

Nanowire Fabrication and Assembly

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What to learn today?

1. Introduction to nanowire

2. Nanowire fabrication

- VLS/CVD
- Solution phase
- Template assisted
- Electrospinning

3. Nanowire assembly

- Magnetic assembly
- DEP assembly
- Surface tension based assembly
- Langmuir-Blodgett technique
- others

4. Lab session (Perry Hall 301)

1. Introduction to Nanowires

Nanowire

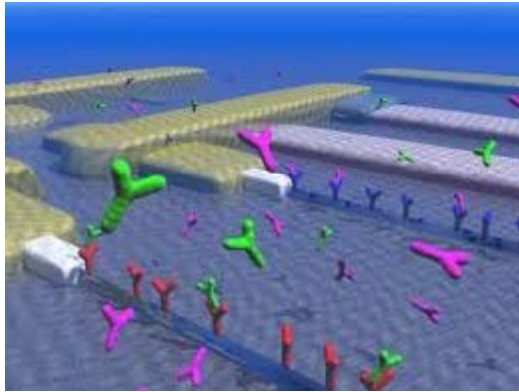
A *nanowire* is an extremely thin wire with a diameter on the order of a few nanometers or less.

“ They represent the smallest dimension for efficient transport of electrons and excitons, and thus will be used as interconnects and critical devices in nanoelectronics and nano-optoelectronics.” (C. M. Lieber, Harvard)

General attributes & desired properties

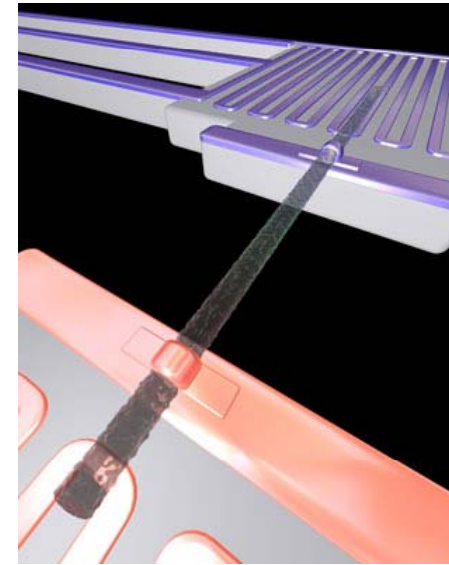
- Diameter – tens of nanometers
- Single crystal formation –common crystallographic orientation along the nanowire axis
- Minimal defects within wire
- Minimal irregularities within nanowire arrays

What a "Nanowire" can do?



Nanowire-based Biosensor

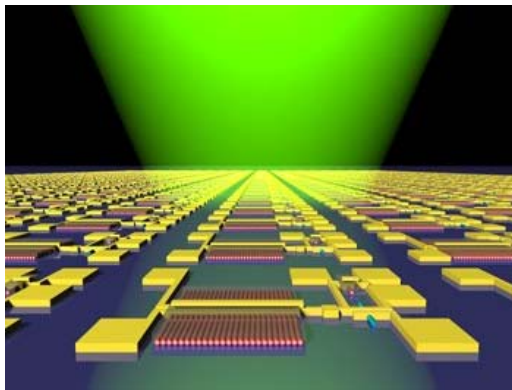
<http://biosingularity.com/2007/02/02/breakthrough-in-nanodevice-synthesis-revolutionizes-biological-sensors/>



Nanowire Thermoelectric Converter

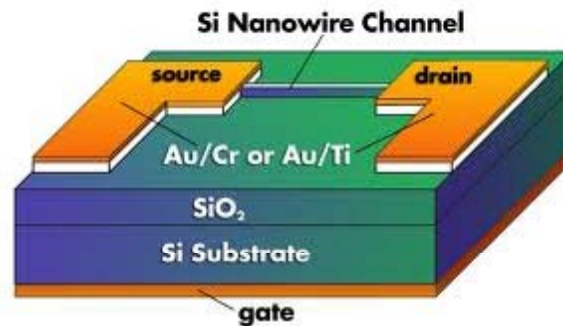
<http://spectrum.ieee.org/energy/renewables/silicon-nanowires-turn-heat-to-electricity>

Nanowire



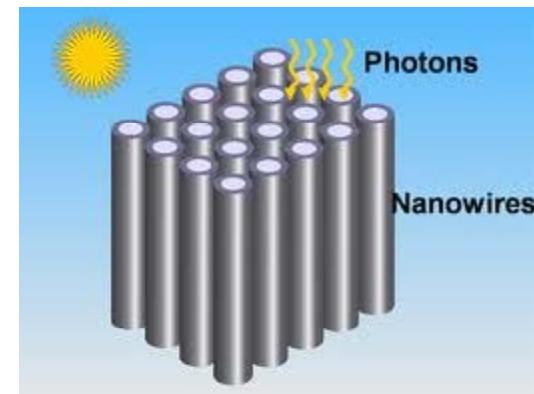
Nanowire circuit

<http://www.lbl.gov/publicinfo/newscenter/features/2008/MSD-nanowire-circuit.html>



Nanowire Transistor

http://www.nist.gov/public_affairs/techbeat/tb2005_0630.htm



Nanowire Solar Cell

<http://spie.org/x26848.xml>

Arts of Nanowire



Ge-Catalyzed ZnO Nanowire Forest



ZnO Nanowire Comb

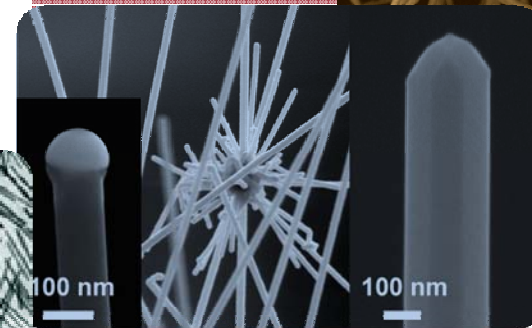
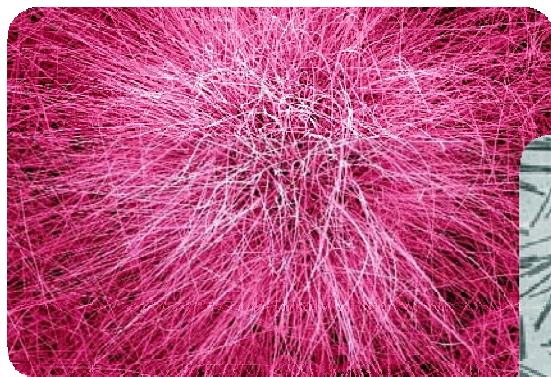
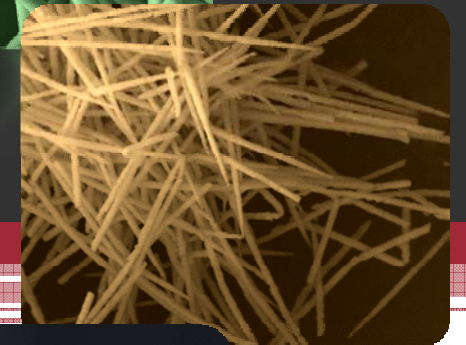
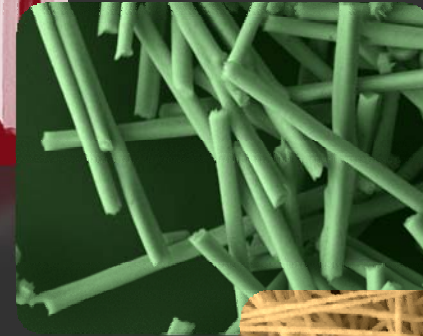


Ga-Catalyzed SiO₂ Nanowire Assembly



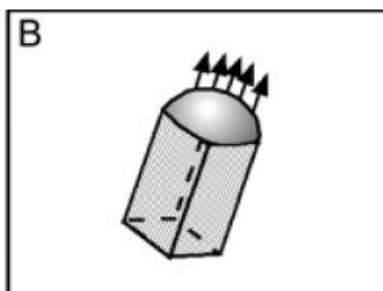
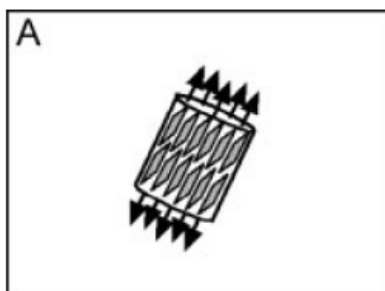
ZnO Nanowire Flower

2. Nanowire Fabrication



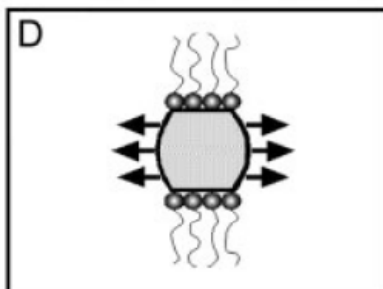
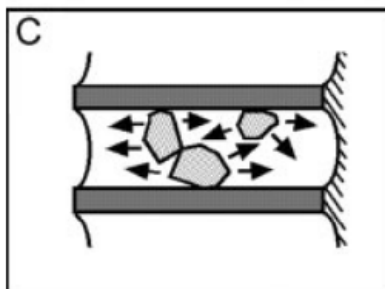
Ways of growing 1-D nanostructures

Guide along
a preferred
crystal
direction



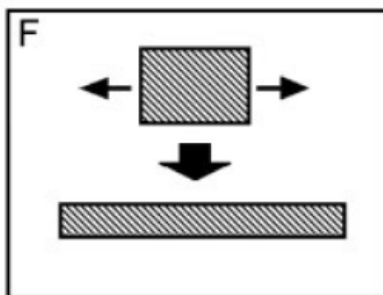
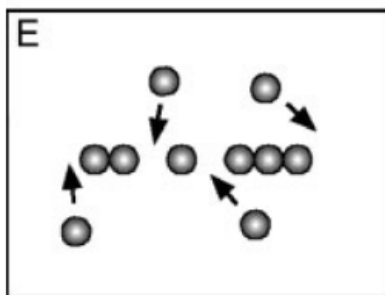
Confinement by liquid
droplet

Hard
template
directed



Soft template directed

Self-assembly



Top-down

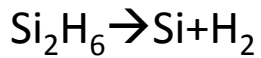
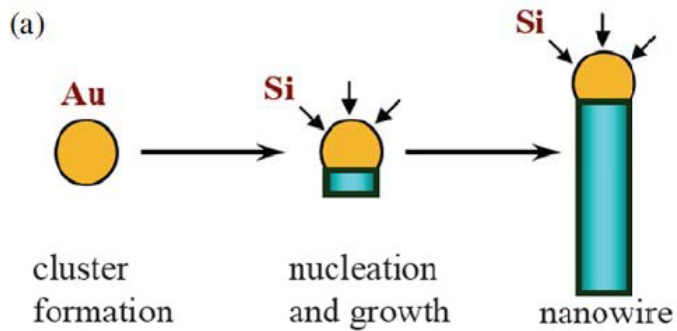
- A) Dictation by the anisotropic crystallographic structure of a solid
- B) Confinement by a liquid droplet as in the vapor-liquid-solid (VLS) process
- C) Direction through the use of a template
- D) Kinetic control provided by a capping reagent (soft-template)
- E) Self-assembly of 0-D nanostructure
- F) Size reduction of a 1-D microstructure



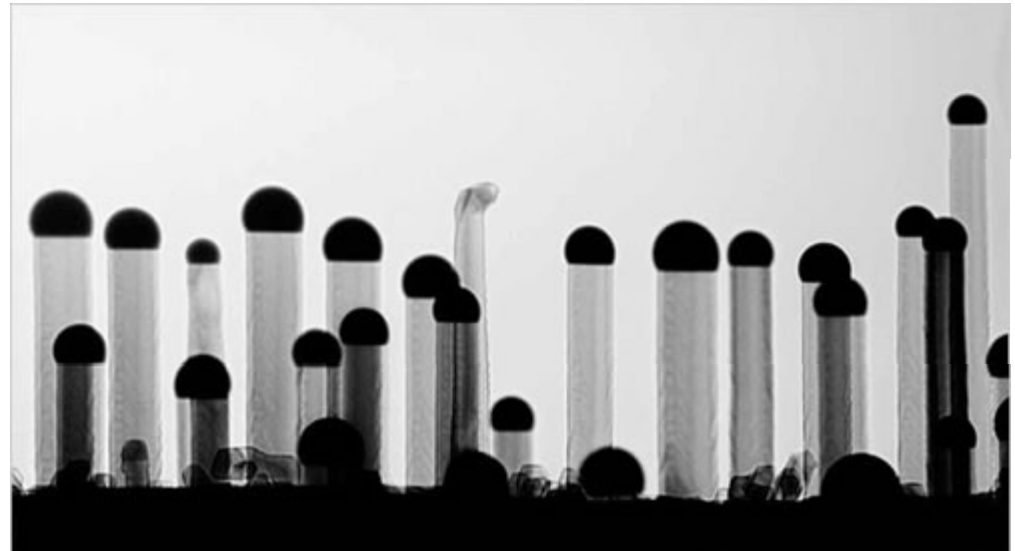
Nanowire Fabrication Method

- Vapor phase growth
 - CVD (chemical vapor deposition)/VLS (vapor-liquid-solid)
- Liquid phase growth
 - Soft template: surfactant assisted
 - Hard template: Electroplating
- Electrospinning

Vapor phase growth

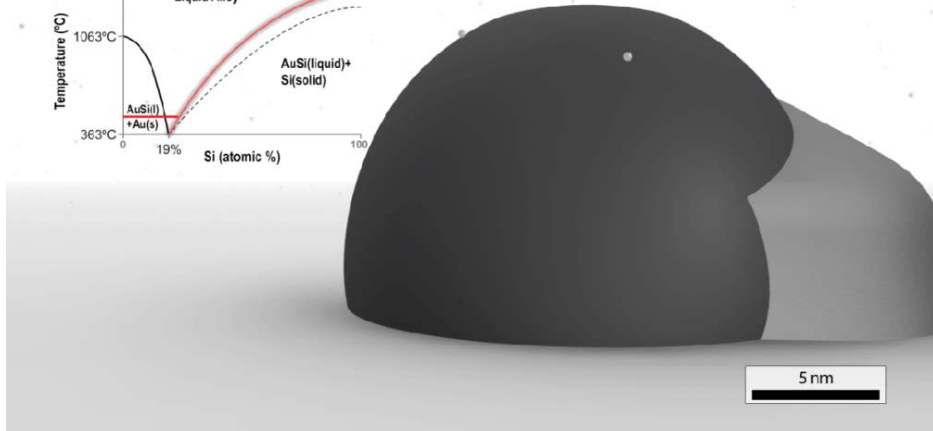
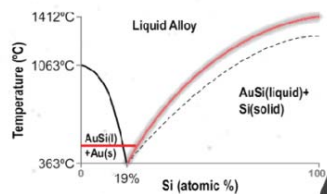


Supersaturation

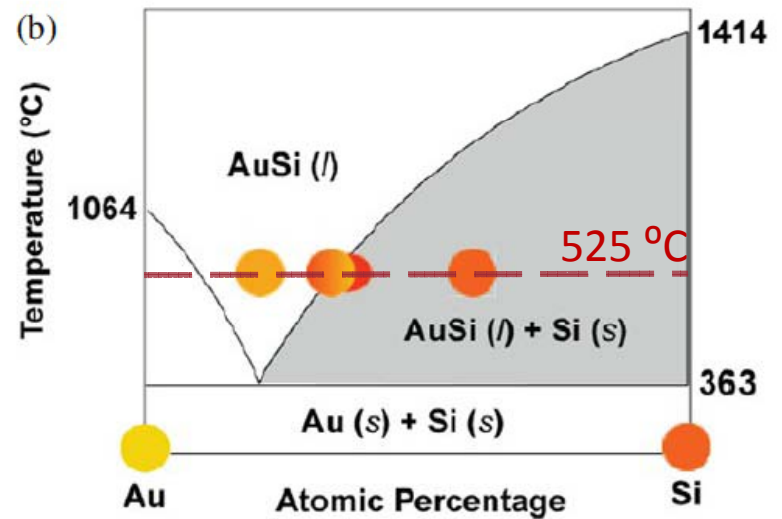


S. Kodambaka *et al*, Phys. Rev. Lett. 96, (2006)

Si Nanowire Growth.

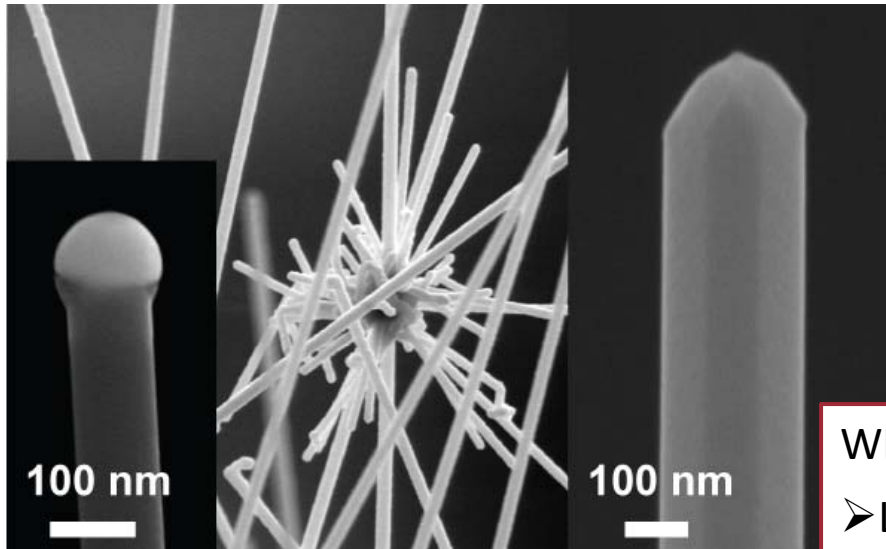


J. Phys. D: Appl. Phys. 39 (2006)



CVD

Chemical vapor deposition (CVD) is a chemical process used to produce high-purity, high-performance solid materials.



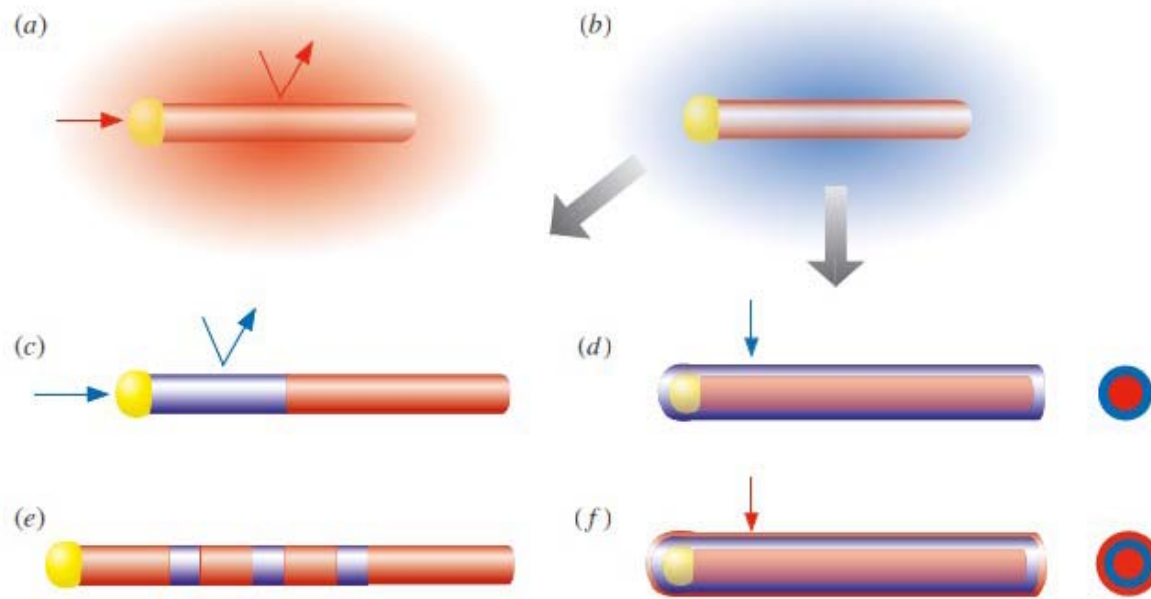
Catalyst: Au

Nanowire: Si

Why CVD?

- Low temperature and low cost
- Adaptable to wide variety of structures
- Low defect density
- Rapid growth
- Direct growth on substrates
- Scalable to large areas and reactor volumes

Heterostructure Nanowires

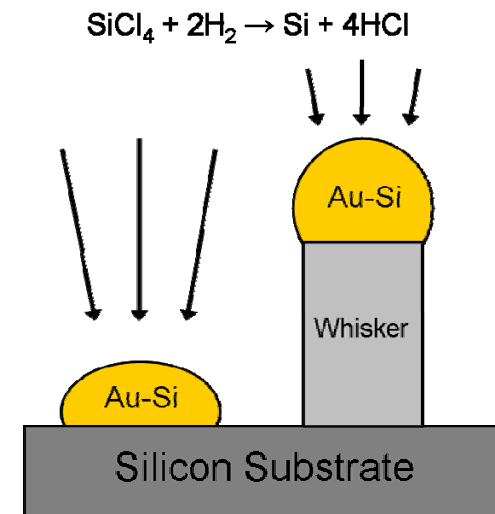
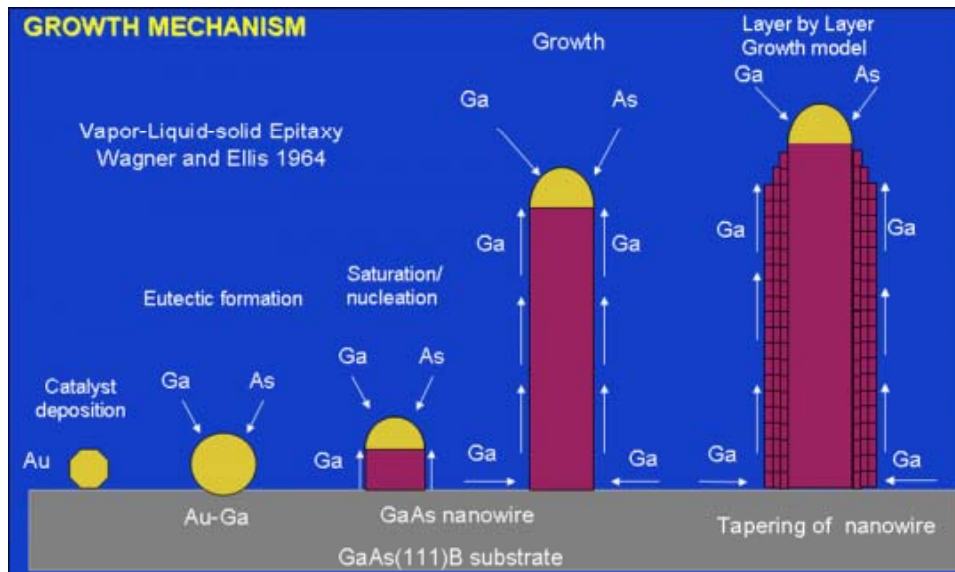


(a) Preferential reactant incorporation at the catalyst (growth end) leads to 1D axial growth.

(b) A change in the reactant leads to either (c) axial heterostructure growth or (d) radial heterostructure growth depending on whether the reactant is preferentially incorporated (c) at the catalyst or (d) uniformly on the wire surface.

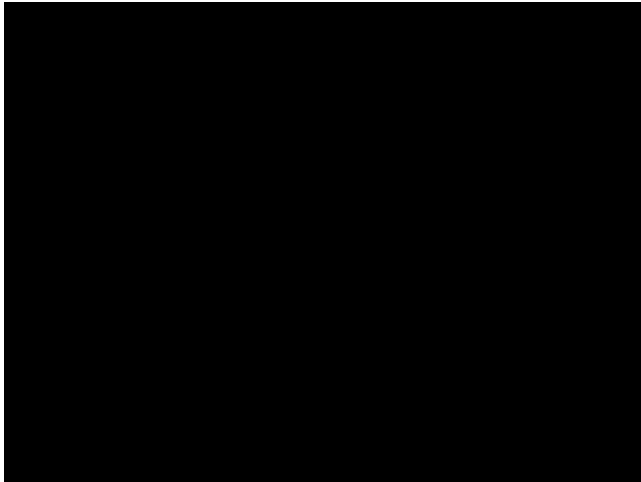
Alternating reactants will produce (e) axial superlattices or (f) core-multi-shell structures

VLS (Vapor-Liquid-Solid)



- Produce crystalline nanowires of some semiconductor materials.
- Requires a catalyst, such as Au, Pt.
- Control: turning off the source can adjust the final length of the nanowire; switching sources can create compound nanowires with super-lattices of alternating materials.

Real Video of Nanowire growth



In situ TEM video

Au catalysed Si nanowire nucleation at 590°C.

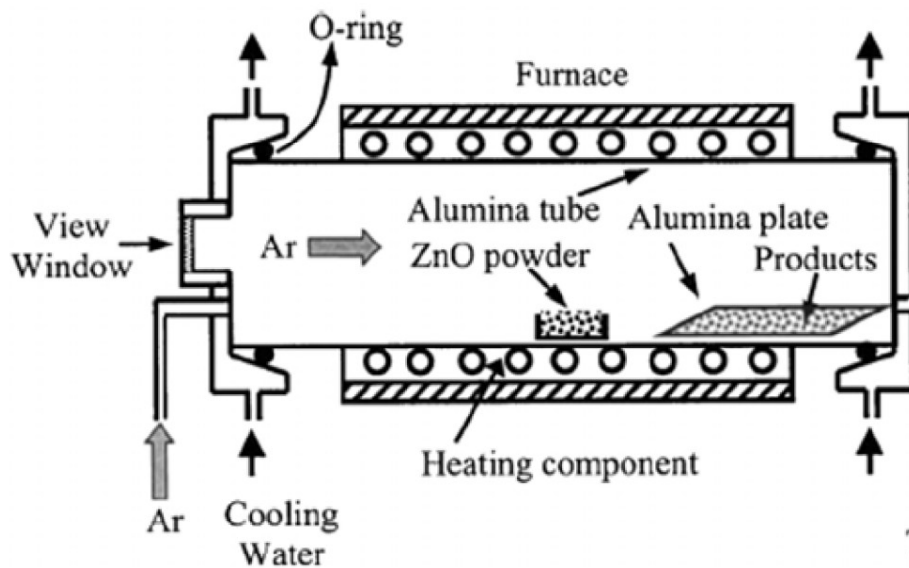
The nominally 2nm thick Au film supported on a SiO_x membrane is initially exposed to $\sim 1.3 \times 10^{-4}$ mbar Si₂H₆.

After ~ 108 s the disilane pressure was increased to $\sim 5 \times 10^{-3}$ mbar.

Three important stages:

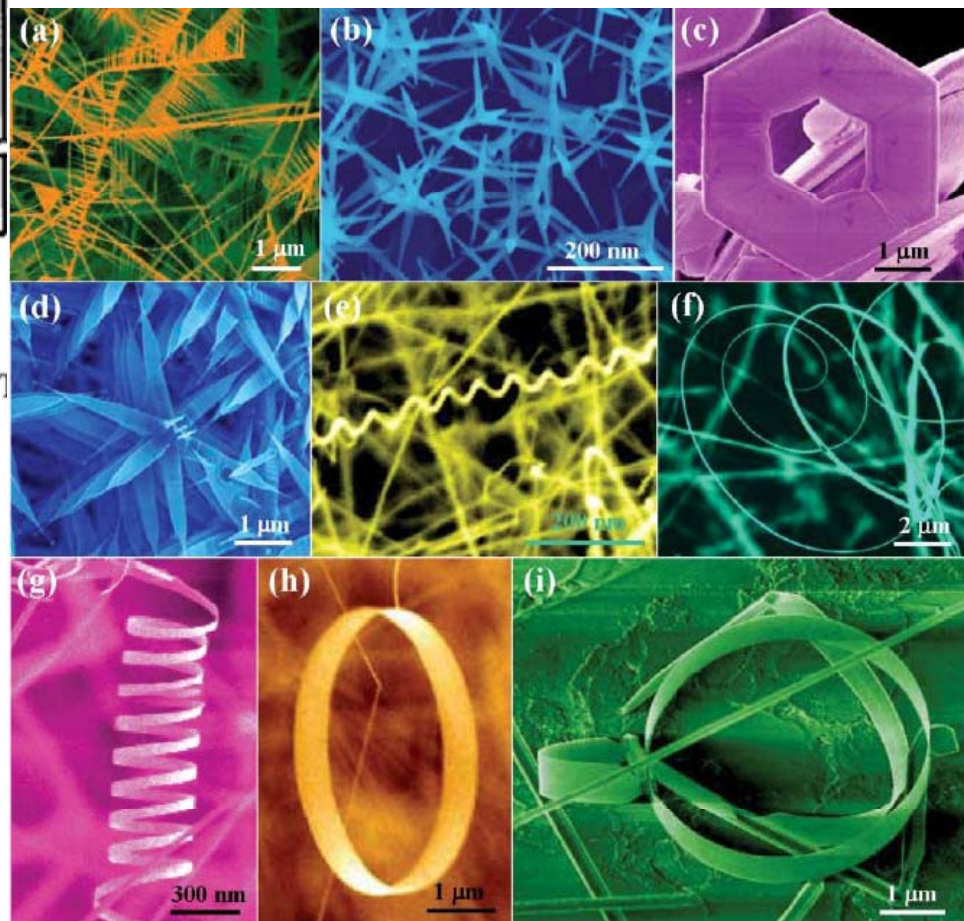
1. Preparation of the catalyst
2. Nucleation
3. Growth

Thermal evaporation and condensation



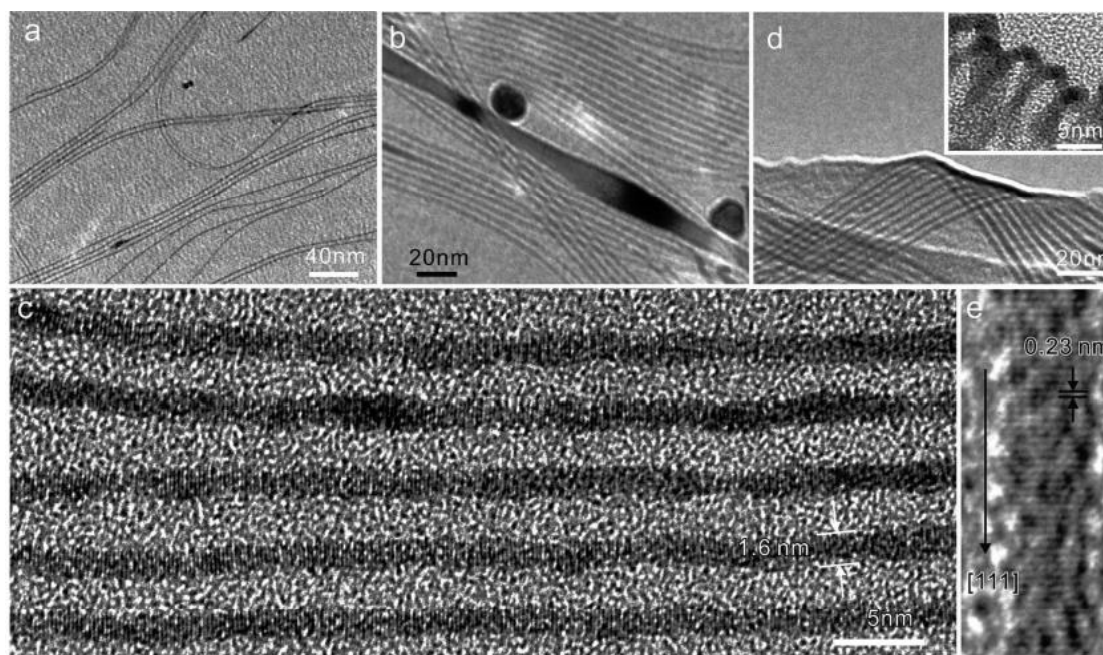
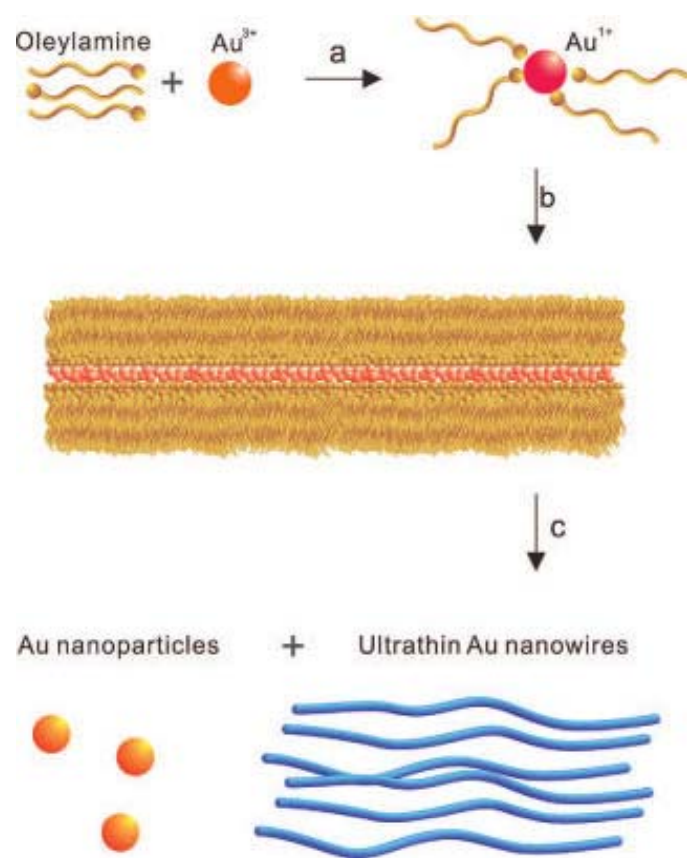
ZnO morphologies depends on:

- Source material
- Substrate temperature
- Argon flow rate
- Coating thickness



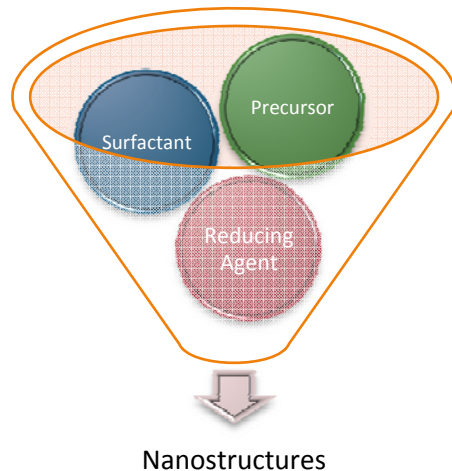
Liquid Phase Growth

Chemical Reduction Method-Soft template



(a-d) TEM images of the ultrathin Au nanowires (<2 nm);
(e) HRTEM image of an individual Au nanowire showing the (111) lattice planes

Chemical Reduction Method



1. Precursor

is a compound that participates in the chemical reaction that produces another compound.

- Salt: HAuCl_4 , AgNO_3 , CuSO_4 ...

3. Reducing agent

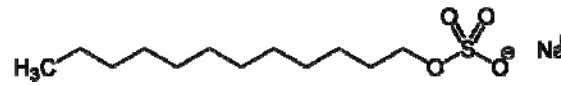
-is the element or compound in a reduction-oxidation (redox) reaction that donates an electron to another species.

- Phosphite, NaBH_4 , ...

2. Surfactant

-usually organic compounds that are amphiphilic, containing both hydrophobic groups (their tails) and hydrophilic groups (their heads).

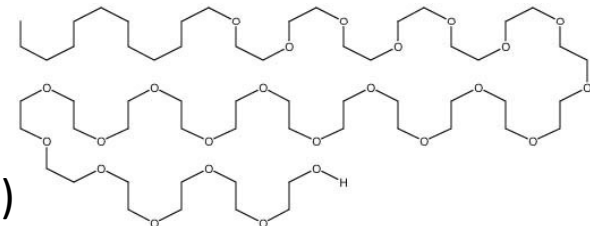
- SDS (Sodium dodecyl sulfate), anionic surfactant



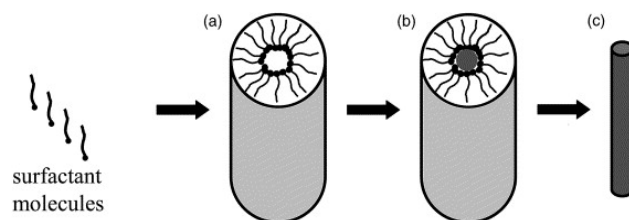
- CTAB (Cetrimonium bromide), cationic surfactant



- Polyoxyethylene (HO-(CH₂CH₂O)_n-H), nonionic surfactant



Chemical Reduction Method

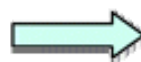


I. Synthesis of seed

2.5×10^{-4} M HAuCl_4 +
 2.5×10^{-4} M Na-citrate



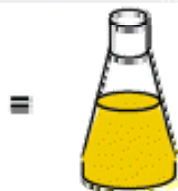
+ 0.6 mL 0.1 M
Ice-cold aq NaBH_4



Gold nanoparticle seeds
(\sim 4nm diameter)

II. Stock solution

Stock solution
 2.5×10^{-4} M HAuCl_4
+ 0.1 M CTAB

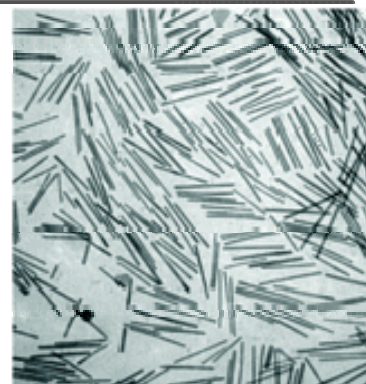
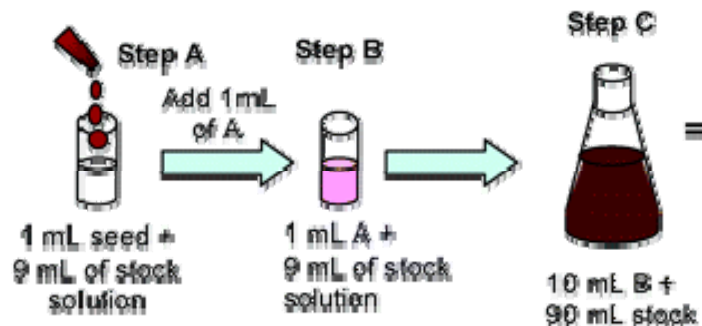


Addition of
Ascorbic acid



Reduction
of Au^{3+} to
 Au^{1+} results
in disappearance
of color

II. Three step protocol for nanorod synthesis

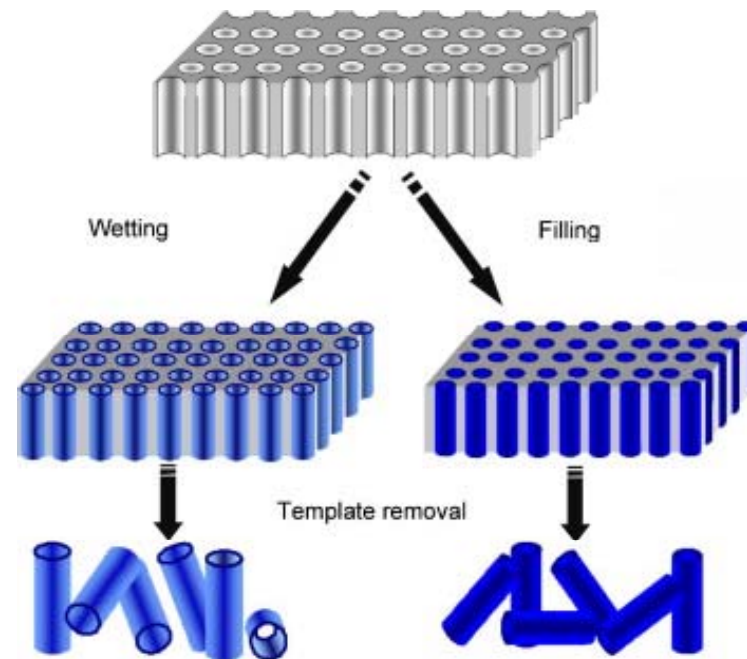
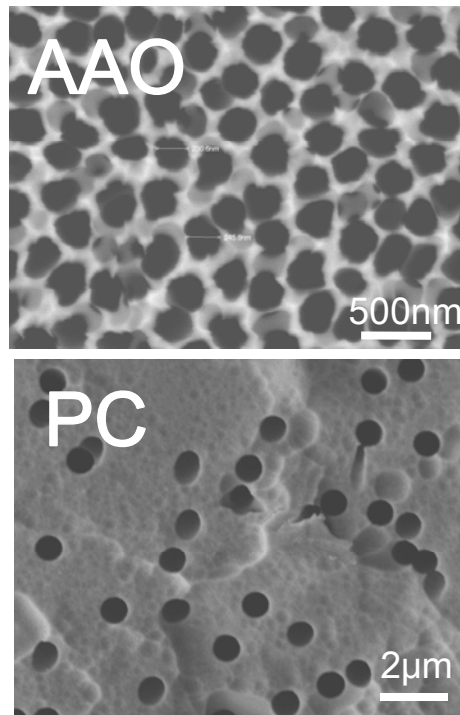


Electroplating-hard template assisted

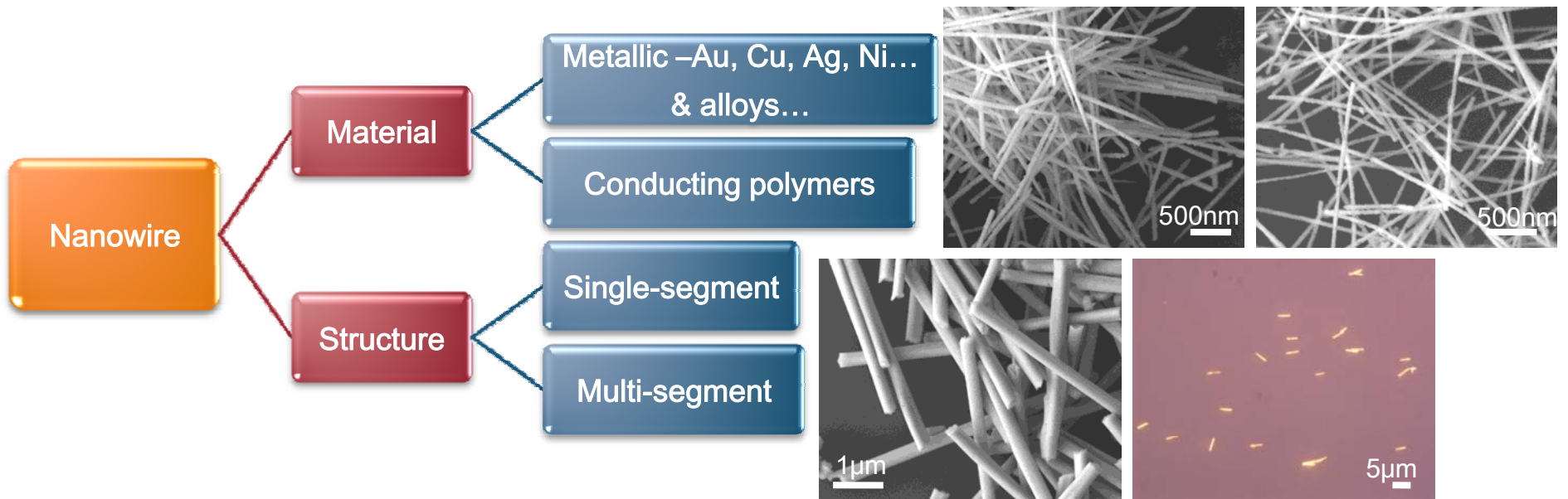
Electrochemical deposition

- Ensures fabrication of electrically continuous wires since only takes place on conductive surfaces
- Applicable to a wide range of materials
- Very high aspect ratios may be achieved

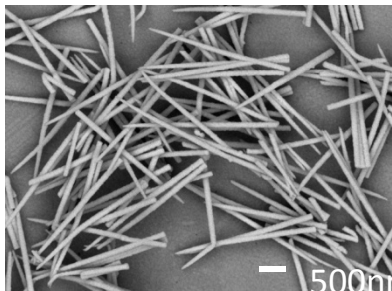
Hard Template: AAO (anodic aluminium oxide) or PC (polycarbonate) membrane.



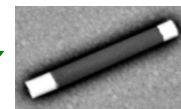
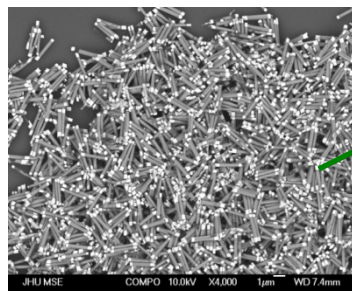
Electrodeposition



Nanowires with one- and multi-component segments



One-component nanowires
(gold nanowires, $d=50\text{nm}$)

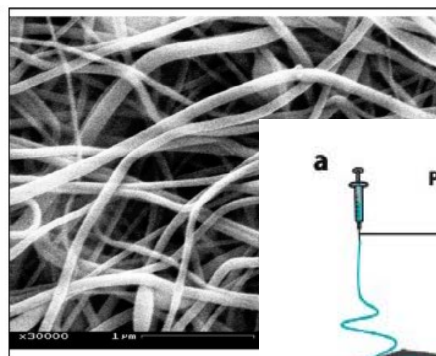
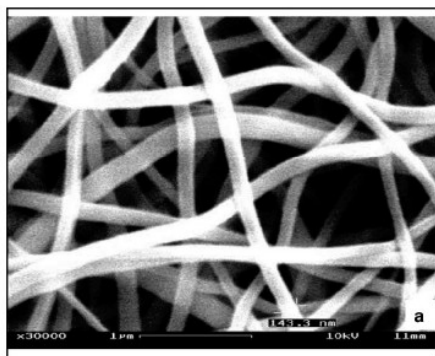


Gold-Nickel-gold
($d=200\text{nm}$)

Multi-component nanowires

Electrospinning

Electrospinning Setup



PVP/H₂PtCl₆ composite nanowire
Nano Lett., 2009, 9 (4), pp 1307–1314

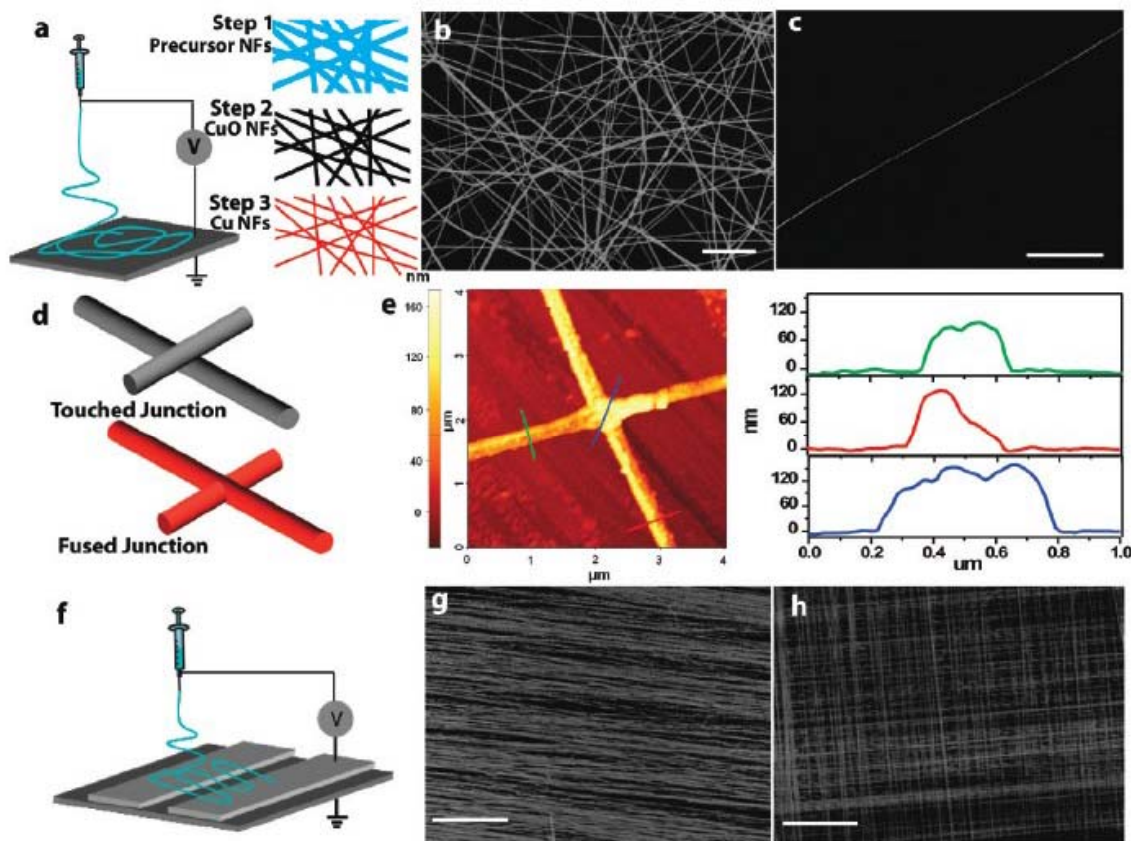
Easily form thin film

Polymer fibers

Polymer + Salt Precursor

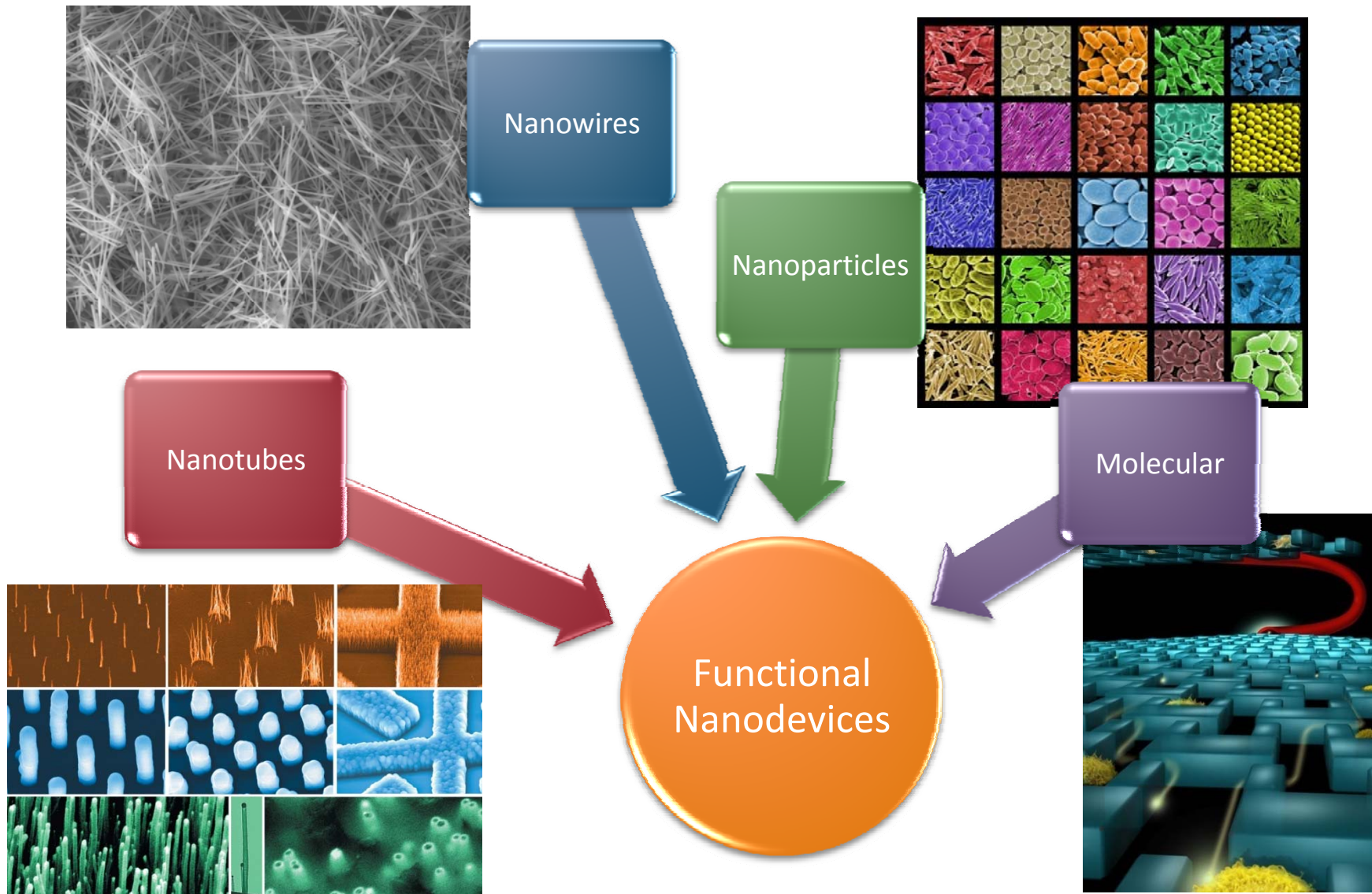
PVA/CuAc₂ composite fibers

Nano Lett., 2010, 10, pp 4242–4248



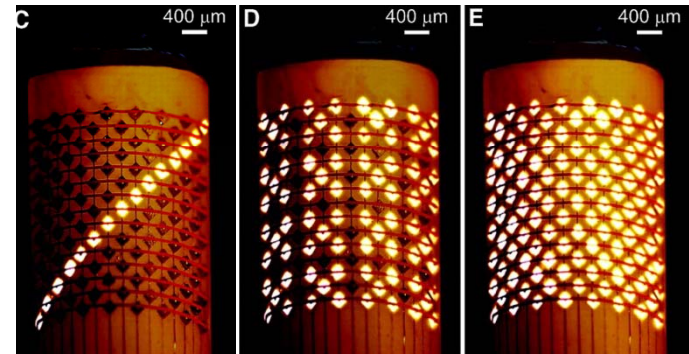
3. Nanowire Assembly

Why do we study “assembly”?



Methods of Self-assembly

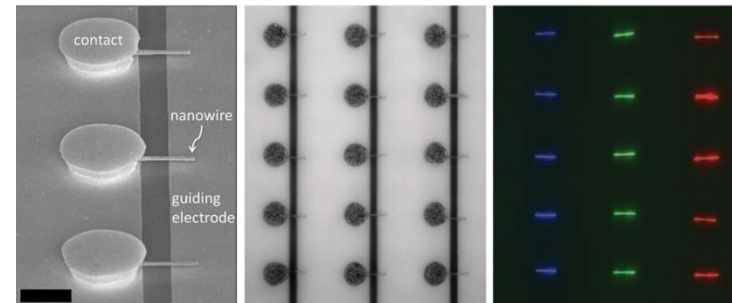
- Electro-static self-assembly (ESA)
- Fluidic self-assembly (FSA)
- Gravity driven self-assembly
- Molecular self-assembly
- Solder based assembly
- Magnetic forces assisted self-assembly
- Dielectrophoresis assembly (DEP)
- DNA assisted assembly
- Langmuir–Blodgett



Solder-based assembly to integrate device segments onto nonplanar substrates.

Jacobs et al. Science, 2000, Vol. 296

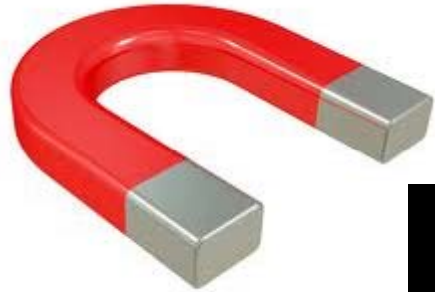
Integrated LEDs



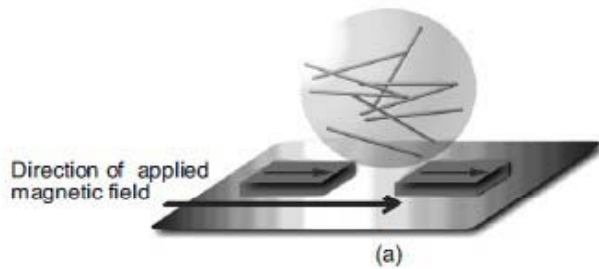
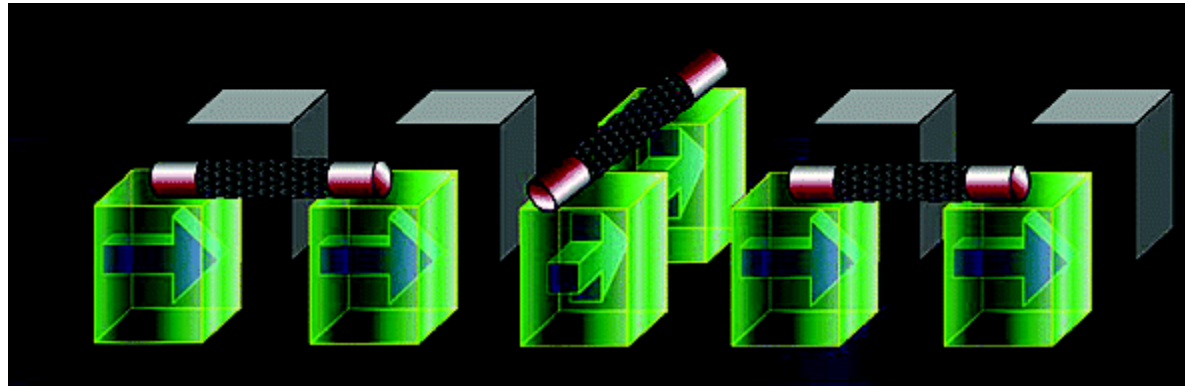
Programmed assembly of DNA-Coated Nanowire Devices.

Thomas et al. Science, 2009, Vol. 323

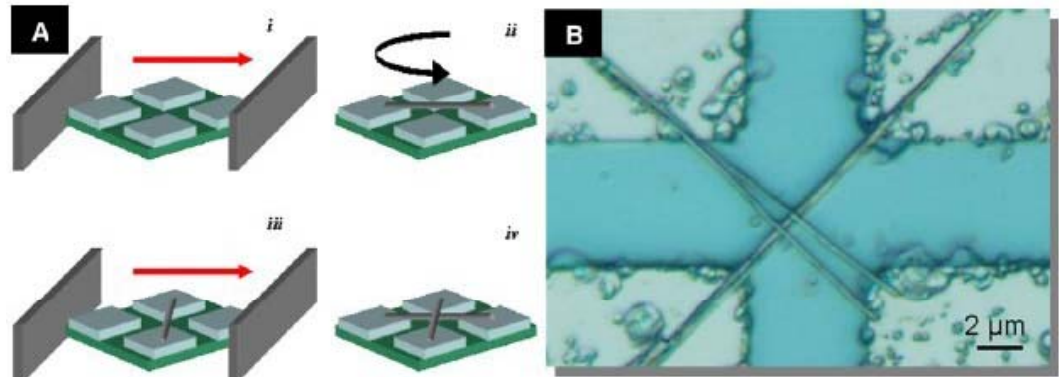
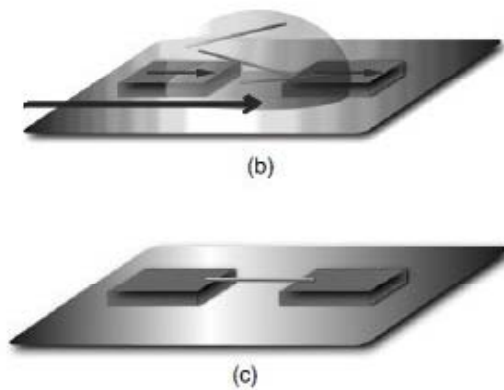
Biomaterial Devices



Magnetic Assembly

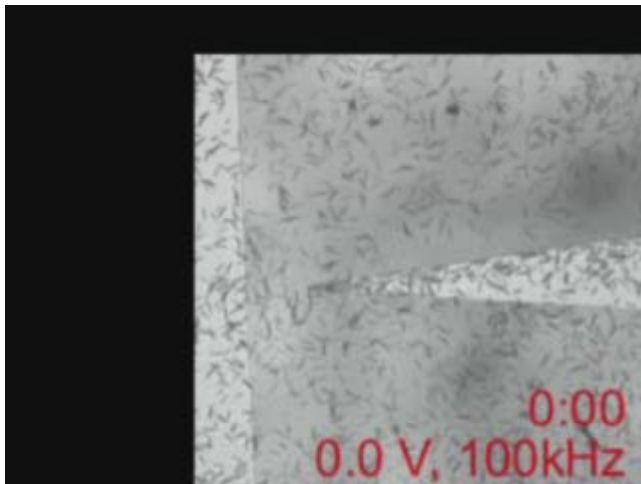
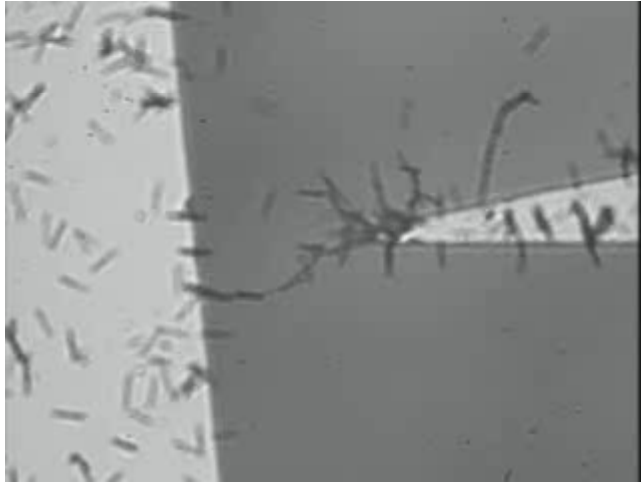


Only magnetic materials can be assembled!
Fe, Ni, Co



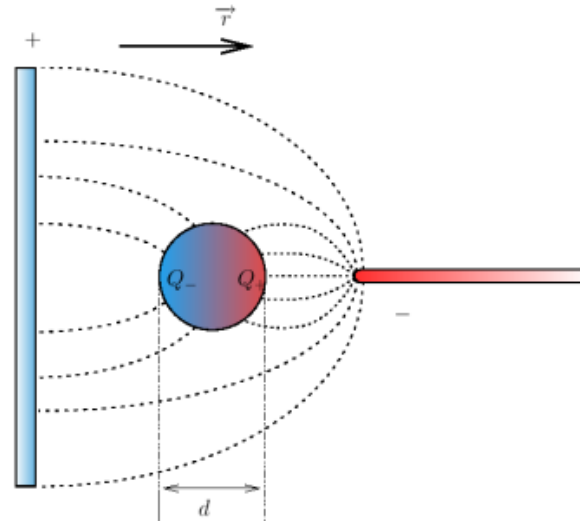
Electrical field-assisted assembly

Vedio: Dielectrophoresis Assembly



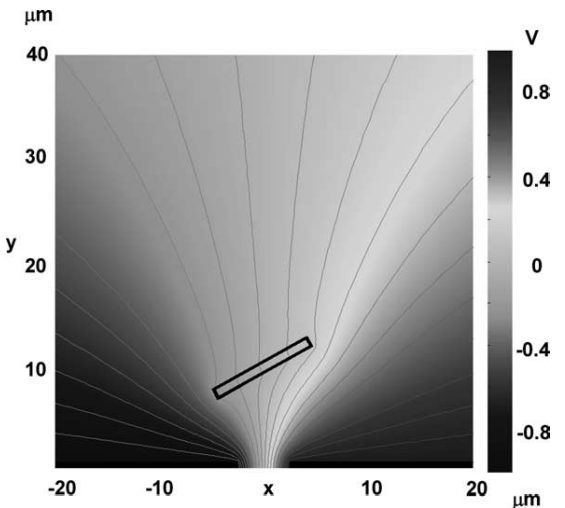
Appl. Phys. Lett. **88**, 233118 (2006)

Dielectrophoresis (or **DEP**) is a phenomenon in which a force is exerted on a dielectric particle when it is subjected to a non-uniform electric field.



$$F_{cylinder} = \pi a^2 L \frac{\epsilon_1 [\epsilon_2 - \epsilon_1]}{\epsilon_2 + \epsilon_1} \nabla |E|^2$$

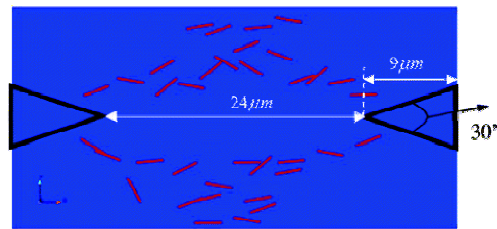
E-magnitude of the electrical field
 ϵ_1 -dielectric constant of the cylinder
 ϵ_2 -dielectric constant of the medium



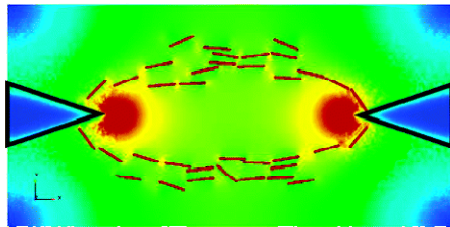
Finite element simulation

H.A. Pohl, *New York*, 1978
 Evoy S et al. *Microelectron. Eng.* 2004

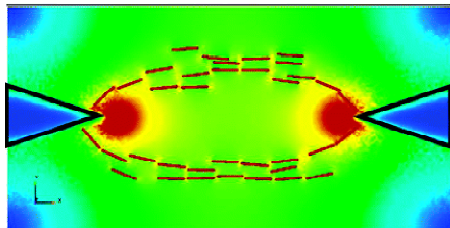
DEP – 2D Assembly



(a)

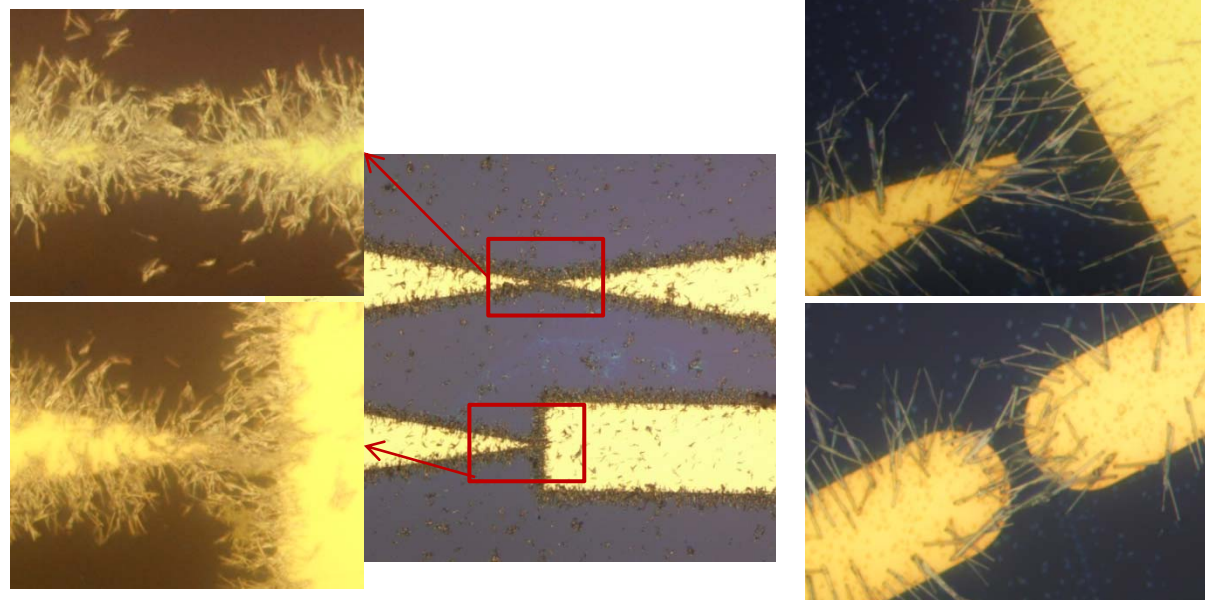
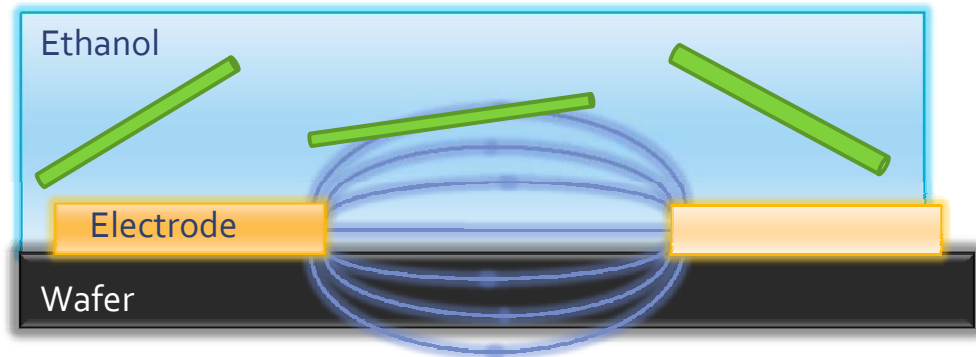


(b)



(c)

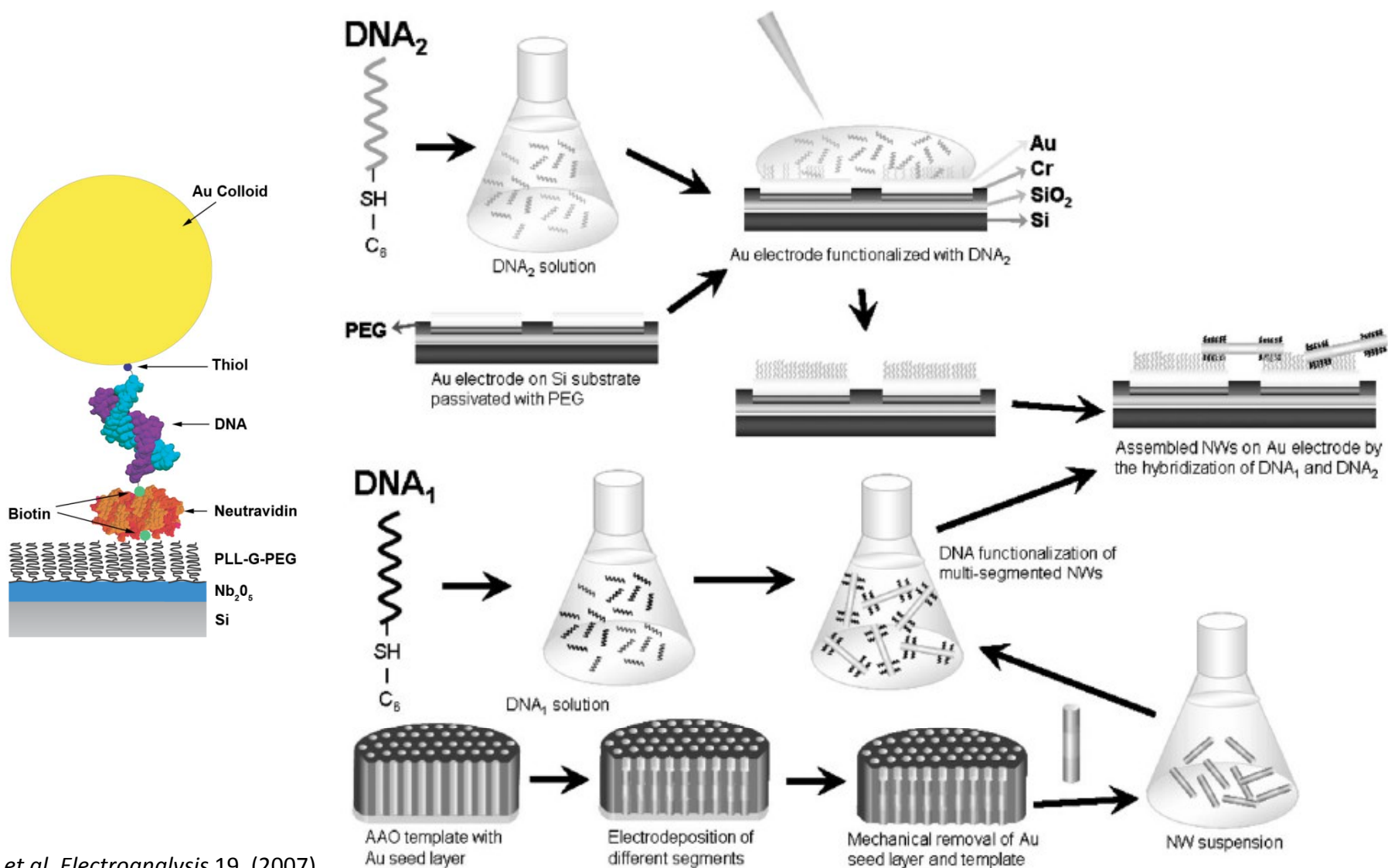
Sequential images of $3\ \mu\text{m}$ -long NWs lining up between triangular-shaped electrodes



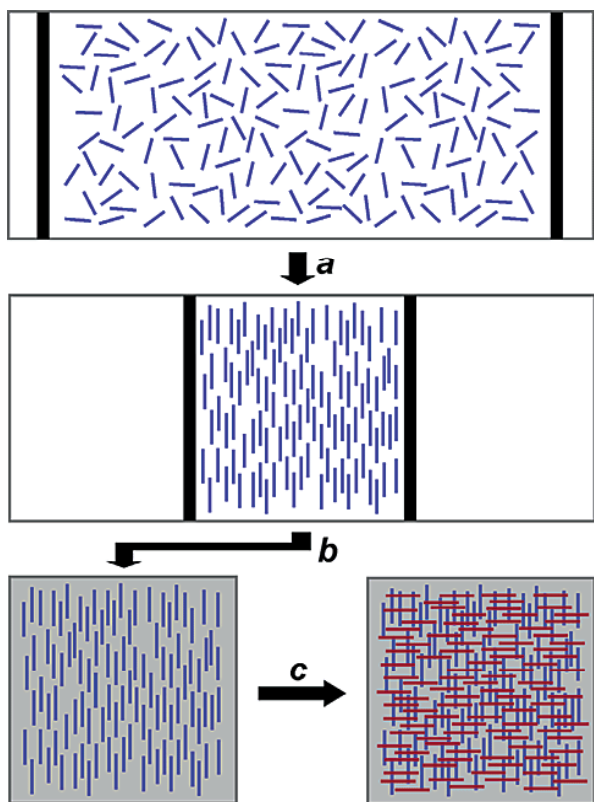
Left: Tin (Sn) nanowires DEP aligned

Right: Indium (In) nanowires DEP aligned

DNA assisted nanowire assembly

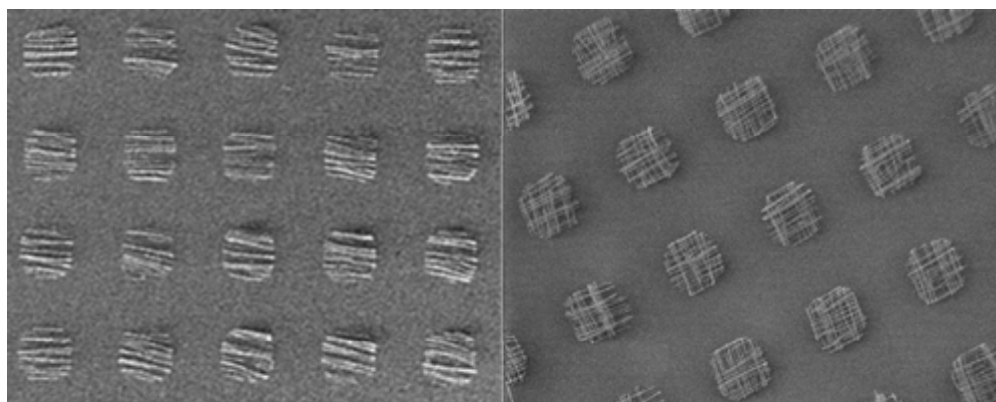


Langmuir–Blodgett technique



NWs (blue lines) in a monolayer of surfactant at the air–water interface are

- (a) compressed on a Langmuir–Blodgett trough to a specified pitch.
- (b) The aligned NWs are transferred to the surface of a substrate to make a uniform parallel array.
- (c) Crossed NW structures are formed by uniform transfer of a second layer of aligned parallel NWs (red lines) perpendicular to the first layer (blue lines)



[Video of Ag nanowire in a LB trough](#)

D. Whang *et al*, *Nano Letters*, 2003, 3 (9)

4. Lab Session I: Electrodeposition of Nanowires in Nanoporous Templates

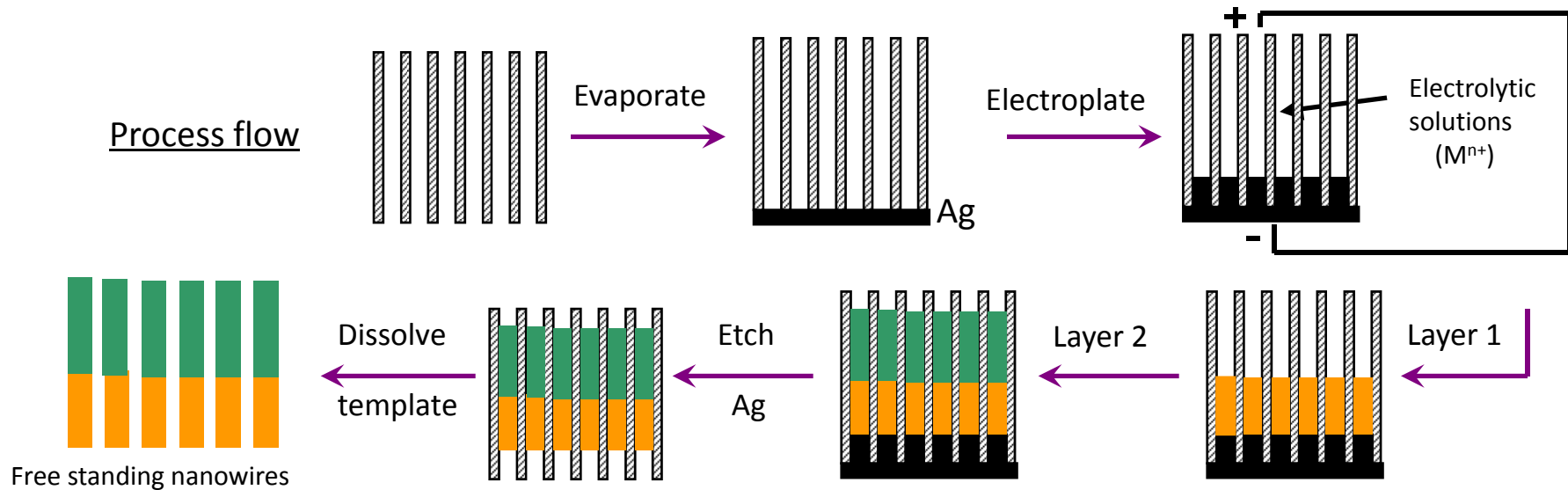
Location:
Engineering Building 301

What to know?

Lab safety!

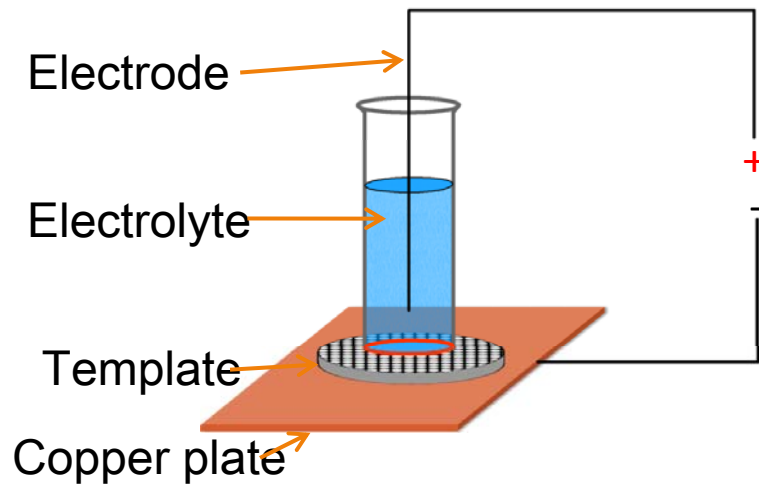
Total Experiment time: 45 min

Multi-segment nanowire fabrication steps



Experiment Setup

Gold nanowire fabrication
 $\text{Au}^{++} + e \rightarrow \text{Au}$



Current control
Current Density:
Ag- 0.5~1 mA/cm²
Au- 1~2 mA/cm²

Ag etching: 6M HNO₃

Template dissolve: 2M NaOH

Nanowire Cleaning: DI Water & Ethanol

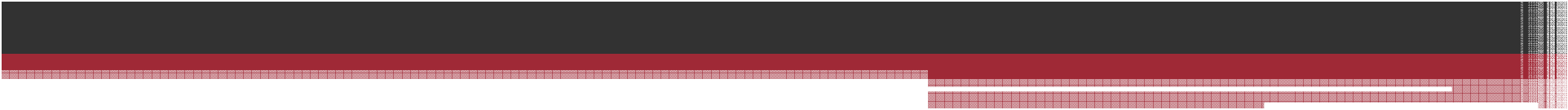


Homework-Lab report

Due date: Apr. 3rd 2013

Laboratory reports should be typed and in the format listed below:

- Lab title
- Lab summary
- Objectives
- Design
- Implementation
- Results and discussions
- Conclusion



Thanks