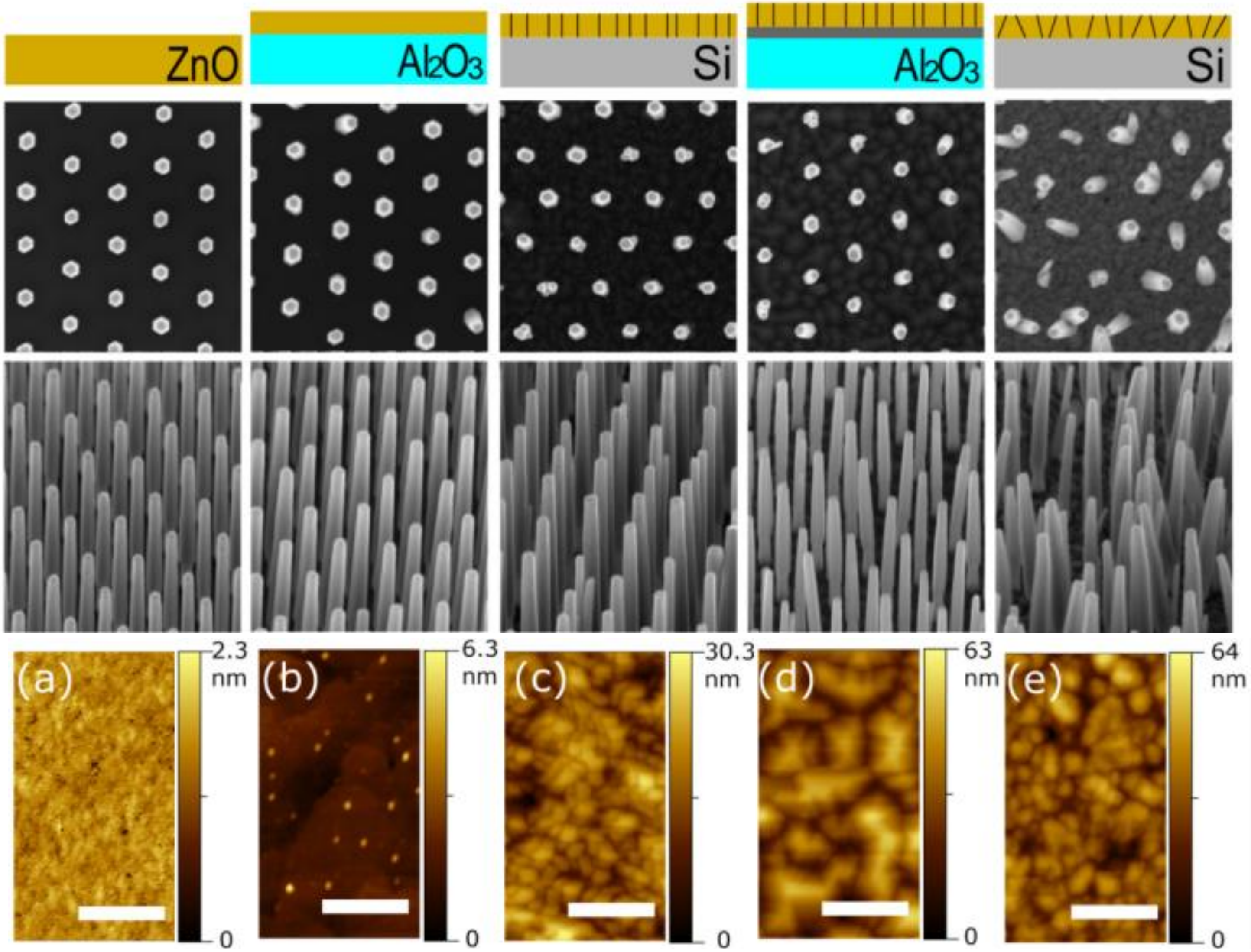
by further alternative nanopatterning methods…


Laser interference lithography


Nanoimprint lithography


AFM lithography

Seed layer engineering

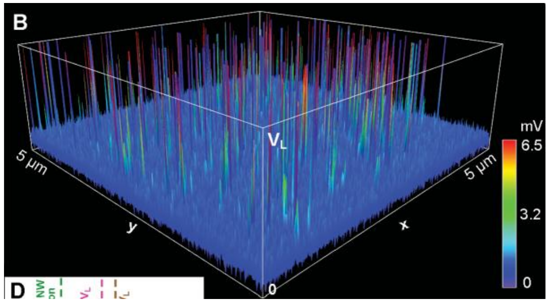


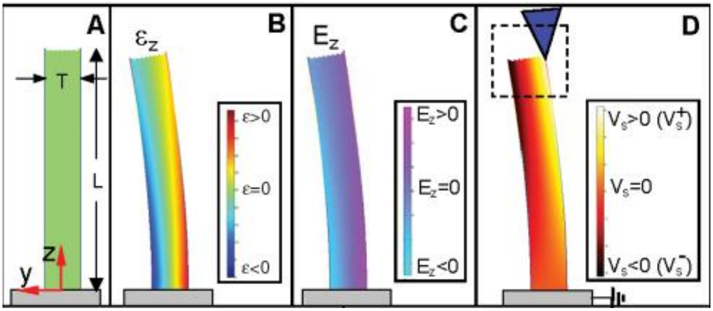
R. Erdélyi et al., Cryst. Gr. & Des., 2011, 10.1021/cg2002755

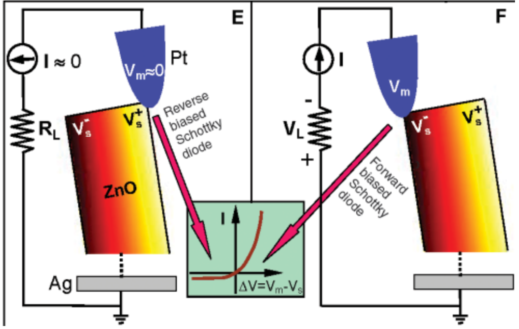
Possible application #1:

Nanogenerator

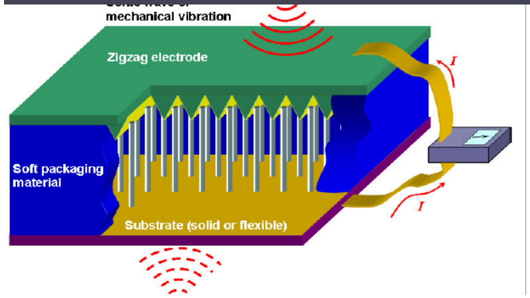
Wang Z.L.: Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays, SCIENCE 312, 14 (2006)

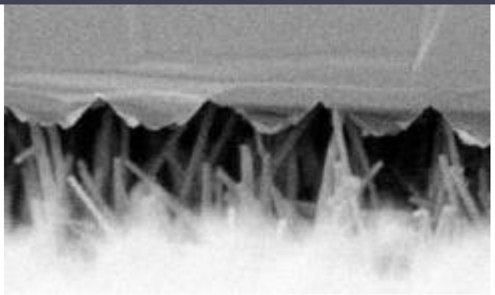


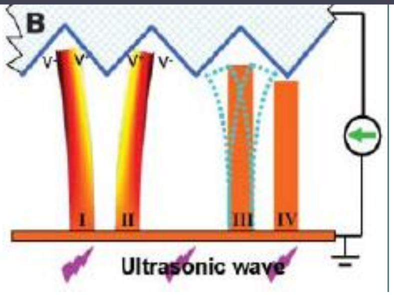




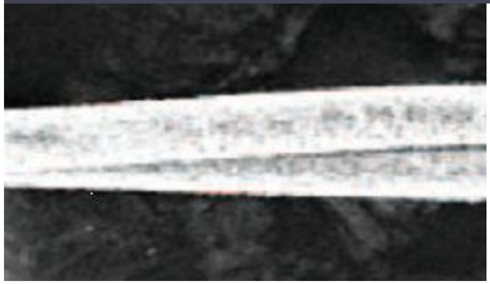
Z. L. Wang et al., Direct-Current Nanogenerator Driven by Ultrasonic Waves, SCIENCE 316 102 (2007)

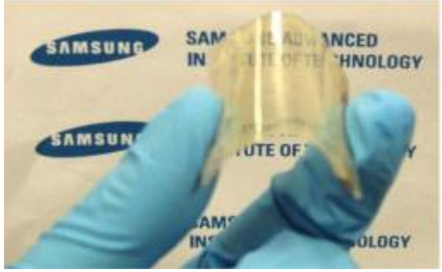






2007- Follow-up works





Fundamental theory of nanogenerator*

Coupled tensor equations

$$\begin{cases} \sigma_p = c_{pq}\varepsilon_q - e_{kp}E_k \\ D_i = e_{iq}\varepsilon_q + \kappa_{ik}E_k \end{cases}$$

$$e_{kp} = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix}$$

Assumptions

- No free charges: $\nabla\vec{D} = \rho_e = 0$
- Perturbation theory

$$\varphi_{\max}^{(T,C)} = \pm\frac{3}{4(\kappa_o + \kappa_\perp)}\left[e_{33} - 2(1+\nu)e_{15} - 2\nu e_{31}\right]\frac{r^3}{l^3}\,y_{\max}$$

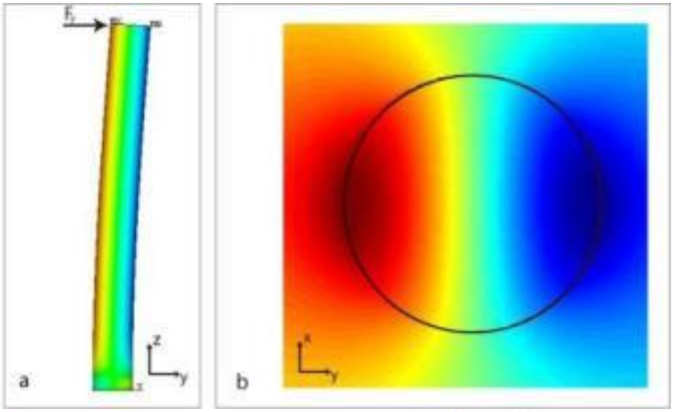
$$y_{\max} = \frac{F_y l^3}{3EI_{xx}} \qquad I_{xx} = \frac{\pi}{4}a^4$$

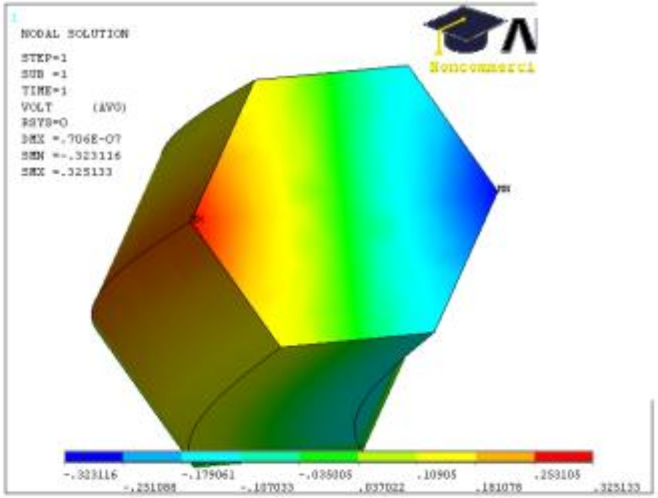
Typical potential difference:

$\Delta\varphi_{calc}$=0.5-1 V » $\Delta\varphi_{exp}$=10-50 mV

+ Practical difficulties

- Less than 1% is active (2 mm^2)
- Low power: I_{DC}~ 100 nA; V~10 mV
- Multilayer: P~ 0,1 μW/cm^2





*Gao Y, Wang ZL, Nano Lett. 7, 2499 (200 7)

Conceptual concerns

- **NW is not insulator**

- resistivity: 10^{-2}-10^{2} Ωcm $\nabla\vec{D} = \rho_e \neq 0$

- screening time constant: 10^{-2} -10^{2} ps

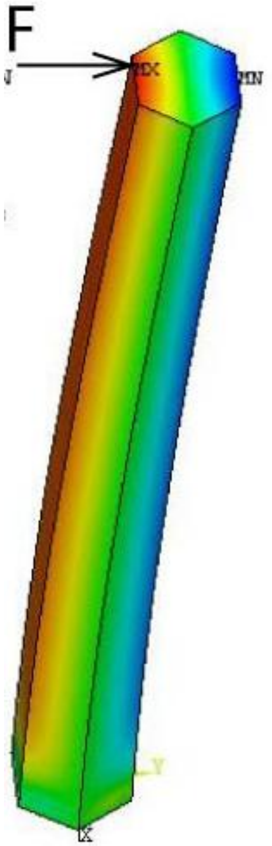
$$\tau_i = RC = \rho\frac{d}{A}\kappa_0\kappa_r\frac{A}{d} = \rho\kappa_0\kappa_r$$

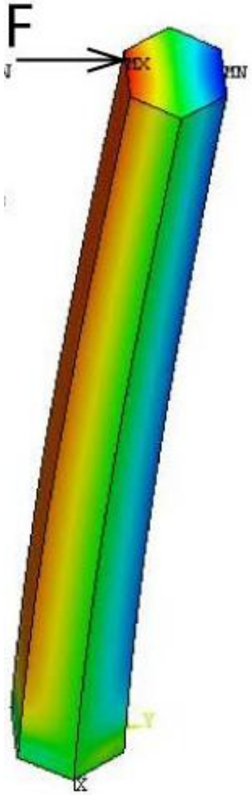
- Rectifying effect is low in the -10-10 mV range*

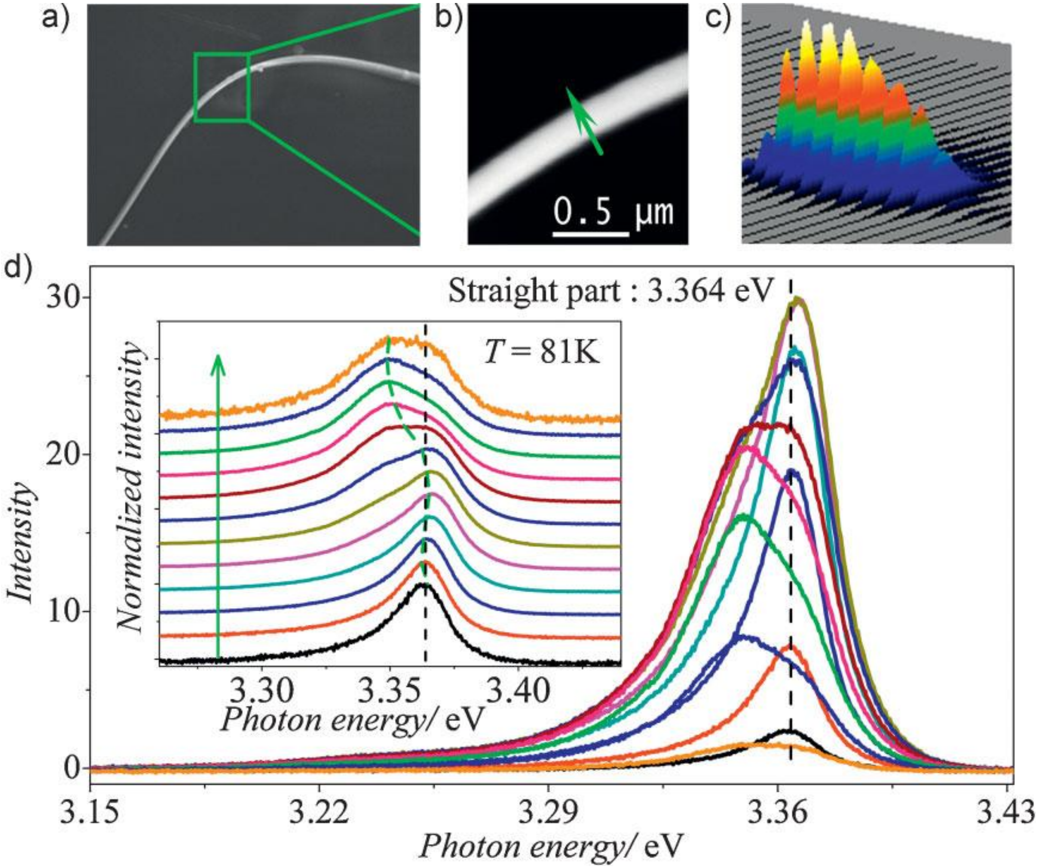
$$J = A^{*}T^{2}\exp\left(-\frac{q\phi_{Bn}}{k_bT}\right)\left[\exp\left(\frac{qV}{k_BT}\right)-1\right]$$

- How can we distinguish the effect of piezoelectricity from stress induced electron band change?

*Alexe M. et al., Adv. Mater. 20, 4021 (2008)







Han X. et al., Adv. Mater. 21, 4937 (2009)

Our goals

1) Systematic investigation on well controlled NRs

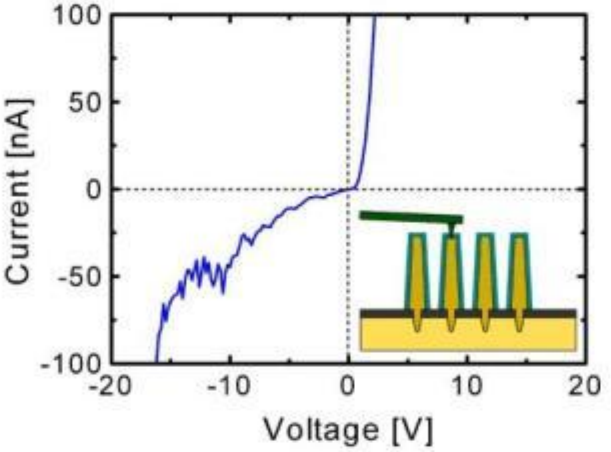
- Electrical
- Mechanical
- Coupled electromechanical

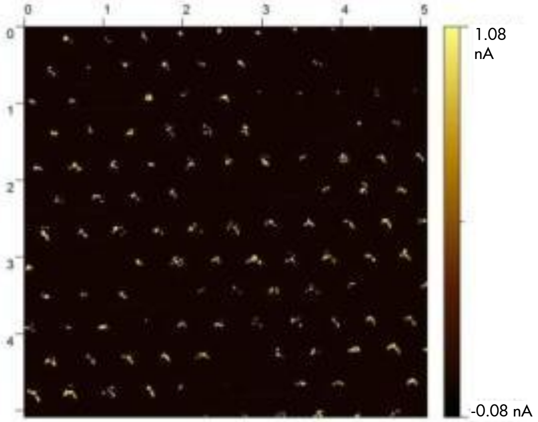
2) Finding the origin of the „nanogenerator effect”

3) Fabrication of new type of energy converter or mechanical sensor

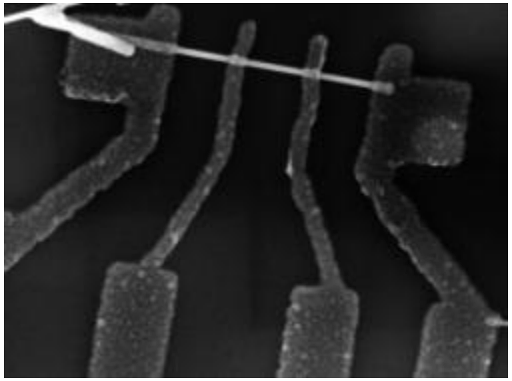
Electrical measurements of ZnO NRs

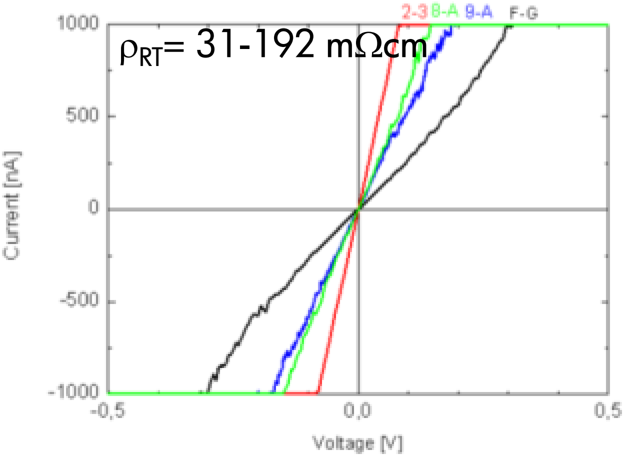
Conductive AFM





Permanent electrical contacts on NR/NW





ρ_{RT}= 31-192 mΩcm

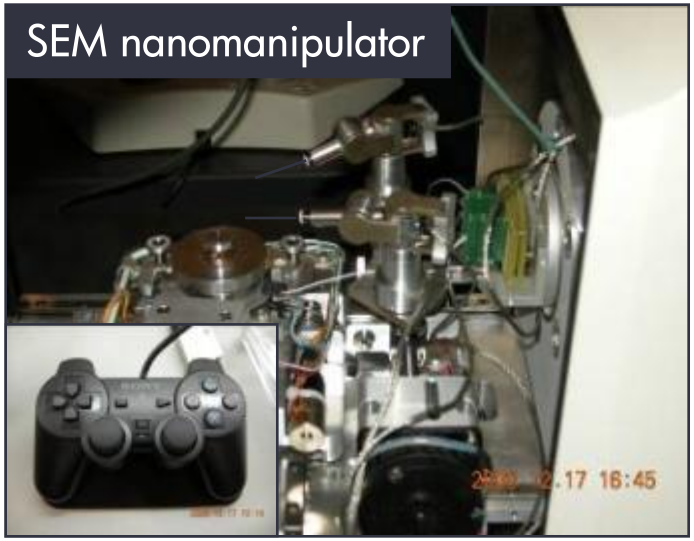
Difficulties

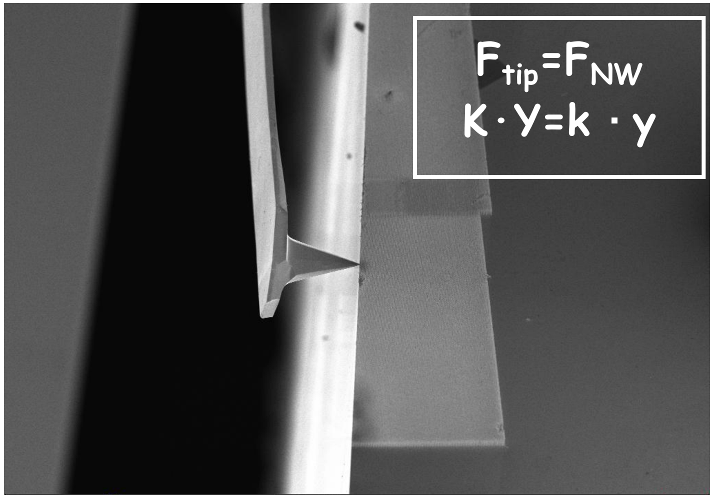
- Resistivity control is poor: from the same growth: 1-10^3 Ωcm, different growths 10^{-3}–10^5 Ωcm*
- Poor chemical resistance of (hydrothermally grown) NWs

*Schlenker et al., Nanotechnology **19**, 365707, (2008)

Nanomechanical test

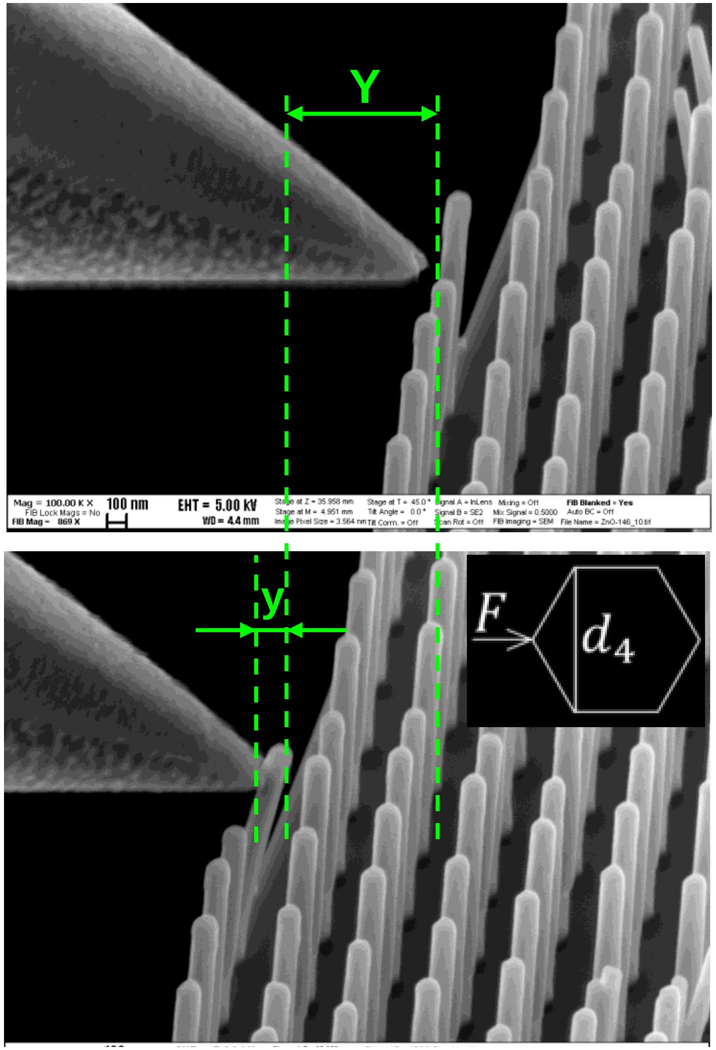
SEM nanomanipulator



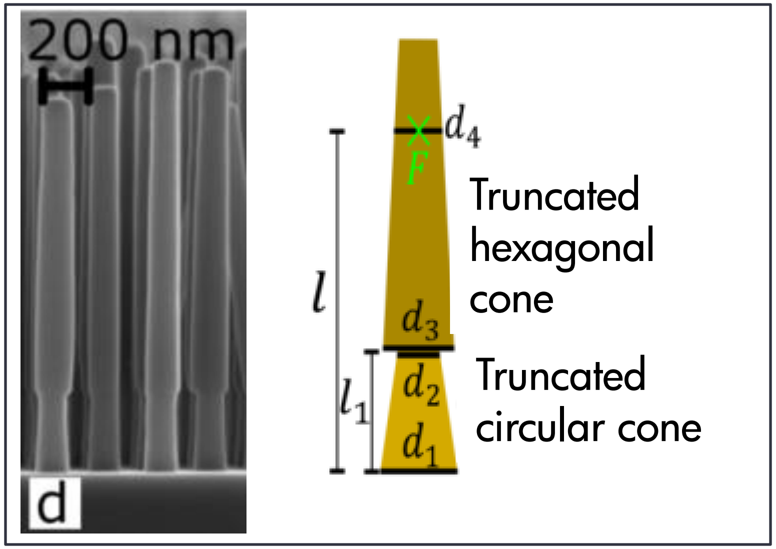


$F_{tip}=F_{NW}$

$K\cdot Y=k\cdot y$



Mechanical test



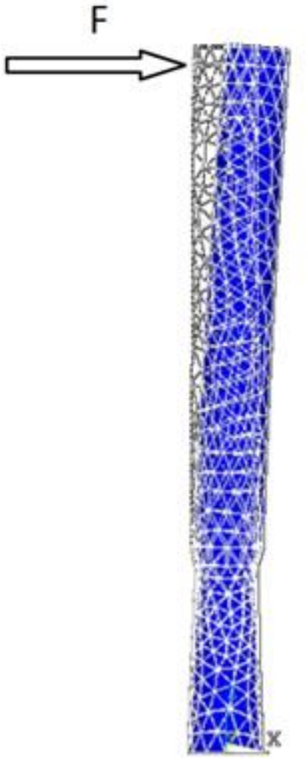
Euler-Bernoulli beam equation:

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\left(EI\frac{\mathrm{d}^2 y}{\mathrm{d}x^2}\right)=q$$

↓

Bending modulus:

$$E_{BM}=\frac{F}{y}\int\frac{x^2}{I}dx$$



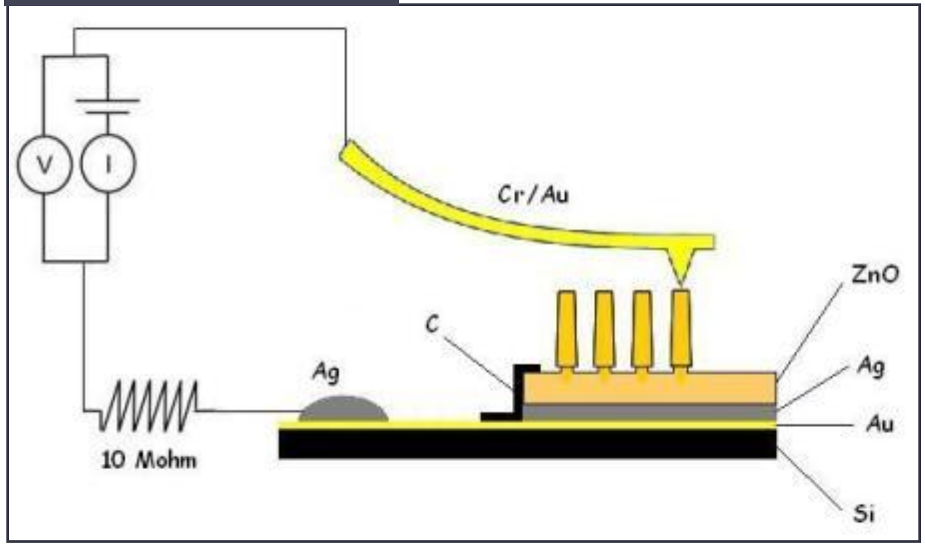
$$E_{BM}=\frac{kY}{y}\left\{\frac{4}{\pi}\int_0^{l_1}\frac{x^2}{\left[\frac{1}{2}\left(d_1-\frac{(d_1-d_2)}{l_1}x\right)\right]^4}dx+\frac{16}{5\sqrt{3}}\int_{l_1}^{l}\frac{x^2}{\left[\frac{1}{\sqrt{3}}\left(d_3-\frac{(d_3-d_4)}{l-l_1}(x-l_1)\right)\right]^4}dx\right\}$$

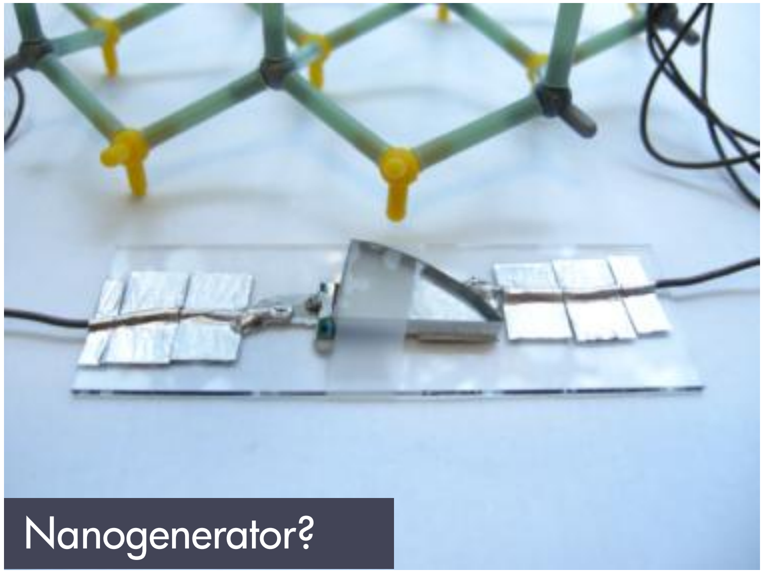
$\langle E_{BM}\rangle=36.0\pm8$ Gpa $<$ $E_{bulk}=140$ Gpa; $E_{BM<11\text{-}20>}\approx E_{BM<10\text{-}10>}$; $E_{BMan.}\approx E_{BMFEA}$

R. Erdelyi, J. Volk et al. to be published in Phys. E

Nanogenerator

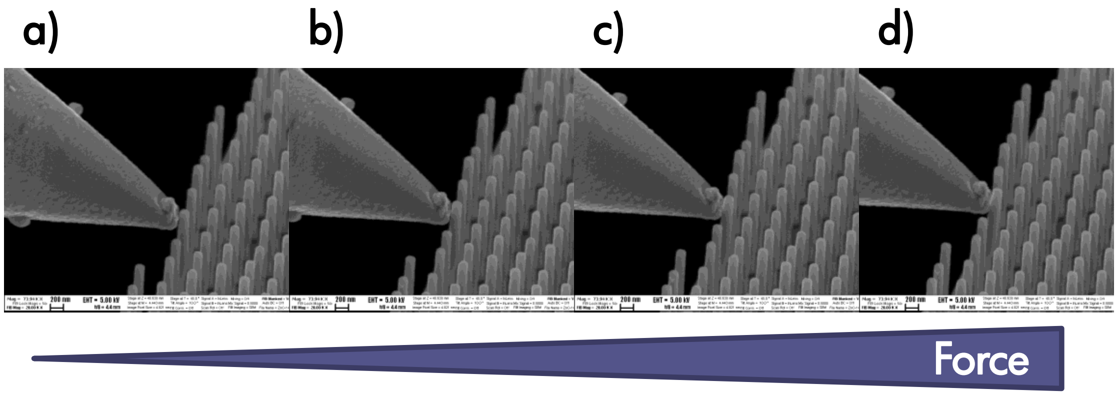
Conductive AFM

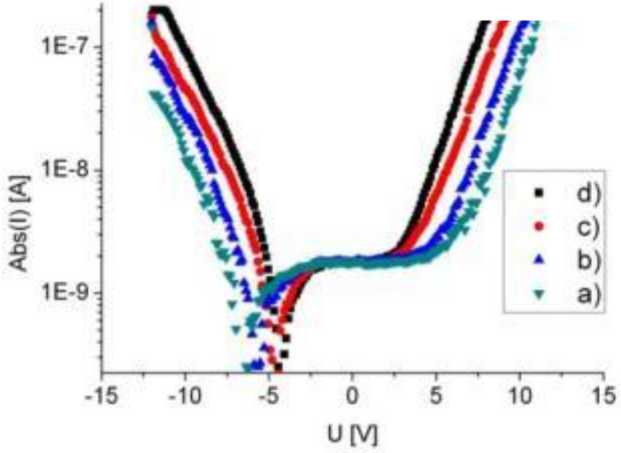


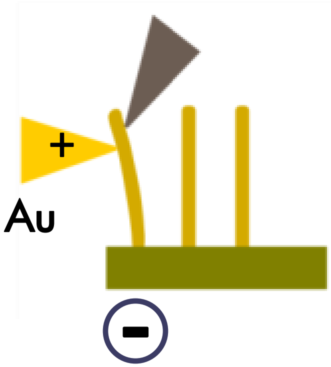

Nanogenerator?

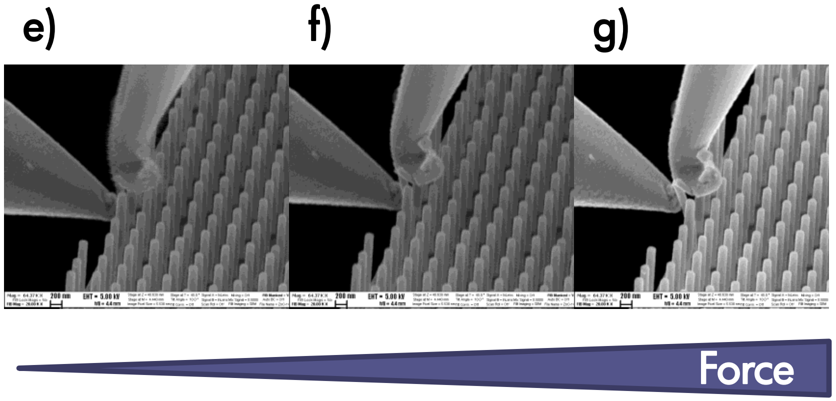
We could not detect any output power.

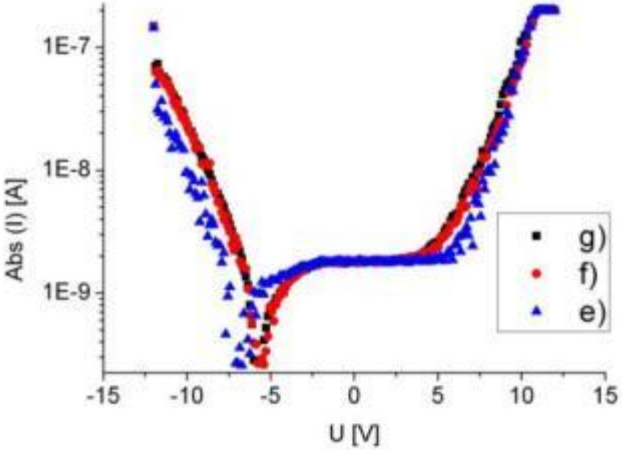
Electromechanical investigation





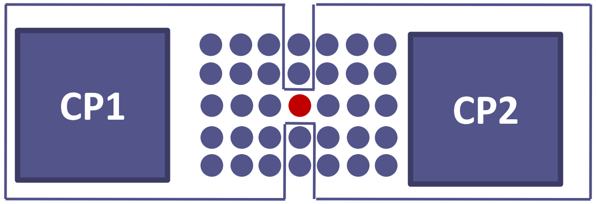


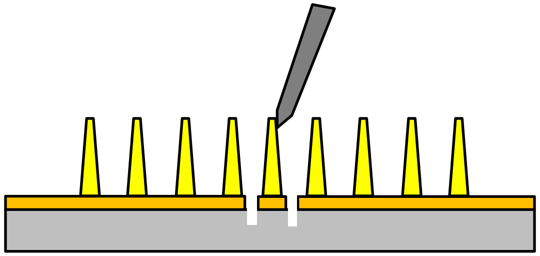


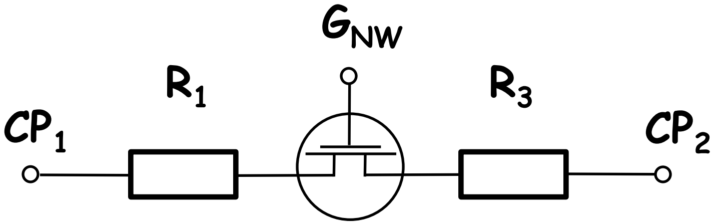


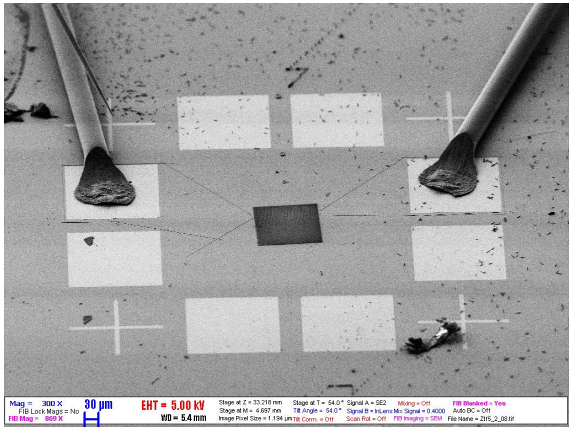
Suitable for force sensing at an operating voltage of ~7V, but permanent contact is needed.

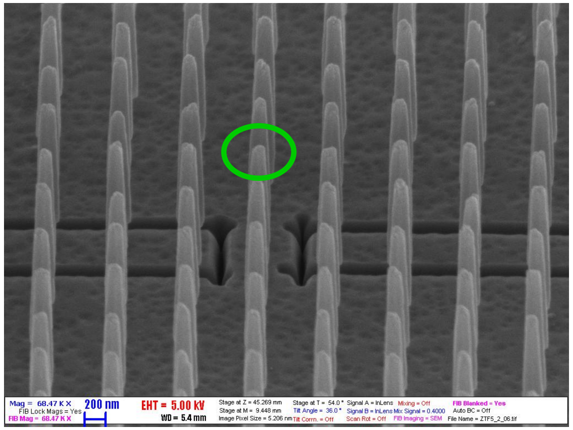
Integrated force sensor

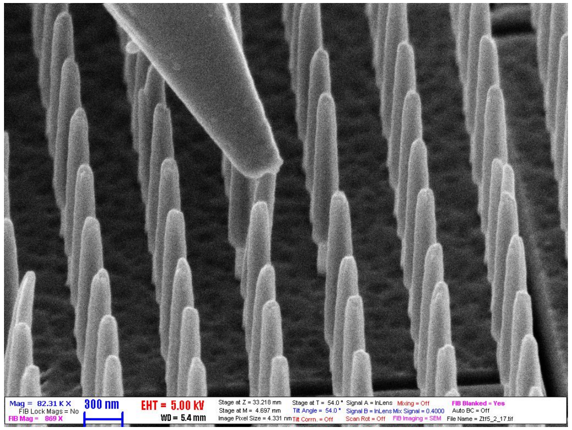






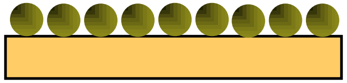




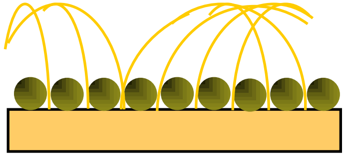


Method #2:

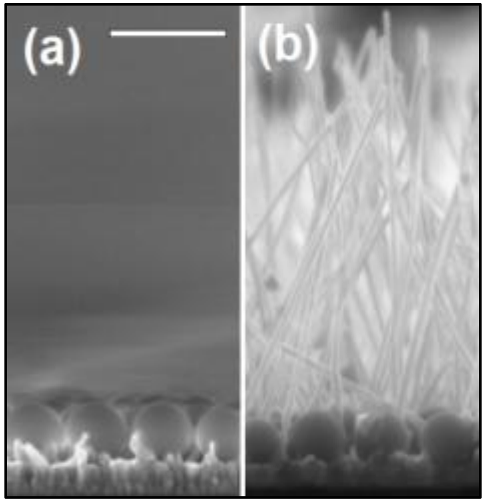
High aspect ration ZnO NWs via nanoparticulate template



LB nanoparticate film

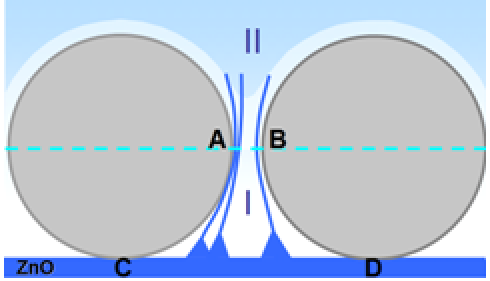


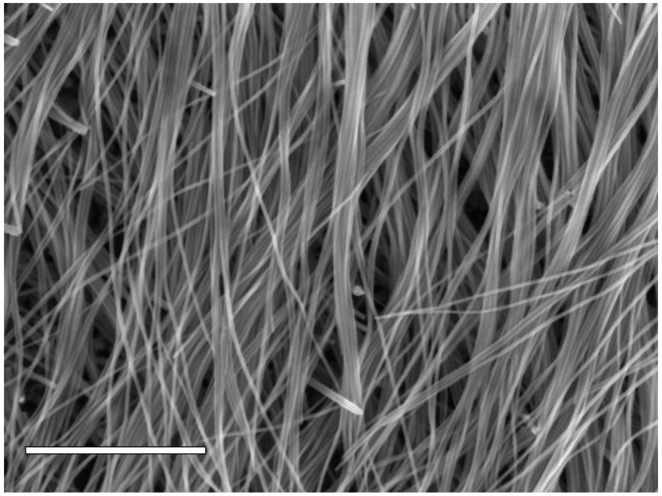
ACG growth

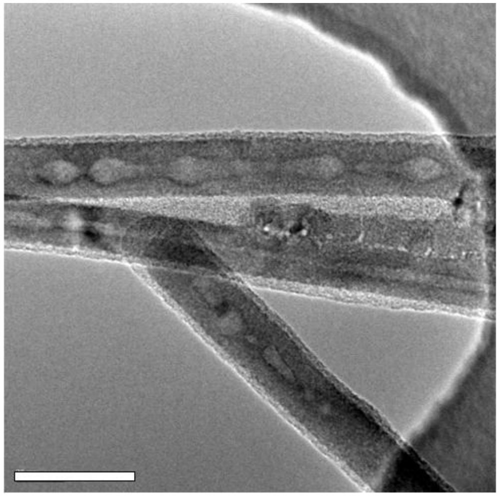


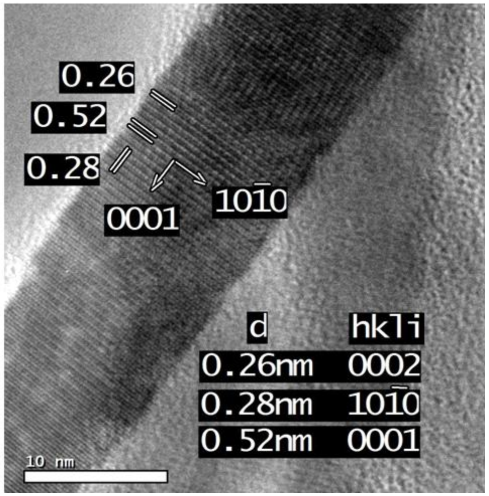
Length: L = 5-20 μm

Diameter: D= 15-30 nm





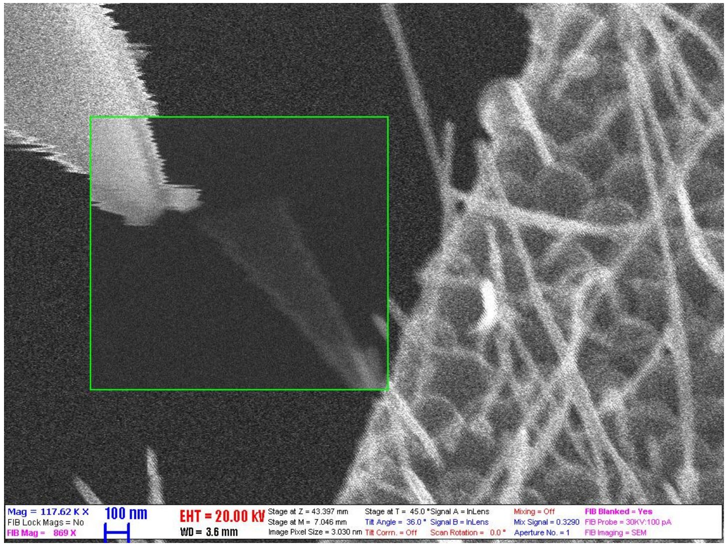


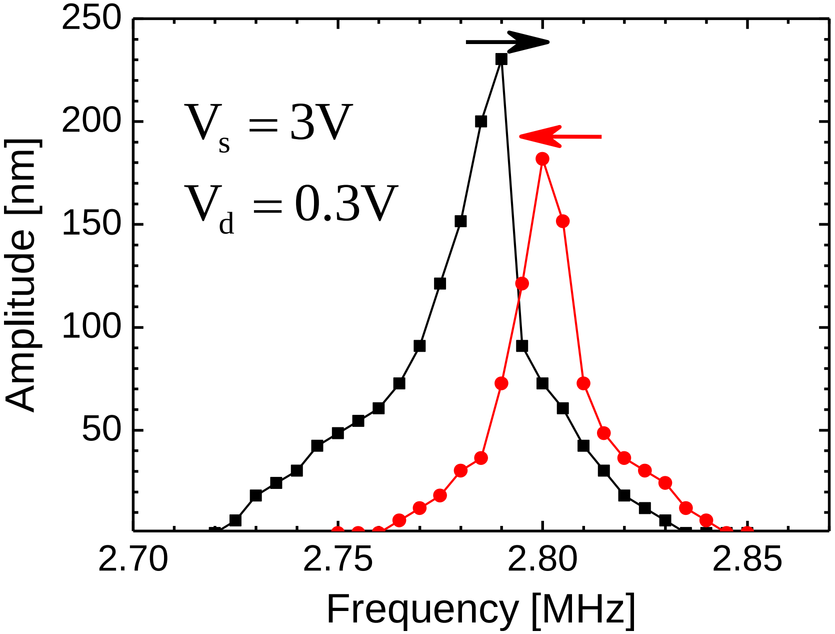


d	hkli
0.26nm	0002
0.28nm	$10\bar{1}0$
0.52nm	0001

Resonance excitation

$$\left.\begin{aligned} V(t) &= V_s + V_d \cos(\omega t) \\ q &= \alpha[\Delta V + V(t)] \\ F(t) &= \beta[\Delta V + V(t)] \cdot q \end{aligned}\right\} \quad F(t) = \alpha\beta\left[\Delta V + V_S + V_d \cos(\omega t)\right]^2$$



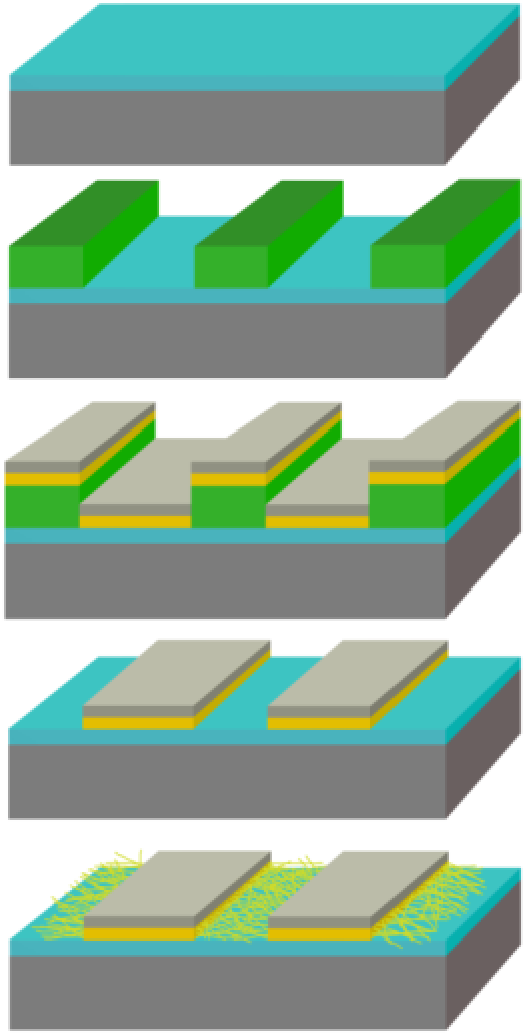


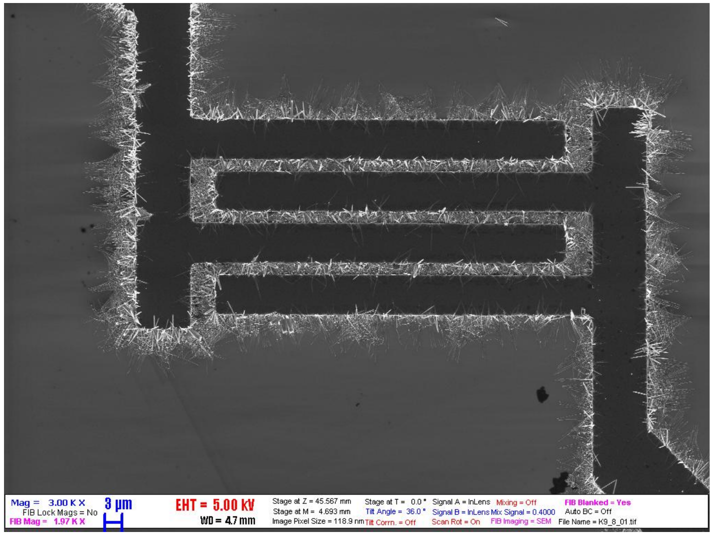
$$\upsilon = \frac{\beta_i^2}{8\pi}\sqrt{\frac{E}{\rho}} \cdot \frac{D}{L^2}$$

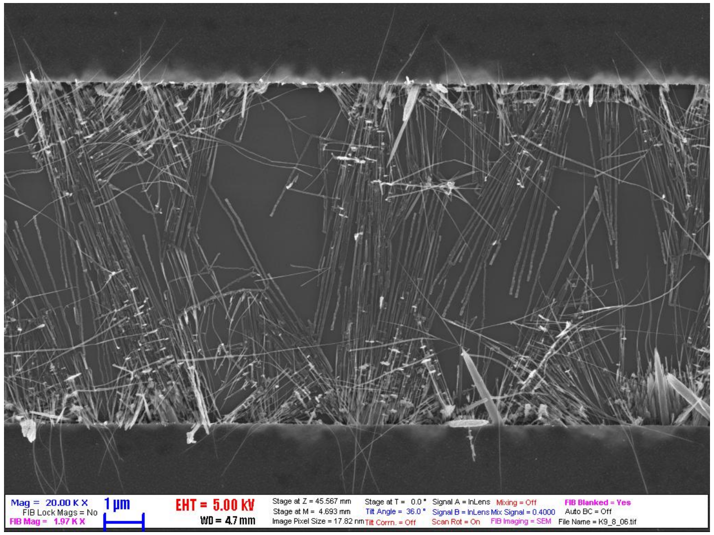
Demonstration with CNT: P. Poncharal, Science 283, 1513 (1999)

Method #3:

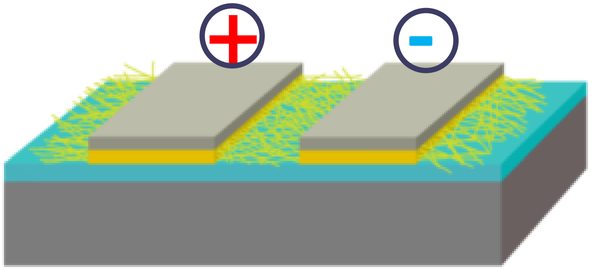
On-chip grown horizontal ZnO nanowires

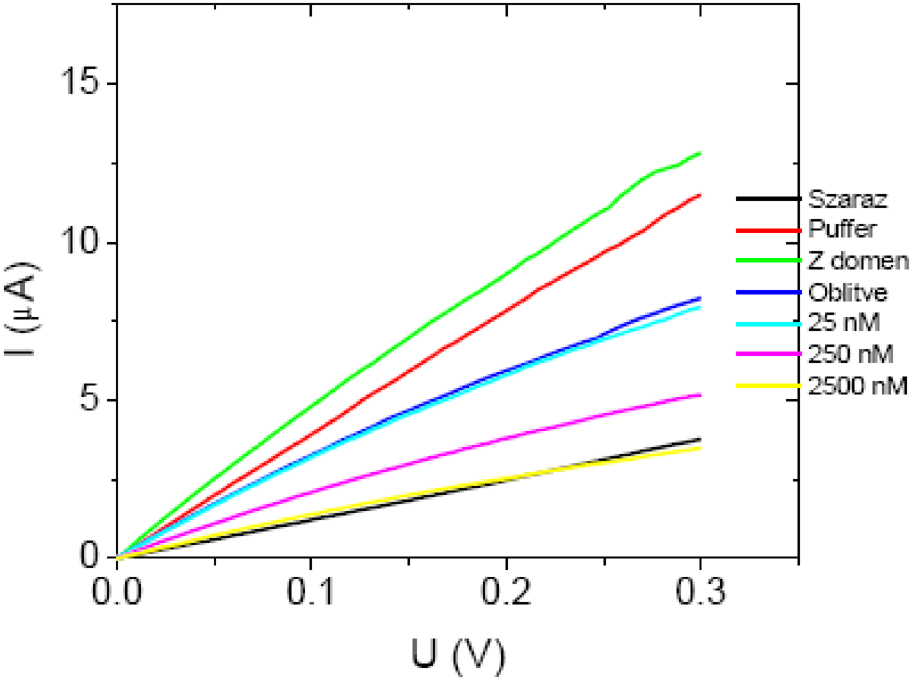


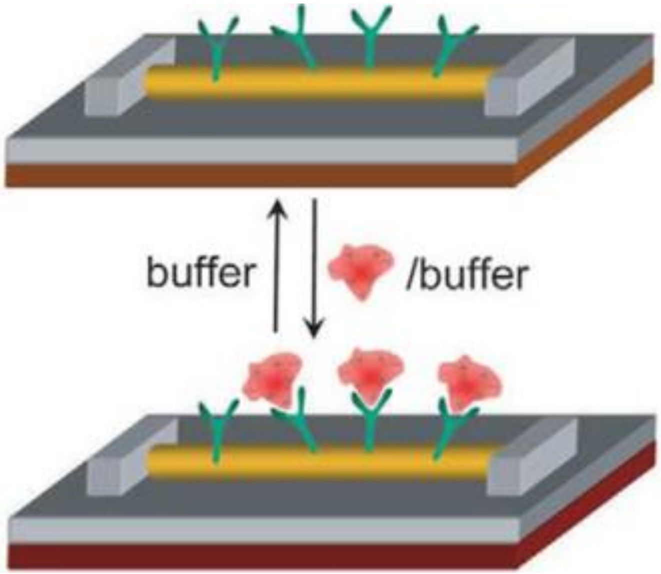




Biological sensor





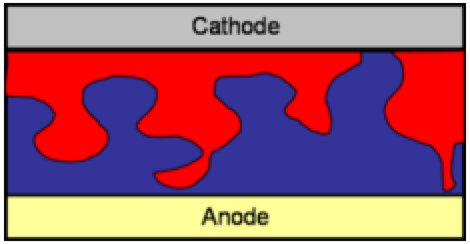


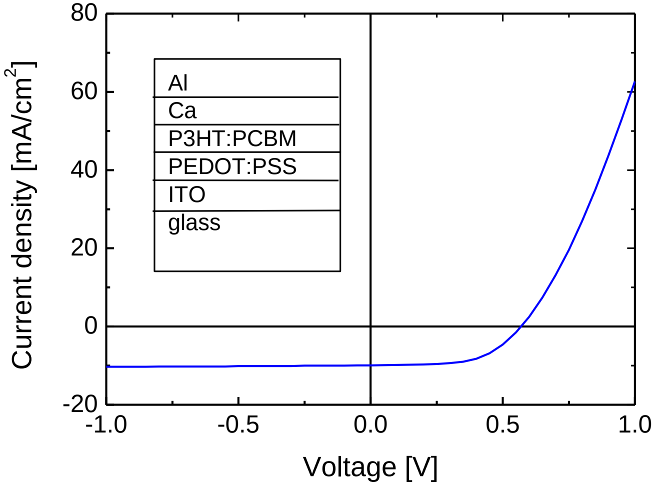
Protein

Z-domain + IgG

Hybrid photovoltaic cell

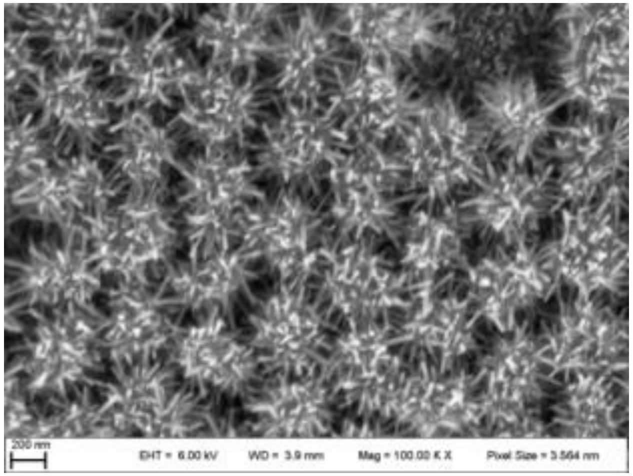
Bulk heterojunction

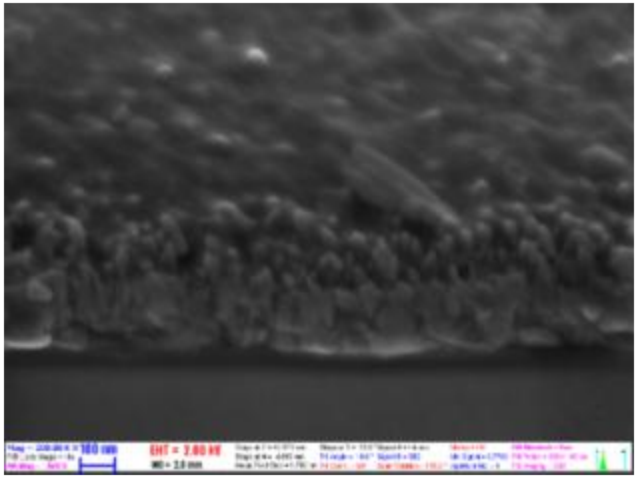




η=3.3%
J_{SC} = 9.9 mA/cm^2
V_{OC} = 550 mV
FF = 0.60

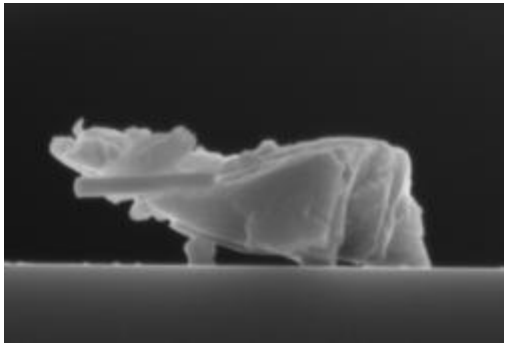
Hierarchial ZnO NWs/p-type polymer

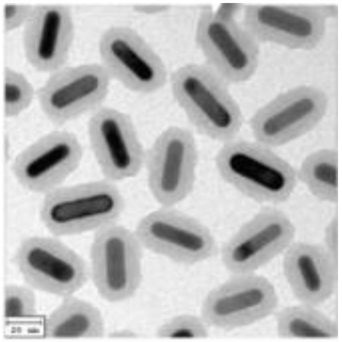


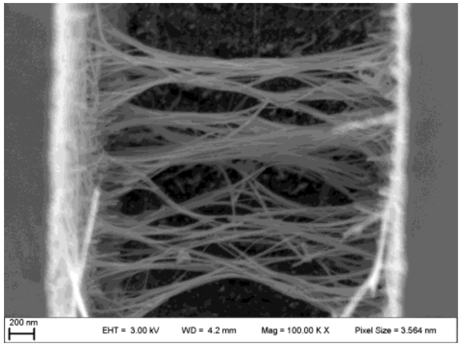


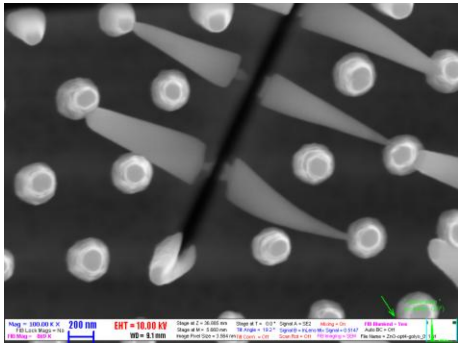
Summary

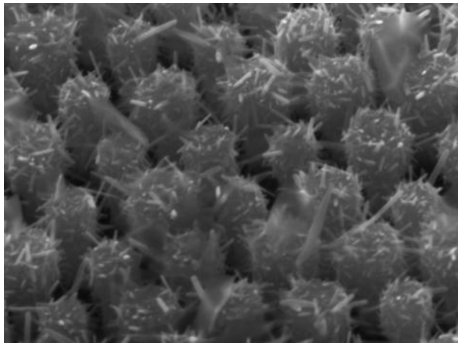
- Geometry, shape and orientation of the ZnO NWs can be well controlled; cheap techniques are available
- Different sensor functions are demonstarted (chemical, biological, force etc.)
- Efficient energy harvesting by ZnO NWs is not available yet, but might be possible in the near future (light or vibration?)
- Compatible and intergatable with Si technology which is important for e.g. automous sensors
- Several difficulties remains: p-type doping, chemical instability of (hydrothermal) ZnO NWs

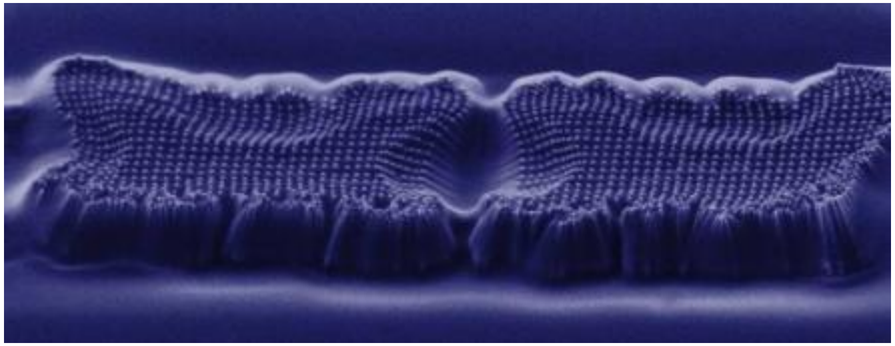


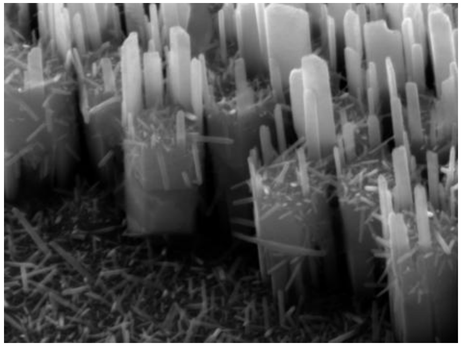


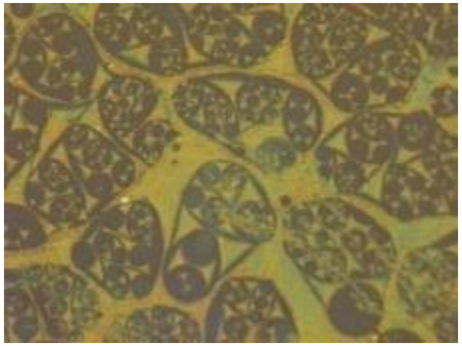


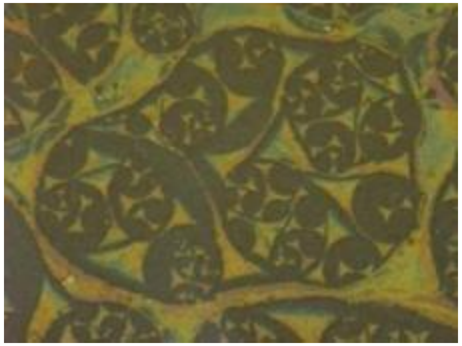


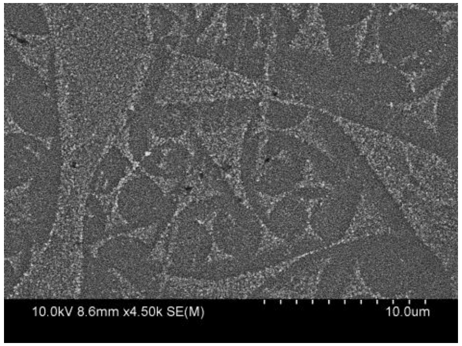


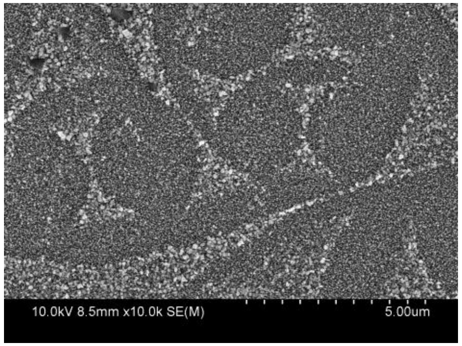












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