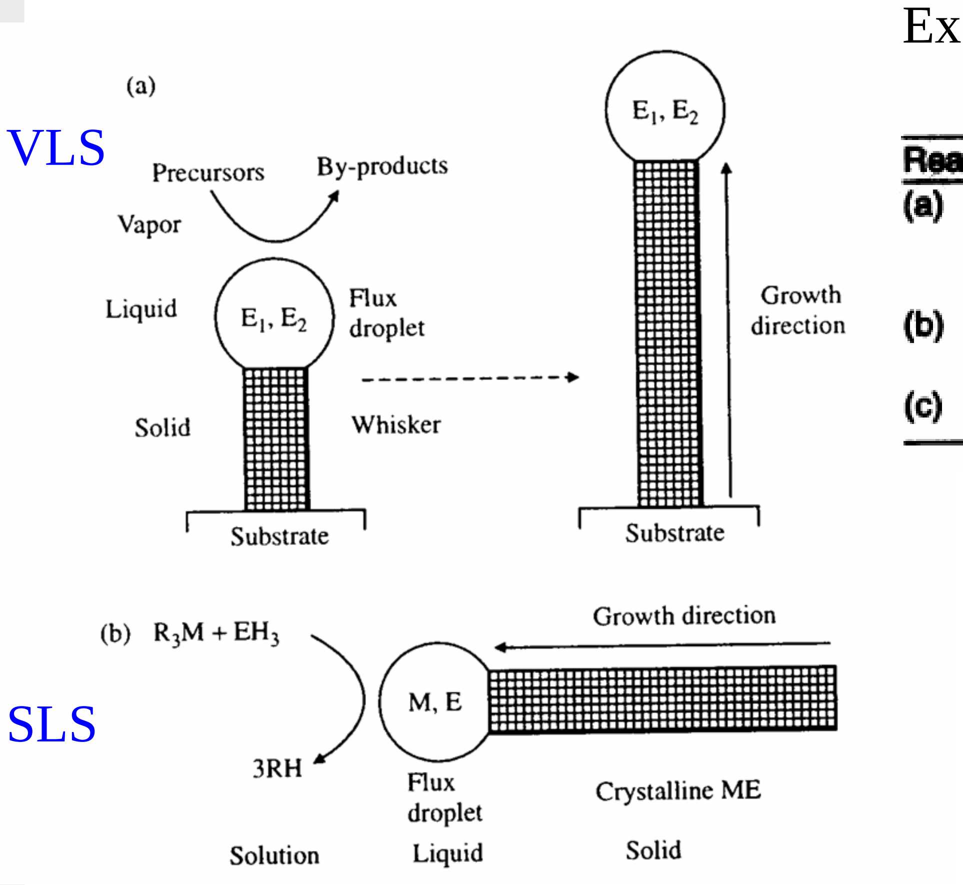
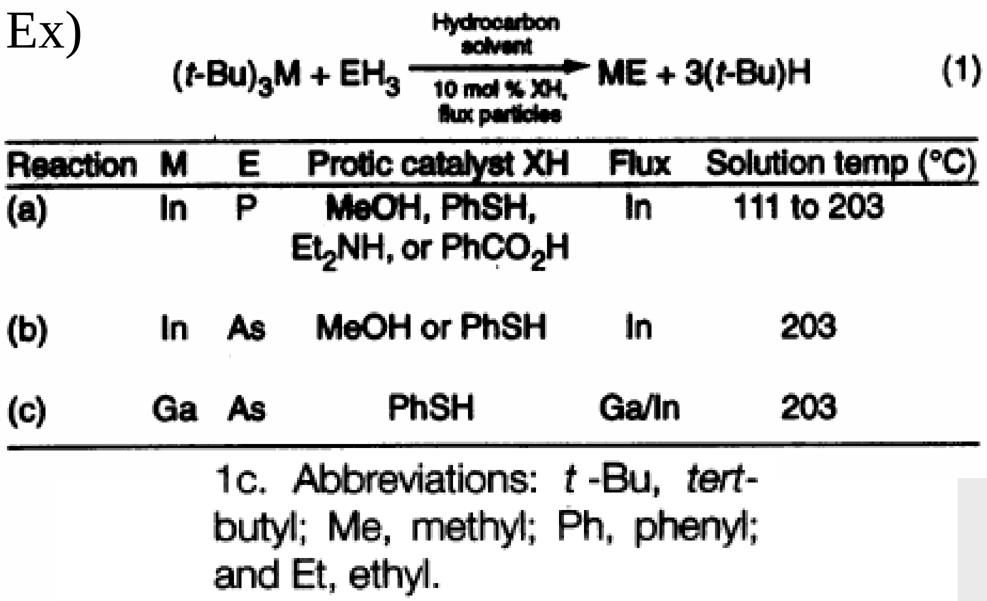
Synthesis of Nano Materials- 1D from Liquid

❑ Solution-Liquid-Solid (SLS) Growth



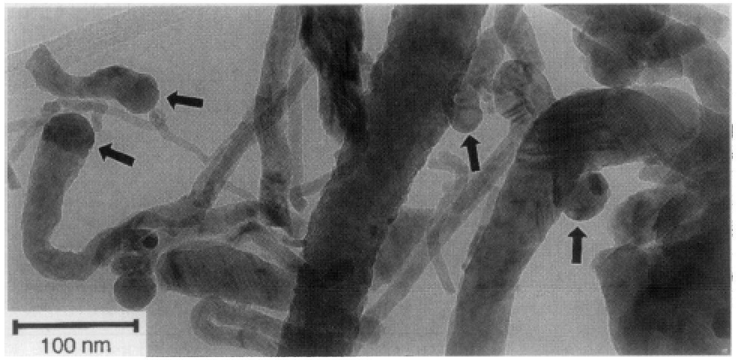
Ex)



$$(t\text{-Bu})_3M + EH_3 \xrightarrow[\text{10 mol \% XH, flux particles}]{\text{Hydrocarbon solvent}} ME + 3(t\text{-Bu})H \qquad (1)$$

Reaction	M	E	Protic catalyst XH	Flux	Solution temp (°C)
(a)	In	P	MeOH, PhSH, Et_2NH, or $PhCO_2H$	In	111 to 203
(b)	In	As	MeOH or PhSH	In	203
(c)	Ga	As	PhSH	Ga/In	203

1c. Abbreviations: *t* -Bu, *tert*-butyl; Me, methyl; Ph, phenyl; and Et, ethyl.



T.J. Trentler, Science 270 (1995) 1791.

Synthesis of Nano Materials- 1D from Liquid

❑ Solution-Liquid-Solid (SLS) Growth

Ex) GaAs (In catalyst)

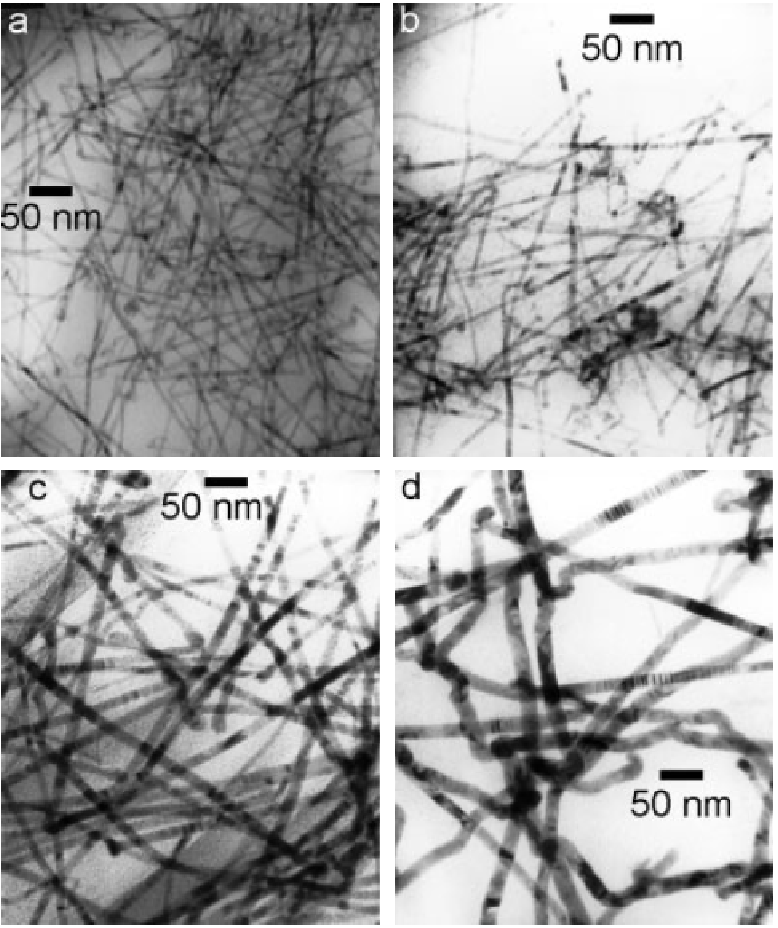
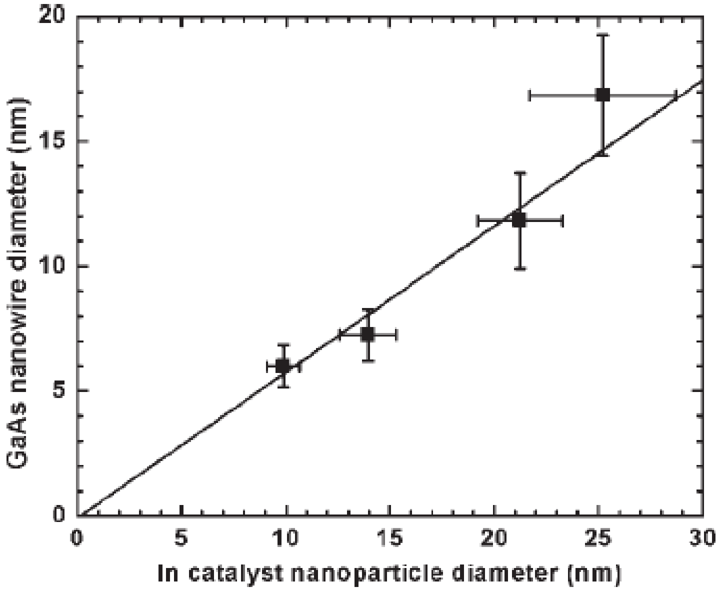


Fig. 1. TEM images of GaAs nanowire specimens of various mean diameter: a) $d_{\text{wire}} = 5.99$ nm, b) $d_{\text{wire}} = 7.25$ nm, c) $d_{\text{wire}} = 11.83$ nm, d) $d_{\text{wire}} = 16.84$ nm.



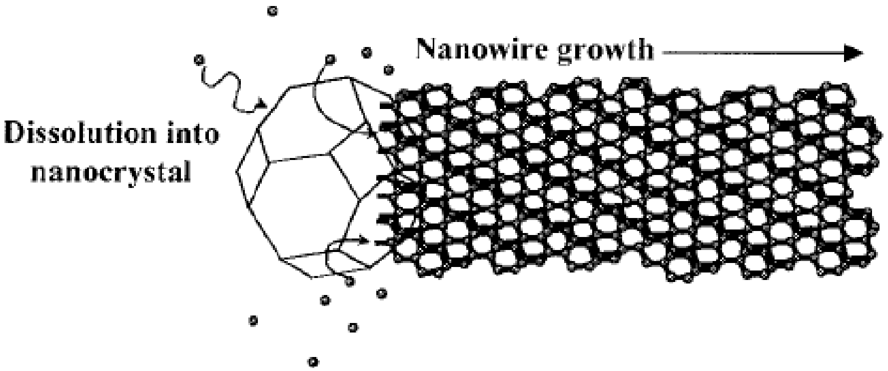
H. Yu, Adv. Mater. 15, 416 (2003)

Synthesis of Nano Materials- 1D from Liquid

❑ Solution-Liquid-Solid (SLS) Growth

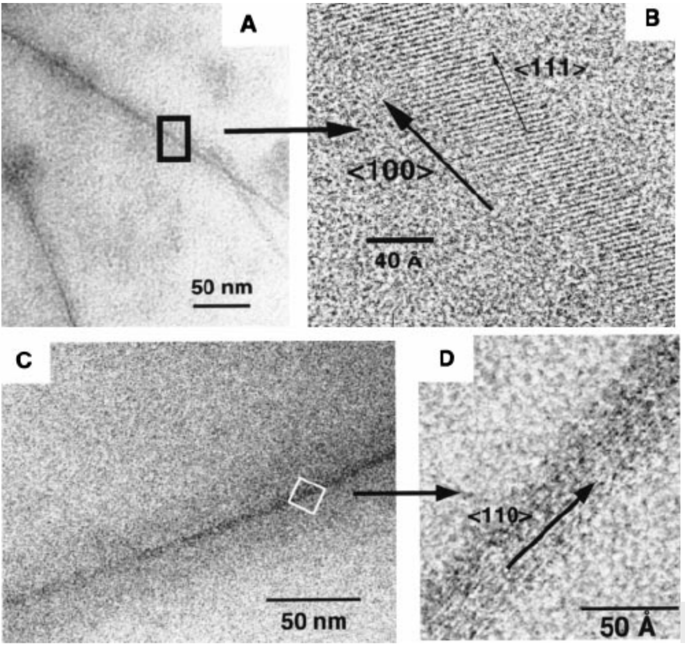
Ex) Si
- Au nanoparticles
  diphenylsilane
  in supercritical hexane

Fig. 1. Schematic of the proposed nanowire growth process. Thermal degradation of diphenylsilane results in free Si atoms that dissolve in the Au nanocrystal until reaching a Si:Au alloy supersaturation, when Si is expelled from the nanocrystal as a crystalline nanowire. This wire is depicted with a preferred <111> orientation.

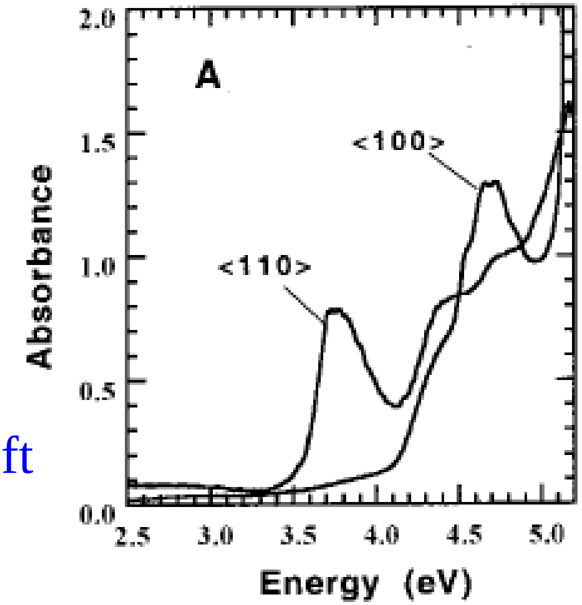


200 bar

270 bar



blue shift



J.D. Holmes, Science 287 (2000) 1471.

Synthesis of Nano Materials- 1D from Liquid

☐ Template-based

- anodized alumina membrane
  radiation track etched polymer
  membrane

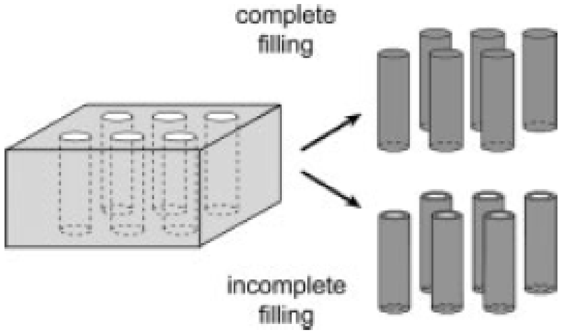


Fig. 7. Schematic drawings illustrating the formation of nanowires and nanotubes by filling and partial filling the pores within a porous membrane with the desired material or a precursor to this material [70,79].

- concerns: wettability of the pore
  inert template
  control of shrinkage during
  solidification- nanorod/nanotube

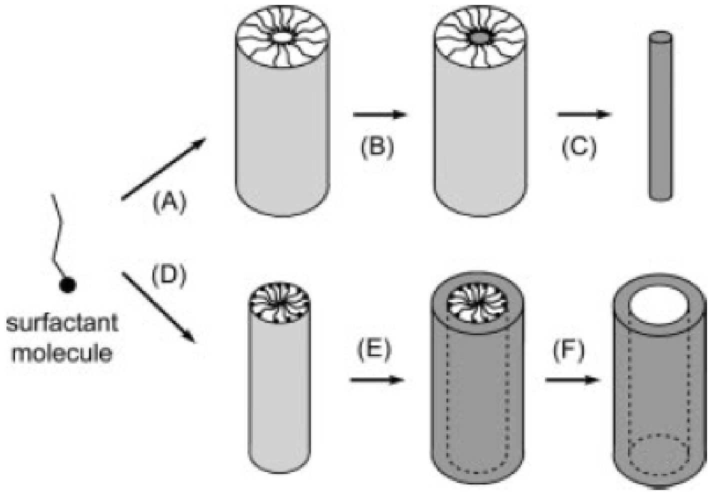


Fig. 8. Schematic illustrations showing the formation of nanowires by templating against mesostructures self-assembled from surfactant molecules: A) formation of a cylindrical micelle; B) formation of the desired material in the aqueous phase encapsulated by the cylindrical micelle; C) removal of the surfactant molecules with an appropriate solvent (or by calcination) to obtain an individual nanowire. D–F) Similar to the processes illustrated in (A–C), except that the exterior surface of an inverted micelle serves as the physical template.

Surfactant molecules self-organized
into rod-shaped micelles

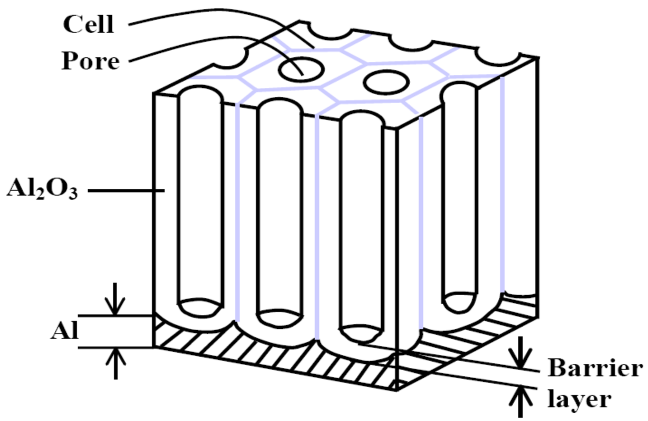
Hydrophobic cationic surfactants:
- CTAB (cetyltrimethylammonium bromide)
- TOAB (tetraoctylammonium bromide)

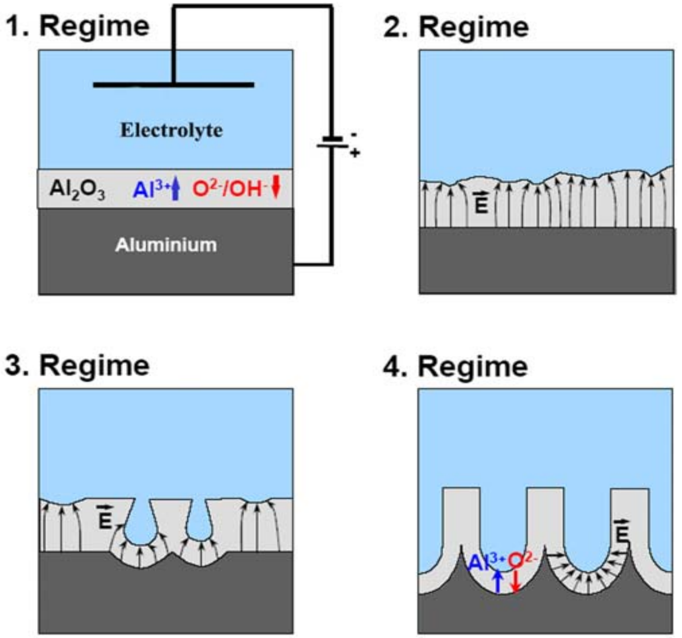
Amphiphilic Block Copolymers:
- hydrophilic-hydrophobic segments

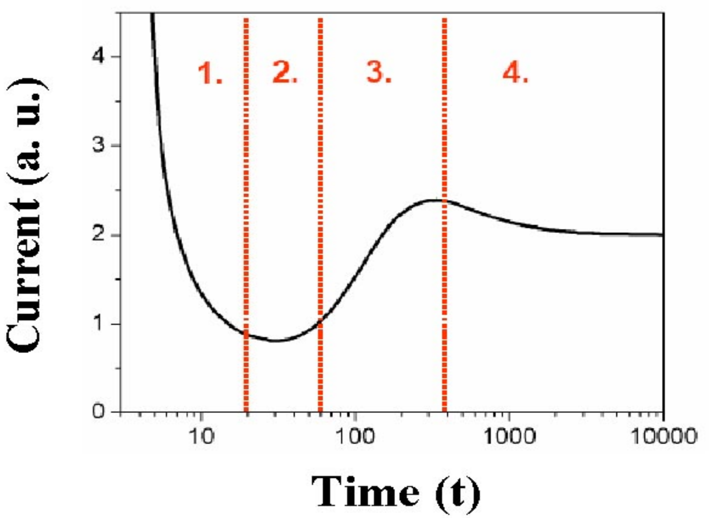
Y. Xia, Adv. Mater. 15, 353 (2003).

Synthesis of Nano Materials- 1D from Liquid

❑ AAO (anodized aluminium oxide) template







1. Regime : initially oxide growth dominates.

$$2Al + 3OH^- \qquad Al_2O_3 + 3H^+ + 6e^-$$

$$2Al + 3O^{2-} \qquad Al_2O_3 + 6e^-$$

2. Regime : dissolution becomes competitive, barrier layer thin, and pore initiate.

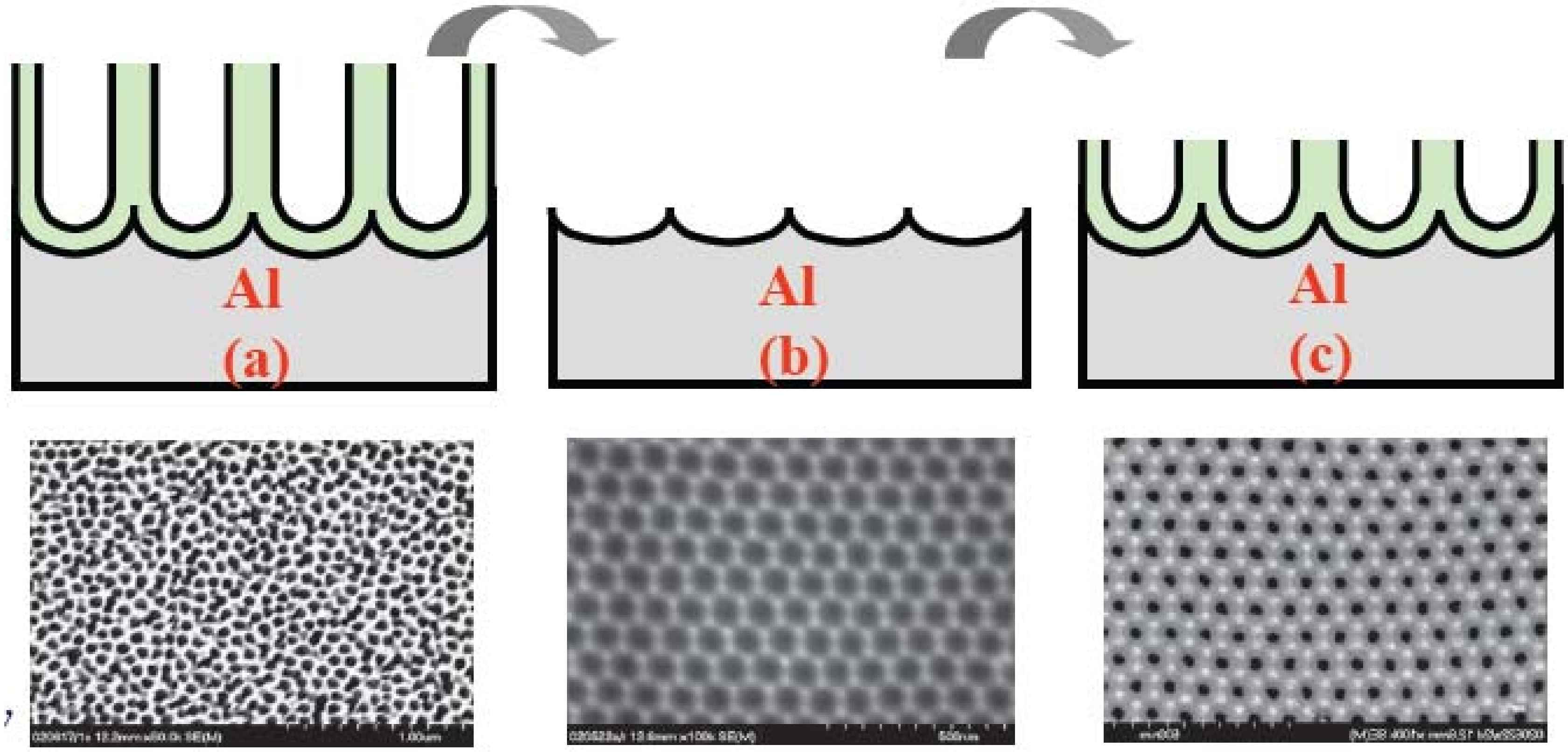
3 & 4. Regime : approaches steady state where both mechanisms occur at roughly the same rate.

V.P. Parkhutik, J. Phys. D 25 (1992) 1258.

Synthesis of Nano Materials- 1D from Liquid

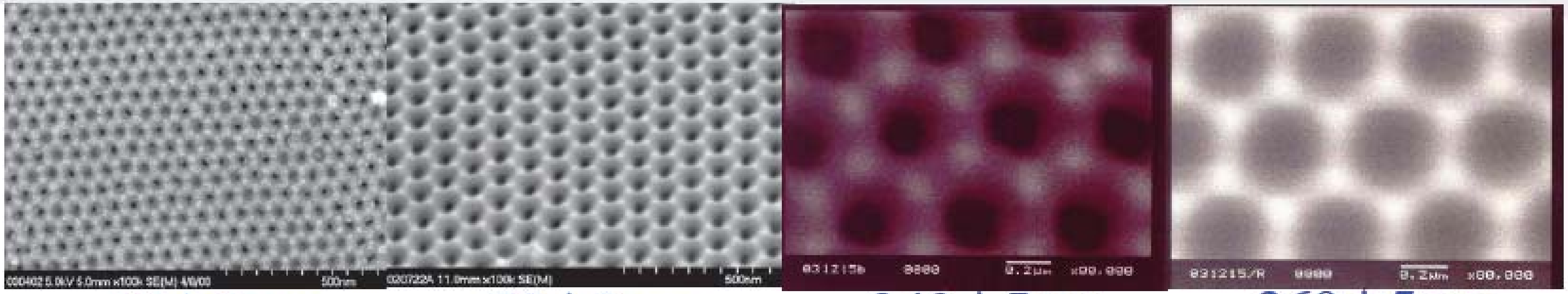
- **AAO (anodized aluminium oxide) template**

1st anodizing removal of porous layer 2nd anodizing



Synthesis of Nano Materials- 1D from Liquid

☐ AAO (anodized aluminium oxide) template



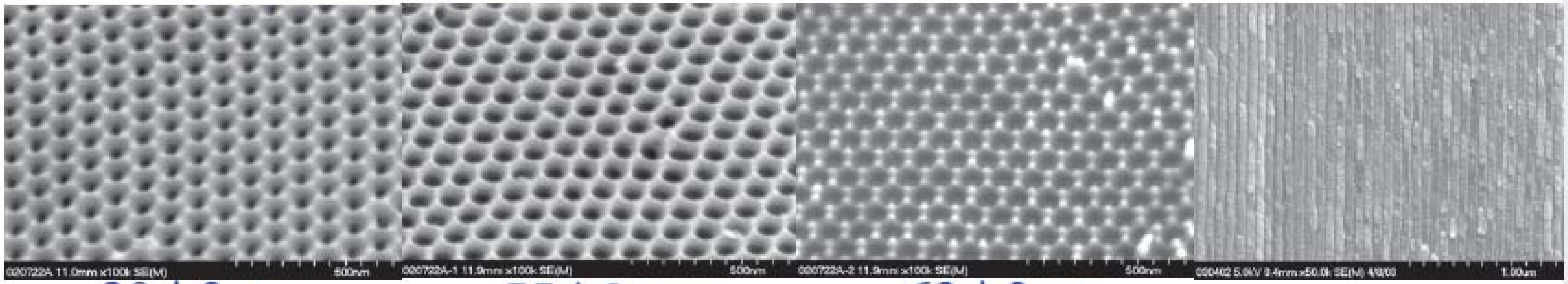
18±2nm sulfuric

30±2nm oxalic

240±5nm 360±5nm phosphoric

Interpore distance : 70~510nm, Pore density : 10^9~10^{11}/cm^2

✓Pore widening with 5 wt% phosphoric acid at 30°C



30±2nm Intitially

55±2nm 30min

63±2nm 60min

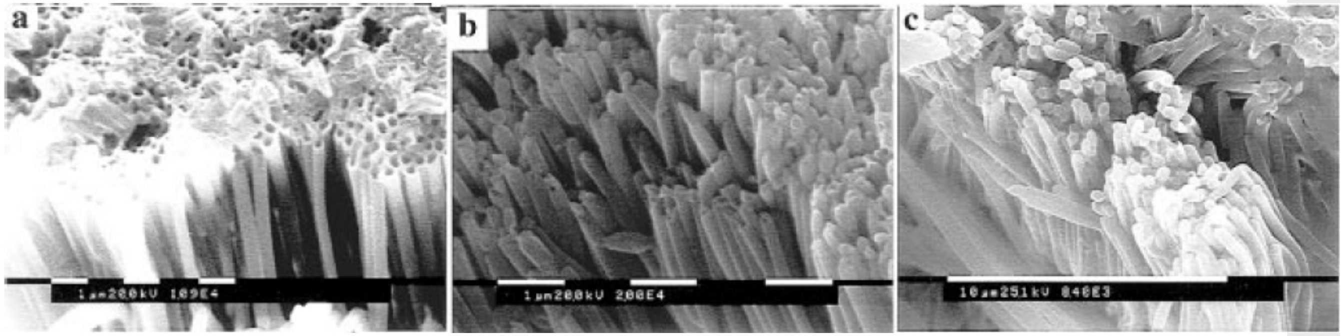
Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (direct filling)-sol-gel

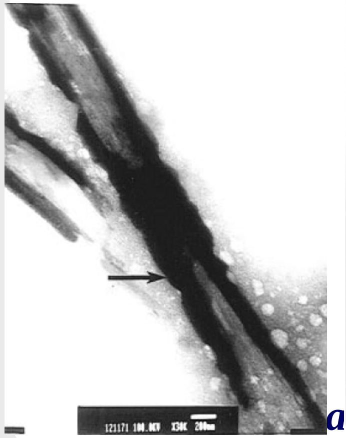
- filling of the template with a stable sol (capillary force)
- drying, firing (400, 120, 550°C), and dissolving in NaOH

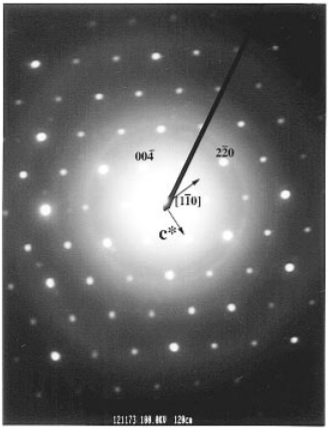
ex) TiO_2, ZnO, WO_4 (titanium isopropoxoide, zinc acetate, WCl_6)

immersion time 5, 25, 60s
tubules → fibrils



crystalline (anatase)
c-axis oriented





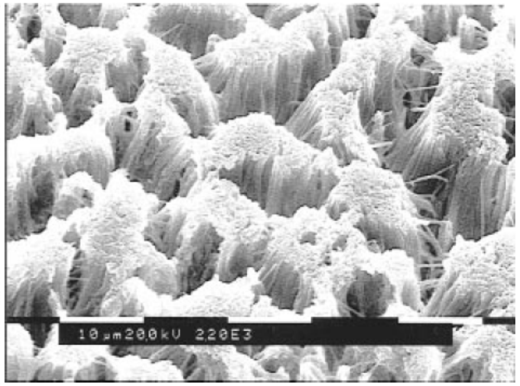


Figure 6. SEM image of 200 nm diameter ZnO fibrils.

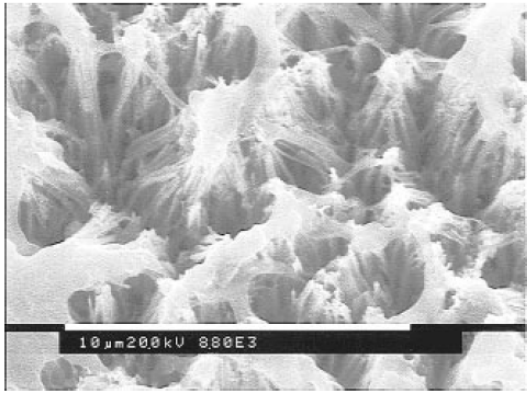


Figure 8. SEM image of 200 nm diameter WO_3 fibrils.

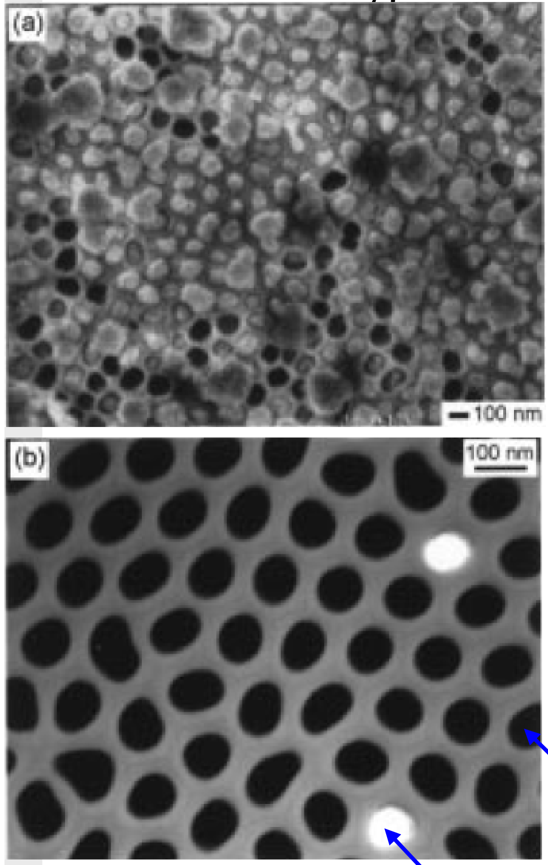
B.B. Lakshmi, Chem Mater. 9 (1997) 857.

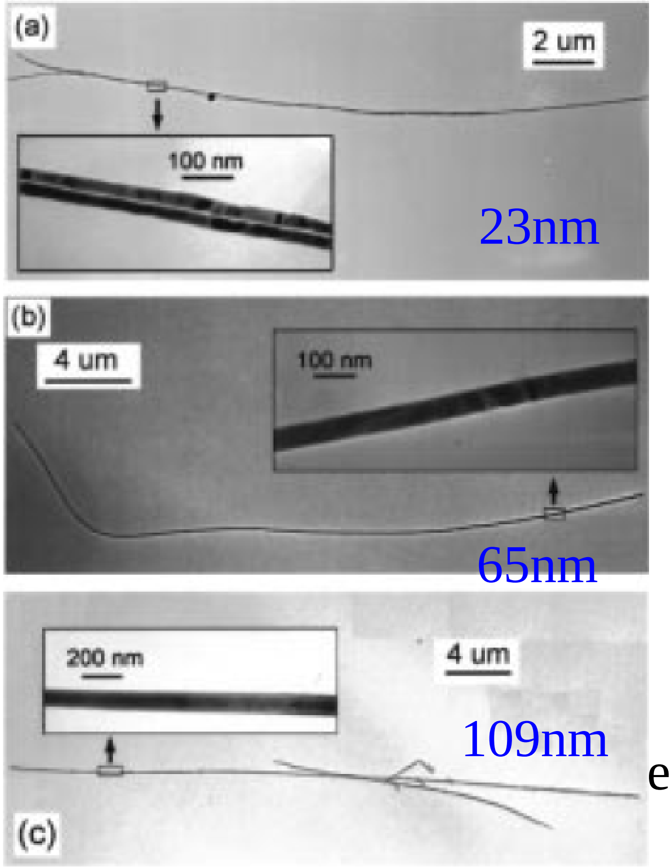
Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (direct filling)-melt

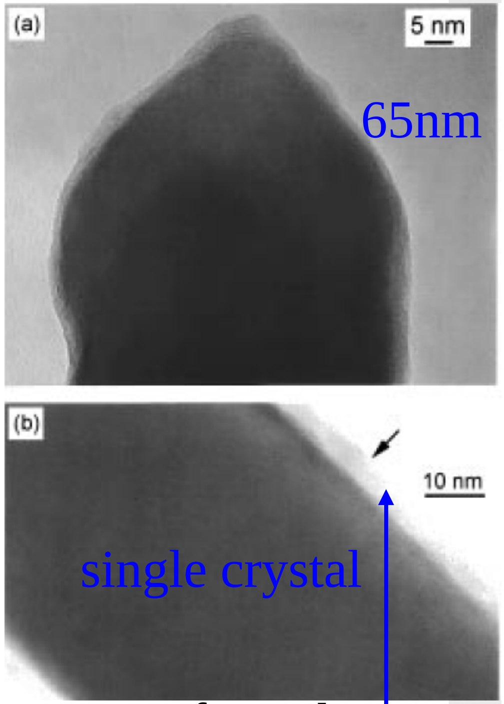
ex) Bi (AAO, 325°C ($T_{m, Bi}$=271.5°C) for 5h, Ar of ~300 bar)

dissolving AAO in $H_3PO_4+CrO_3$





exposure to air for 4h



exposure to air for 48h

amorphous oxide

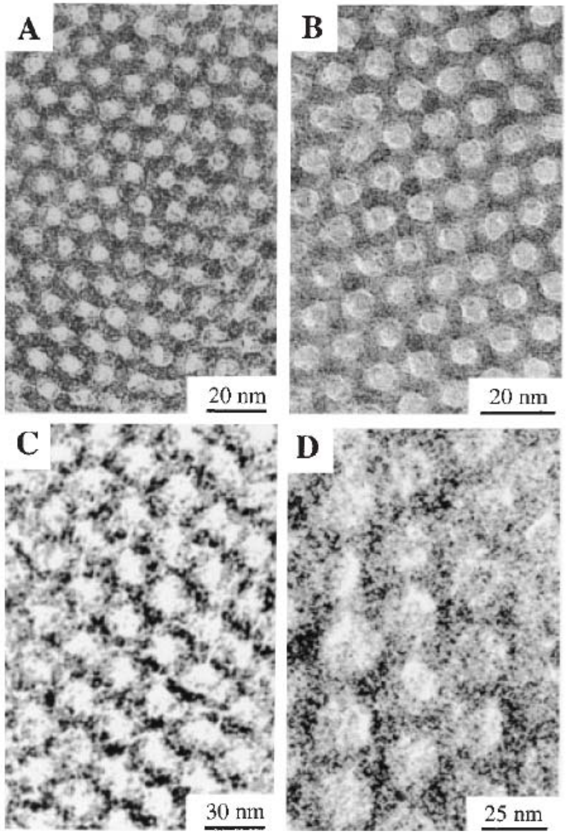
Z. Zhang, Chem Mater. 11 (1999) 1659.

Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (direct filling)-solution

ex) Au, Ag, Pt (mesoporous silica (SBA-15), $HAuCl_4$, $AgNO_3$, $Pt(NH_3)_4(NO_3)_2$) aqueous solution, CH_2Cl_2 treatment, reduction in H_2

SBA-15



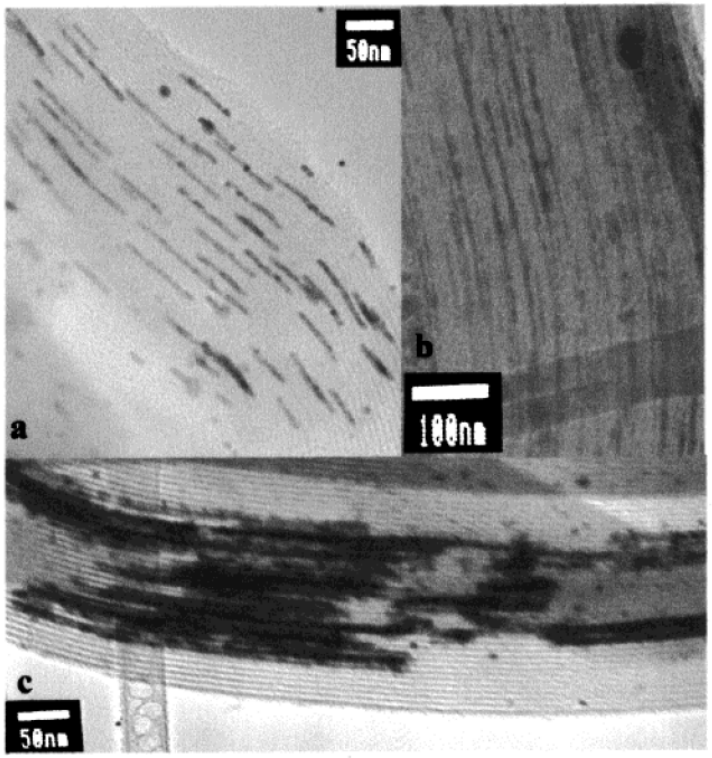


Figure 2. TEM micrographs of nanowires within the framework of SBA-15: (a) Au/SBA-15; (b) Ag/SBA-15; (c) Pt/SBA-15. TEM micrographs were taken with a 2000 FX JEOL instrument operating at 200 kV.

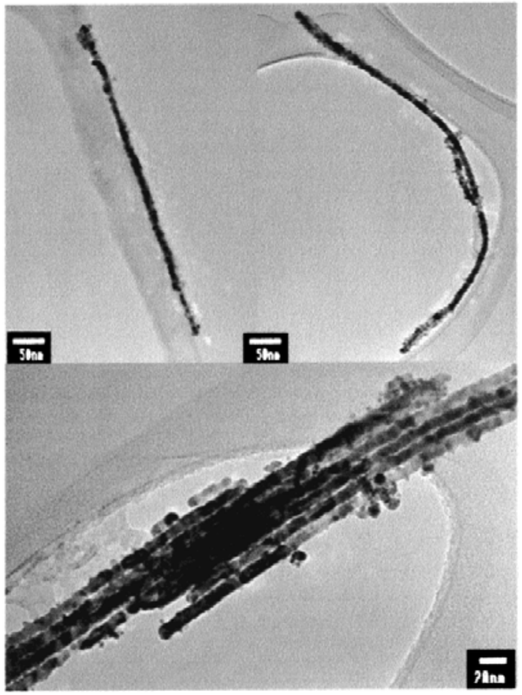


Figure 3. TEM micrographs of the unsupported Pt nanowires obtained by removal of silica framework with aqueous HF solution.

D. Zhang, Science 279 (1998) 548.

Y.-J. Han, Chem. Mater. 12 (2000)2068.

Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (direct filling)-solution

ex)

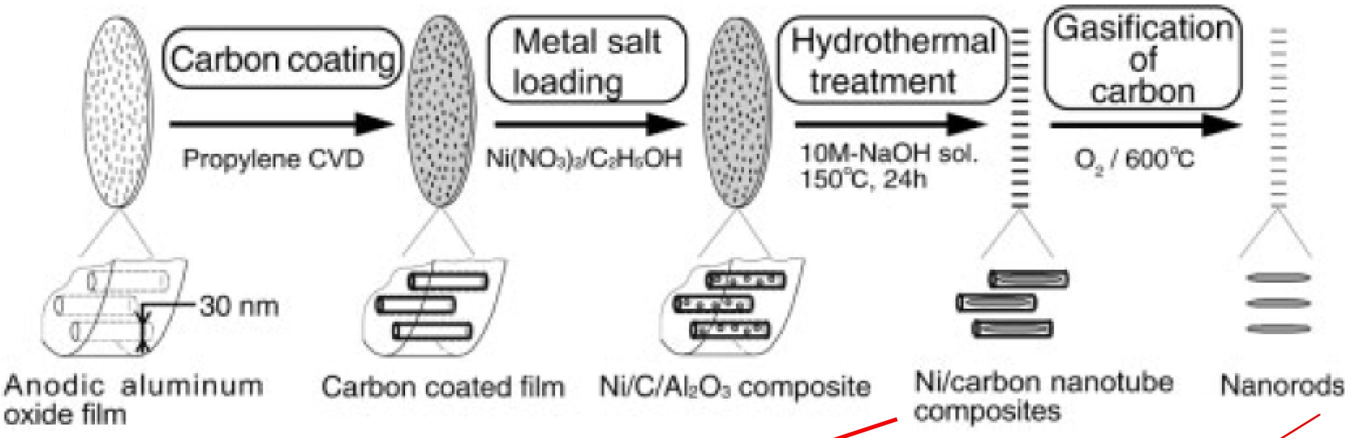
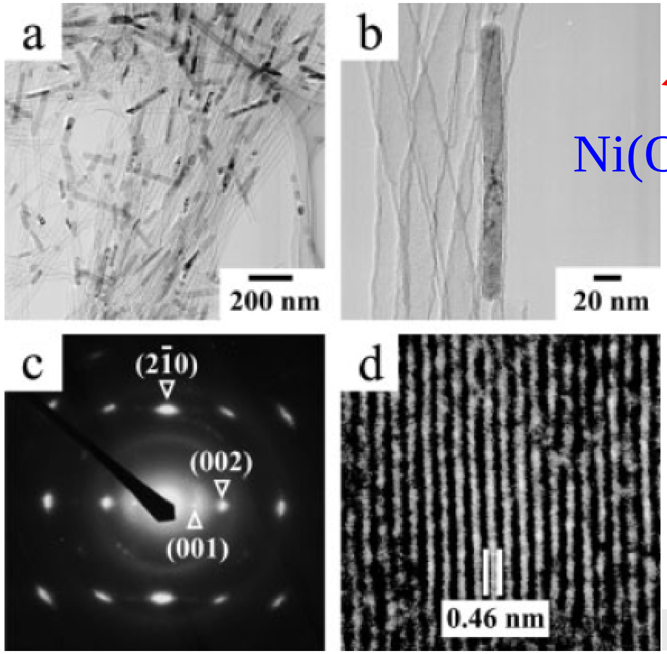
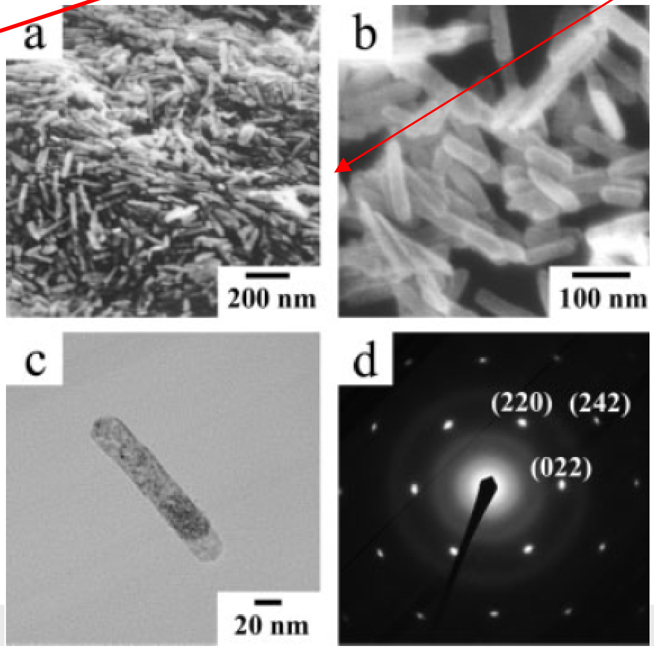


Fig. 1. Schematic illustration of the synthesis of nanorods by hydrothermal treatment in the template.



$Ni(OH)_2$



NiO

K. Matsui, Adv. Mater. 14 (2002) 1216.

Synthesis of Nano Materials- 1D from Liquid

- **Template-based** (direct filling)-polymerization

ex) polypyrole polyacetylene

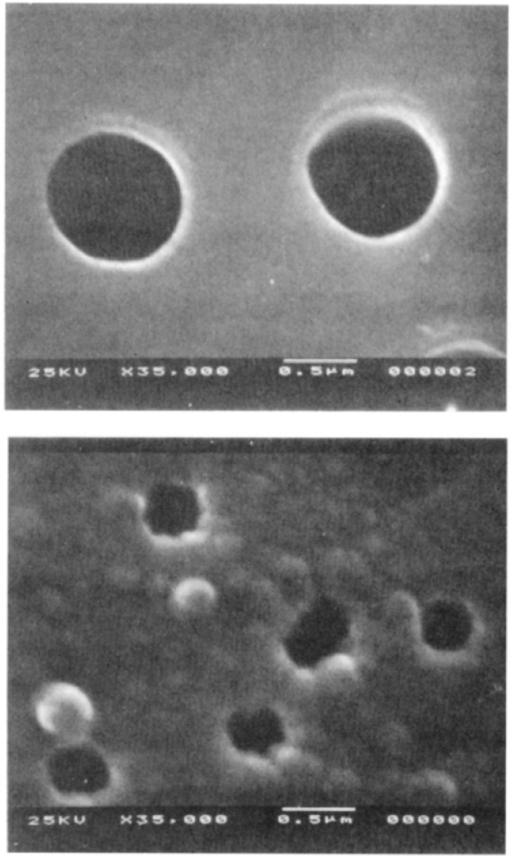


Figure 1. Electron micrographs of surfaces of 1.0 μm pore diameter Nuclepore membrane: (A) virgin membrane and (B) after 1 min polypyrrole polymerization period (see text).

Z. Cai, J. Am. Chem. Soc. 111 (1989) 4138.

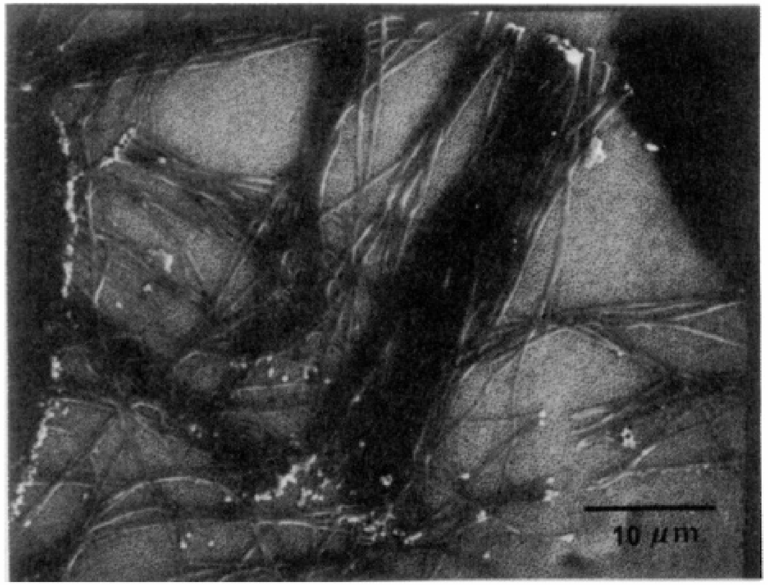


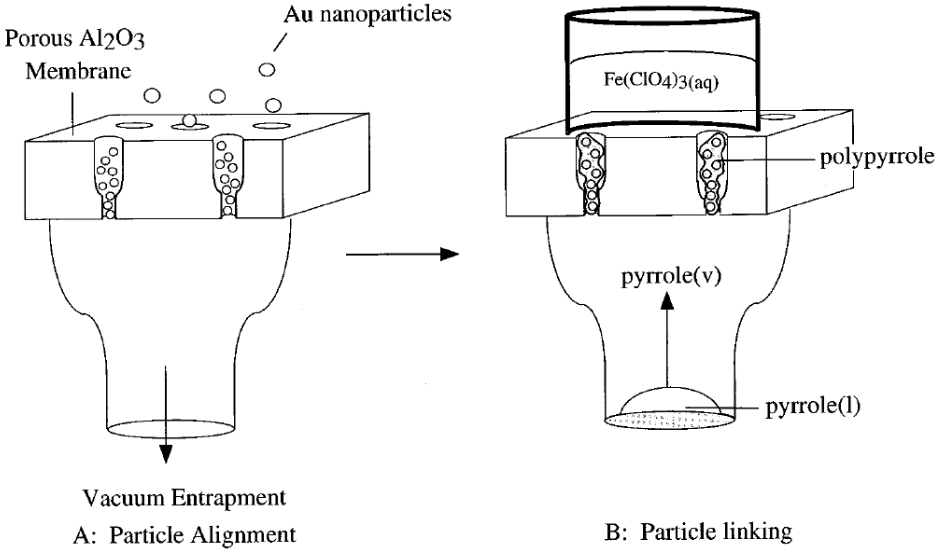
Figure 1. Scanning electron micrograph of template-synthesized polyacetylene fibrils.

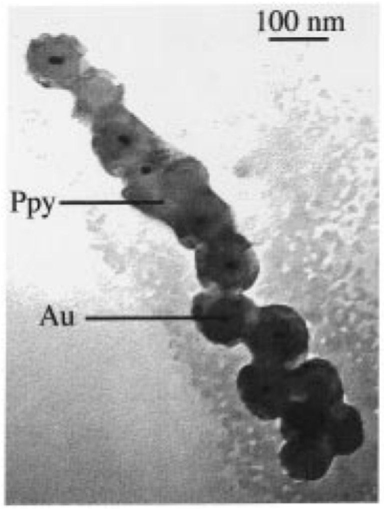
W. Liang, J. Am. Chem. Soc. 112 (1990) 9666.

Synthesis of Nano Materials- 1D from Liquid

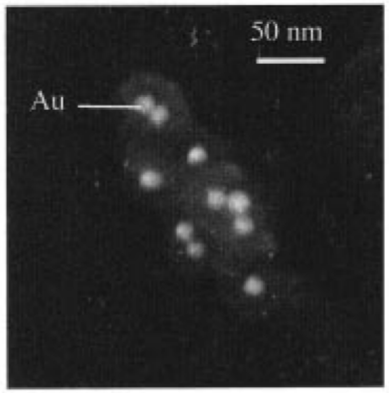
- **Template-based** (direct filling)-polymerization

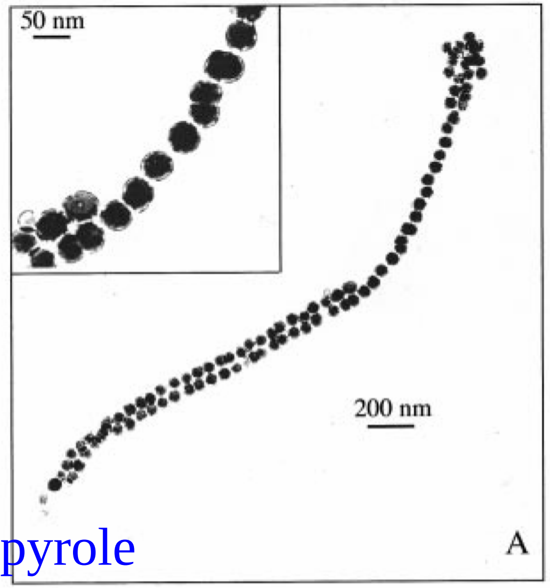
ex) composite





Ag/polypyrole





polypyrole

S. M. Marinakos, Chem Mater. 10 (1998) 1214.

Synthesis of Nano Materials- 1D from Liquid

- ❑ **Template-based** (direct filling)

ex) silica (TEOS)-surfactant (PEO-PPO-PEO)

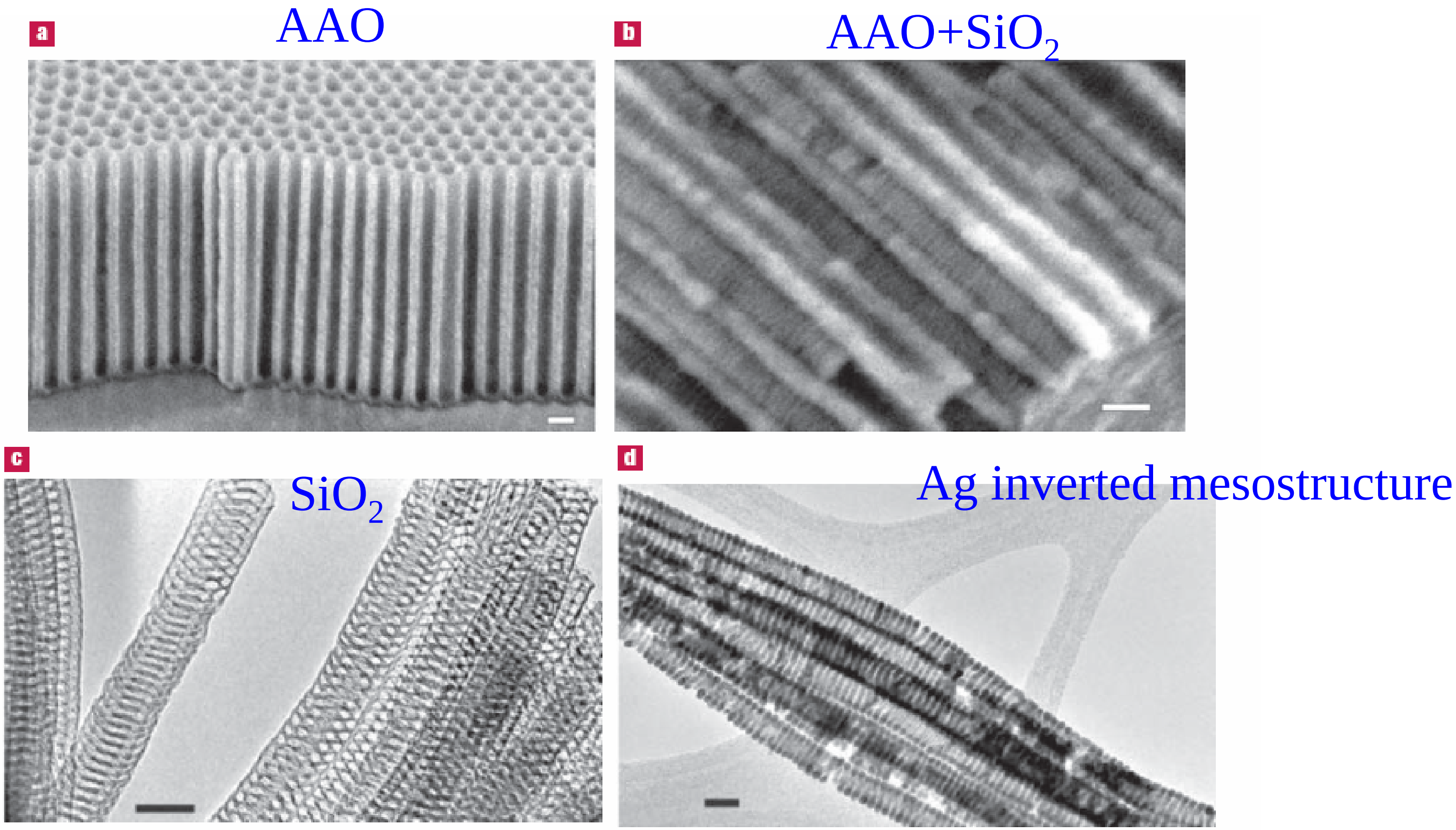


Figure 1 SEM images of PAA membrane and TEM images of free-standing mesoporous silica fibres and silver mesostructured nanowires. **a**, SEM image of the starting PAA membrane. **b**, SEM image of the PAA membrane cross-section after loading with mesoporous silica. **c**, TEM image of free-standing mesoporous silica fibres. **d**, TEM image of Ag nanowires with inverted mesostructures after their release from the oxide matrix. Scale bars: 100 nm in **a** and **b**, and 50 nm in **c** and **d**.

Y. Wu, Adv. Mater.
3 (2004) 816.

Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (direct filling)

ex) silica (TEOS)-surfactant (PEO-PPO-PEO)

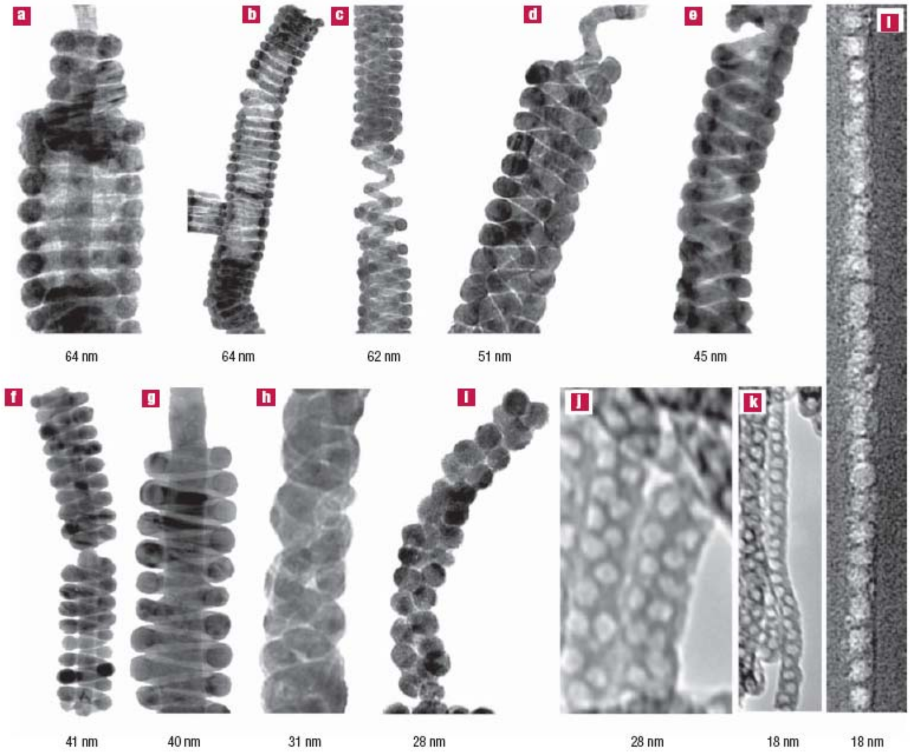


Figure 3 Representative TEM images of mesostructures formed inside alumina nanochannels with differing confinement dimensions. The confining nanochannel diameter is indicated underneath each image. **a–i**, Silver inverted mesostructures prepared by backfilling the confined mesoporous silica; **j–k**, free-standing mesoporous silica fibres; **l**, mesoporous silica embedded inside the alumina nanochannels obtained using a focused ion beam for sample preparation. The structures are **a**, three-layer stacked doughnuts; **b**, S-helix; **c**, core–shell D-helix, in which the core and the shell are both S-helix; **d**, core–shell triple-helix, in which the shell is a D-helix and the core is a S-helix; **e**, D-helix; **f**, **g**, S-helix with a straight core channel; **h**, D-helix; **i**, **j** inverted peapod structure with two lines of spherical cages packed along the long axis of the alumina nanochannel; **k**, **l**, inverted peapod with one line of cages.

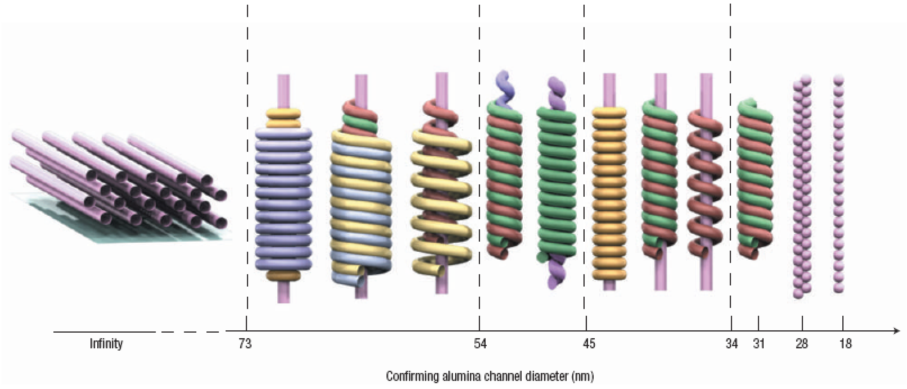


Figure 4 Summary of the experimentally observed confined mesostructural evolution with varying alumina nanochannel diameters.

a-i: Ag inverted mesostructure

Y. Wu, Adv. Mater.
3 92004) 816.

Synthesis of Nano Materials- 1D from Liquid

☐ **Template-based** (electrochemical deposition)

Basic Terminologies

☐ **Reduction/Oxidation, Electron Accepter/ Donor, Oxidizing/ Reducing Agent**

☐ **Half-cell reaction/ Overall reaction**

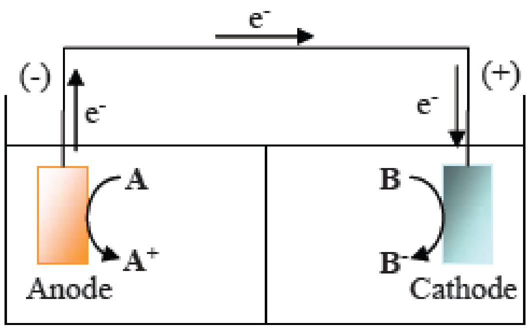
☐ **Anode/ Cathode**

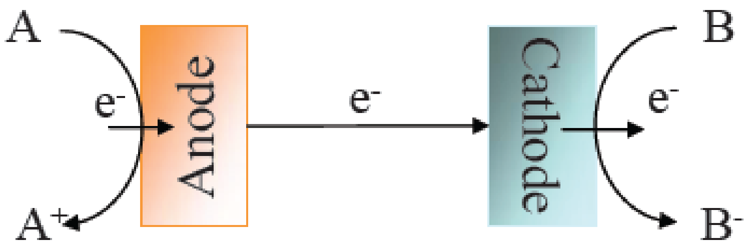
$$\text{Anode} \quad A \longrightarrow A^{+} + e^{-}$$

$$\text{Cathode} \quad B + e^{-} \longrightarrow B^{-}$$

$$A + B \longrightarrow A^{+} + B^{-}$$

Oxidized	Reduced
Electron donor	Electron acceptor
Reducing agent	Oxidizing agent





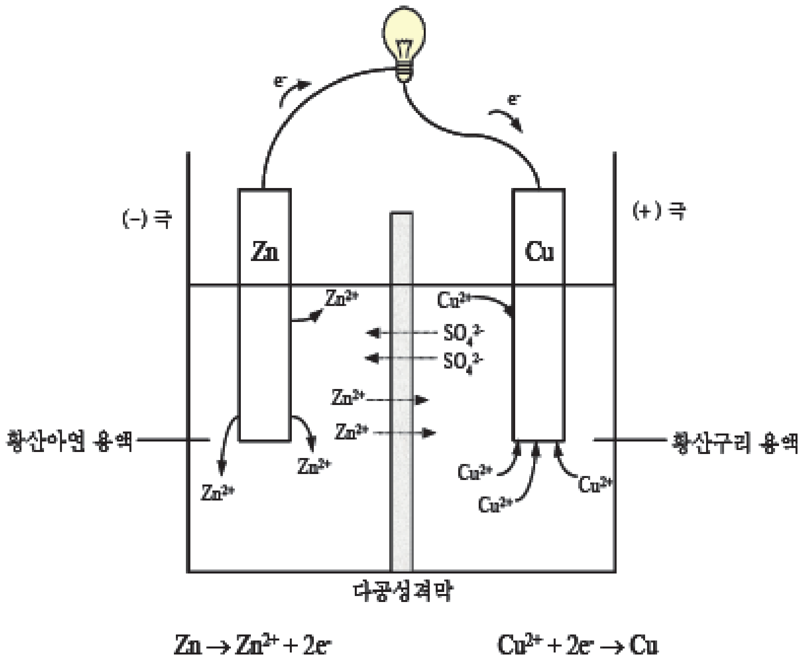
Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (electrochemical deposition)

Electrochemical Cells – Two Electrode System

❑ **Components of the cell**

- Electrodes
    - Anode
    - Cathode
- Solution
    - Electroactive species
    - Supporting electrolyte
    - Solvent
- Separator
- Wire
- Voltmeter, Ammeter



* Electron transfer (or redox reaction) always accompanies ion transfer.

Synthesis of Nano Materials- 1D from Liquid

❑ Template-based (electrochemical deposition)

When a metallic salt is dissolved in water, it dissociates to form positively charged ions. The solution that contains these charged ions is referred to as an electrolye or a plating solution. By passing a sufficient amount of electric current through this electrolyte, one can reduce the metal ions to form solid metal. This process is most commonly referred to electroplating or electrochemical deposition.

Electrodeposition is carried out in a three electrode electrochemical cell that contains a "working electrode" (PAA template), a "reference electrode" (Ag/AgCl), and a "counter electrode" (platinum gauze). For electrodeposition to occur the working electrode must be conducting. Unfortunately, PAA is a ceramic and so a 100 nm layer of platinum (or some other conducting metal) must be deposited on the back side of the PAA template prior to beginning electrodeposition.

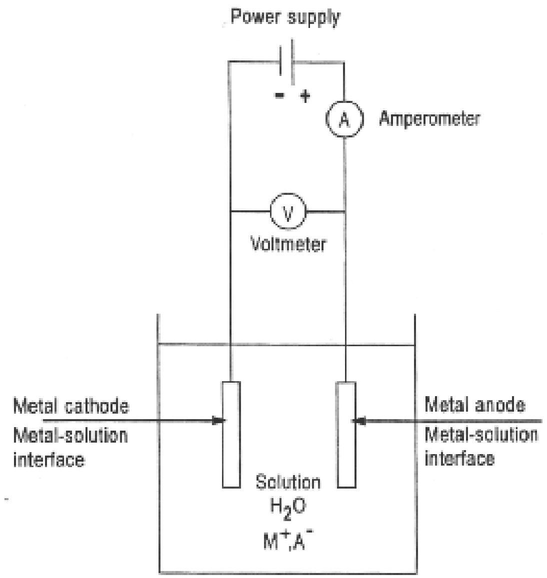
http://cobweb.ecn.purdue.edu/~mdasilva/Electrodeposition.shtml

Synthesis of Nano Materials- 1D from Liquid

☐ **Template-based** (electrochemical deposition)

This in turn allows the positively charged ions to be accelerated towards the bottom of the pores once the open side of the template is exposed to the electrolyte and the current is applied to the conducting layer. When the ions reach the bottom of the pores, it sees the electrons that are supplied from the applied current and gets reduced to its metallic form. This is shown by the following reaction where "M" represents some metal of "n" valency. In can therefore be expected that for a 3+ gold cation in solution, 3 electrons would be required to reduce the cation into its metallic form.

$$\mathbf{M^{+n} + ne^{-} ==> M}$$



Synthesis of Nano Materials- 1D from Liquid

- ☐ **Template-based** (electrochemical deposition)

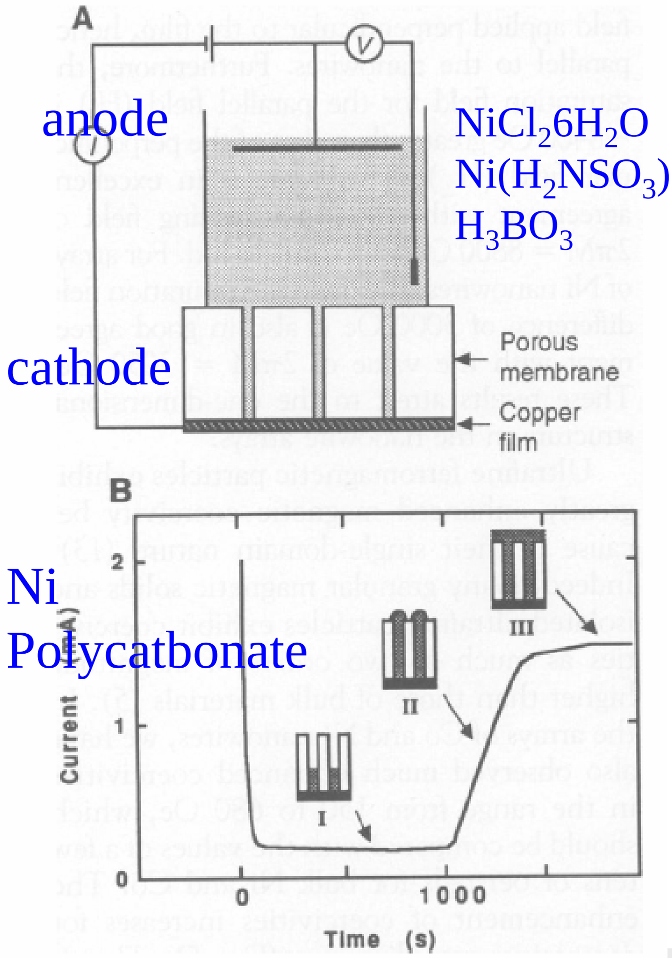
For the electrodeposition of nickel in PAA for example, we might use a nickel chloride salt which dissociates in water to form positively charged nickel cations and negatively charged chloride anions. The platinum conducting layer located on the bottom of the PAA template is negatively charged and so it attracts the positively charged nickel cations. The electrons flow from the platinum layer to the cations to reduce them to metallic form. Meanwhile, the negatively charged chloride anions are attracted to the positively charged platinum electrode (the counter electrode or anode). At the counter electrode, electrons are removed from the platinum grid, oxidizing it to the platinum cations.

The thickness of the nanowire is roughly directly proportional to the time duration of the electrodeposition. In other words, the longer time the specimen remains in the electrolytic bath, the thicker the resulting electrodeposited layer will be. The thickness of a nanowire or nanowire segment can vary from 5 nm to 50 µm.

Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (electrochemical deposition)

ex) Ni



anode

$NiCl_2 6H_2O$
$Ni(H_2NSO_3)_2 4H_2O$
H_3BO_3

cathode

Ni

Polycatbonate

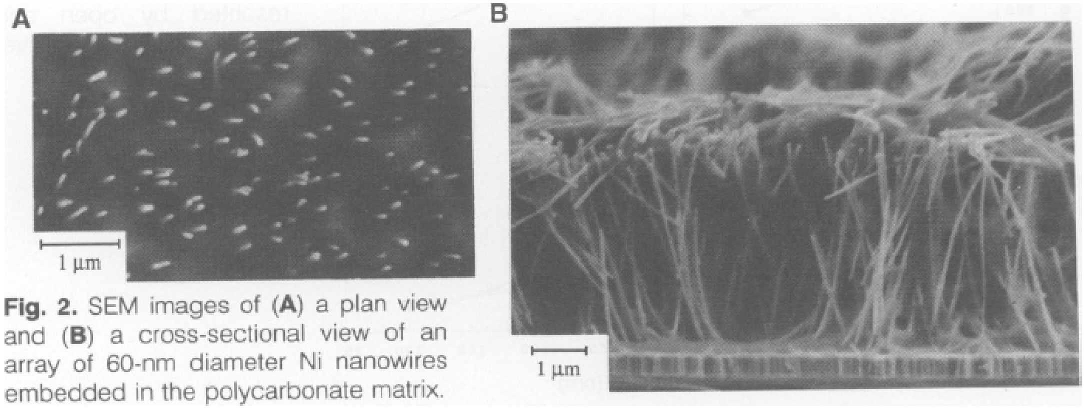
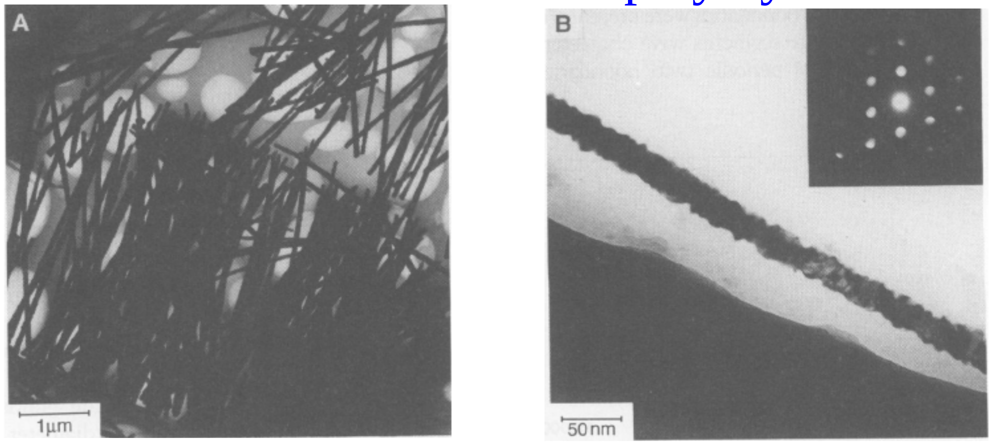


Fig. 2. SEM images of (**A**) a plan view and (**B**) a cross-sectional view of an array of 60-nm diameter Ni nanowires embedded in the polycarbonate matrix.

polycrystalline



T.M. Whitney, Science 261 (1993) 1316.

Synthesis of Nano Materials- 1D from Liquid

- **Template-based** (electrochemical deposition)

  ex) Sb (pulsed)

  - AAO/ $SbCl_3$ $C_6H_8O_7$ H_2O $K_3C_6H_5O_7$ H_2O

single crystal

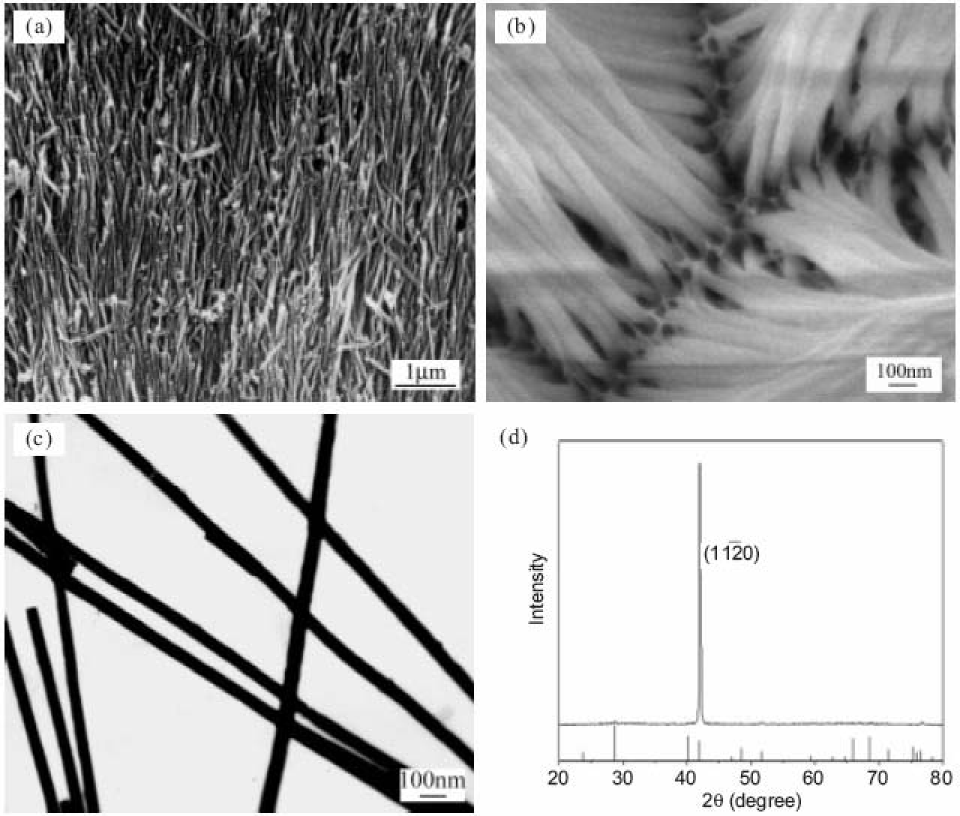
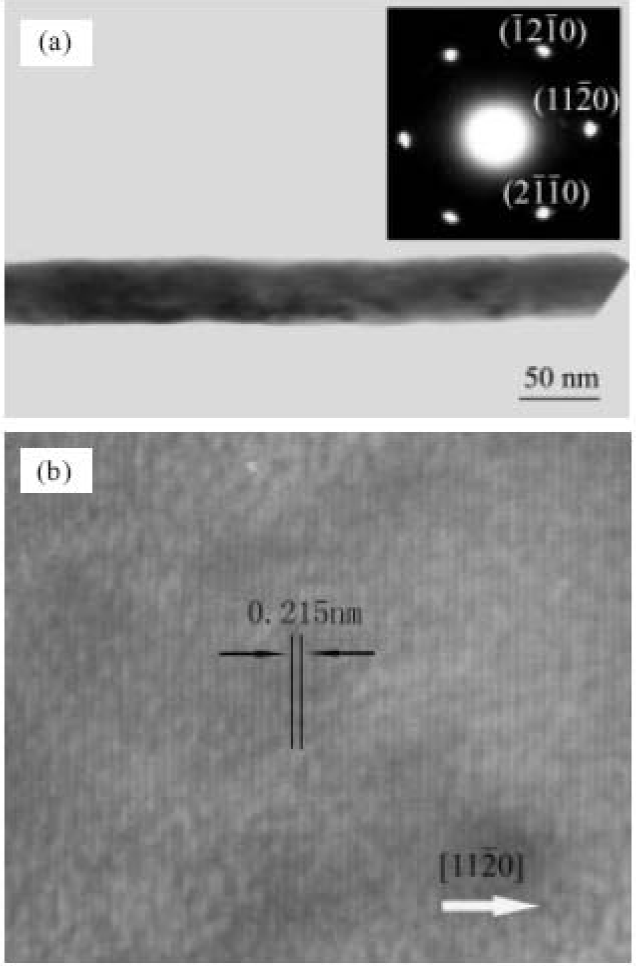


Fig. 1. a) A typical FEM image showing the general morphology of the antimony nanowire array. b) A typical FEM image showing the filling degree of the template and height variation of the nanowires. c) A TEM image of antimony nanowires showing the morphology of individual nanowires. d) XRD pattern of the antimony nanowire array; the sole diffraction peak indicates the same orientation of all the nanowires.



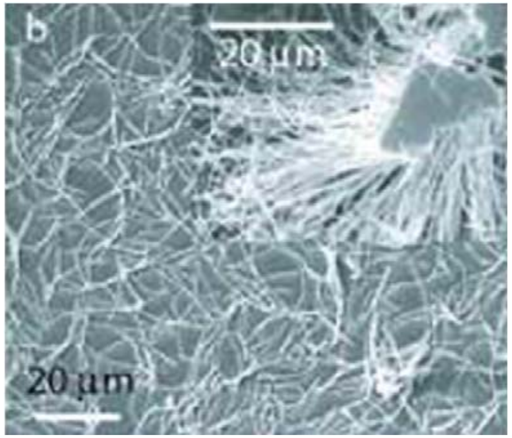
Y. Zhang, Adv. Mater. 14 227 (2002).

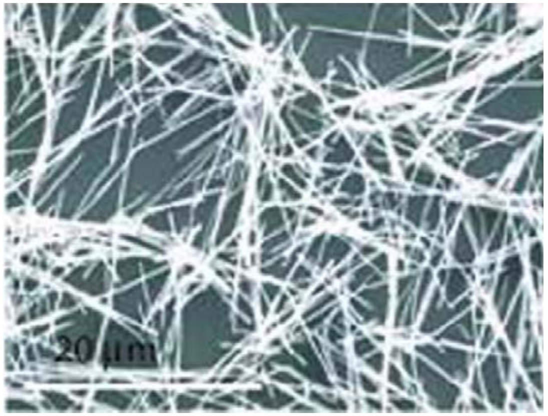
Synthesis of Nano Materials- 1D from Liquid

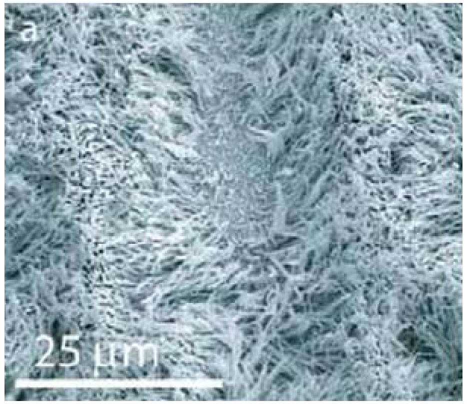
- **Template-based** (electrochemical deposition)

AAO

ex) Ag Cu Au







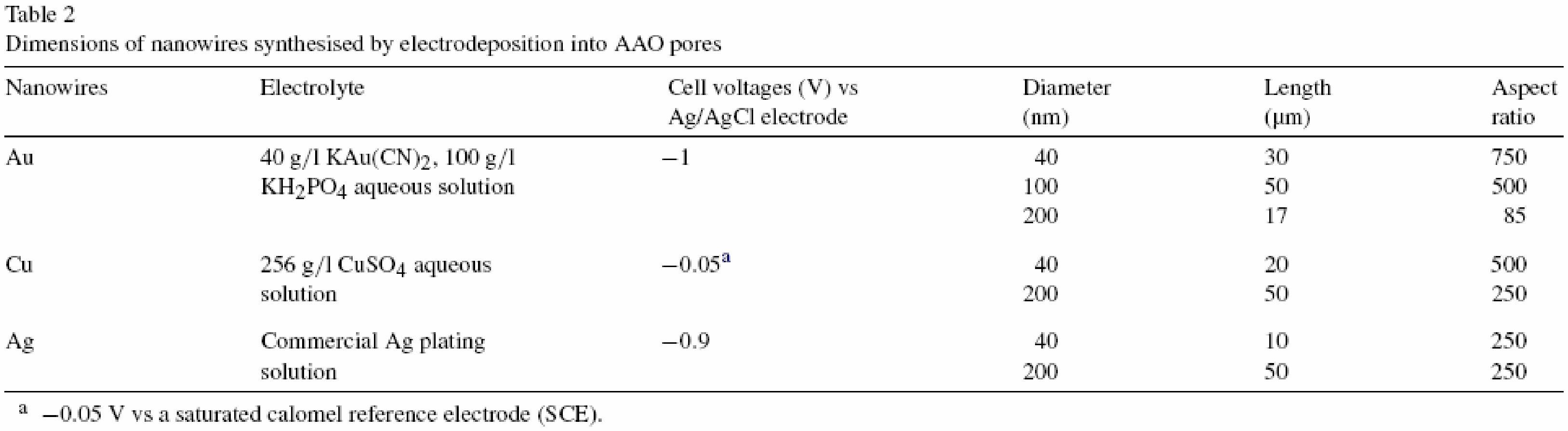


Table 2

Dimensions of nanowires synthesised by electrodeposition into AAO pores

Nanowires	Electrolyte	Cell voltages (V) vs Ag/AgCl electrode	Diameter (nm)	Length (μm)	Aspect ratio
Au	40 g/l $KAu(CN)_2$, 100 g/l KH_2PO_4 aqueous solution	−1	40 100 200	30 50 17	750 500 85
Cu	256 g/l $CuSO_4$ aqueous solution	−0.05[a]	40 200	20 50	500 250
Ag	Commercial Ag plating solution	−0.9	40 200	10 50	250 250

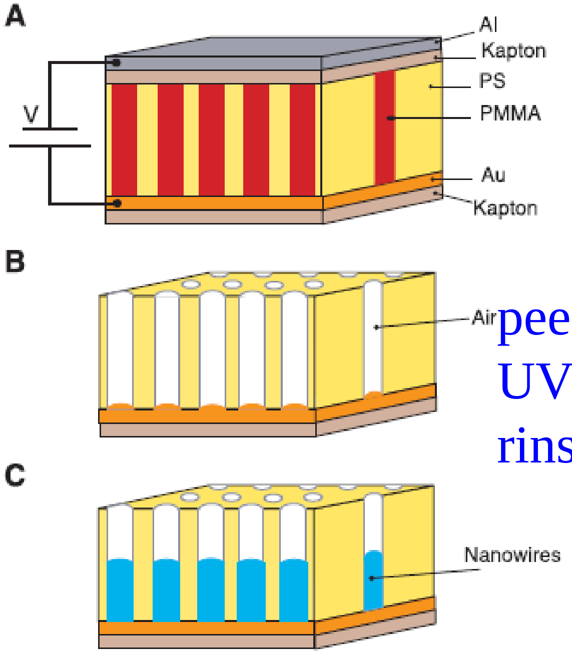
[a] −0.05 V vs a saturated calomel reference electrode (SCE).

B. Wu, J. Colloid Interf. Sci. 303 (2006) 611.

Synthesis of Nano Materials- 1D from Liquid

- **Template-based** (electrochemical deposition)

diblock copolymer, cobalt nanowire



spin casting

annealing above T_g under E

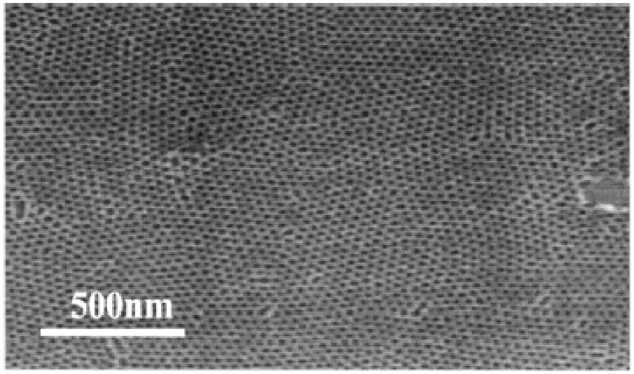
cylinderical microdomain

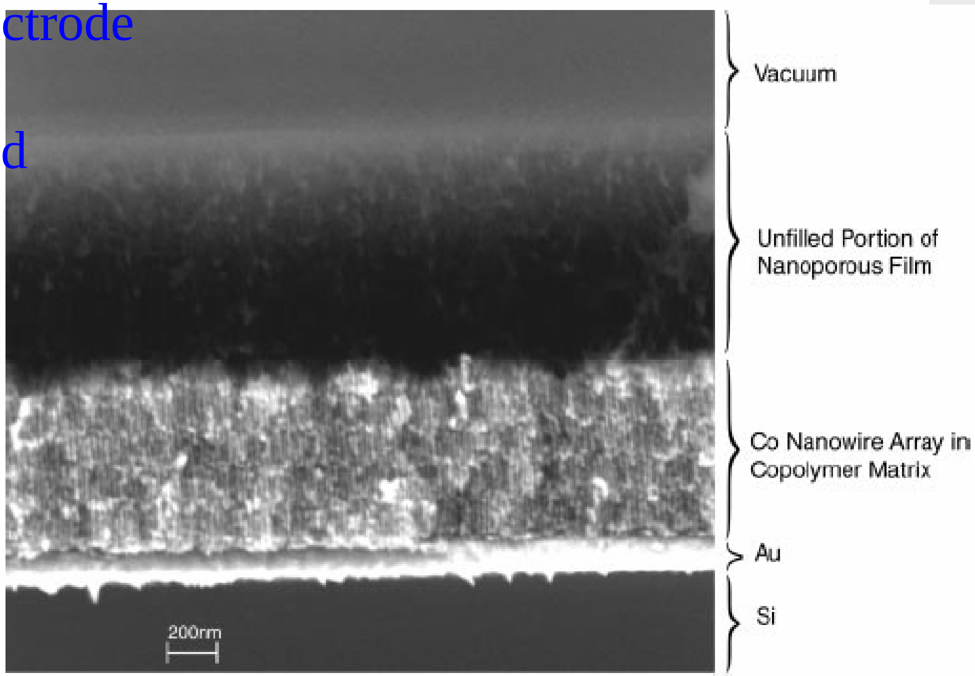
peel away upper electrode

UV exposure

rinse with acetic acid

$CoSO_4 5H_2O$
H_3BO_3

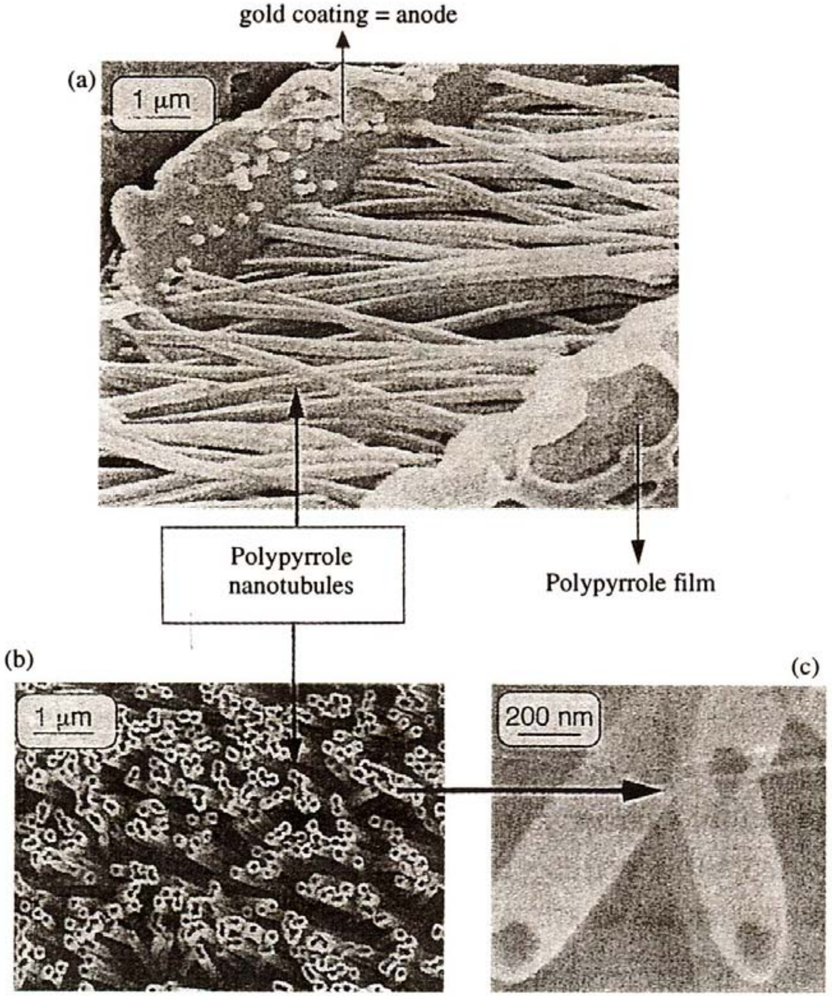




T.P. Russel, Science 290 (2000) 2126.

Synthesis of Nano Materials- 1D from Liquid

- ☐ **Template-based** (electrochemical deposition)



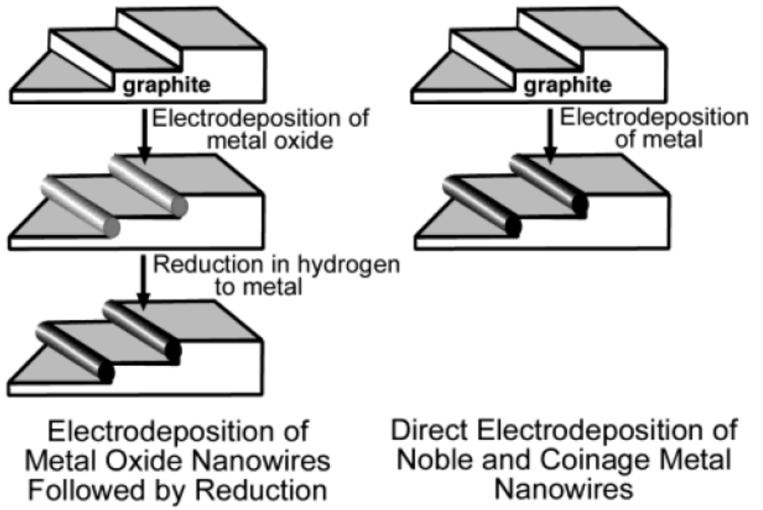
L.Piraux, Nucl. Instrum. Meth. Phys. Res. B131 (1997) 357.

Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (electrochemical deposition)

- graphite surface (Pd, Cu, Ag, Au, MoO_2 → MO)

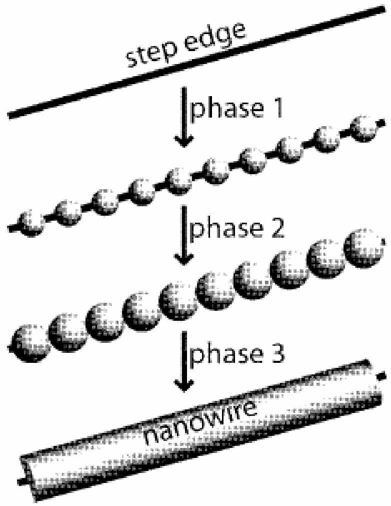
SCHEME 1: Two Methods for Implementing Electrochemical Step Edge Decoration To Produce Metal Nanowires



Electrodeposition of Metal Oxide Nanowires Followed by Reduction

Direct Electrodeposition of Noble and Coinage Metal Nanowires

SCHEME 4: Three Phases of Nanowire Electrodeposition at Step Edges



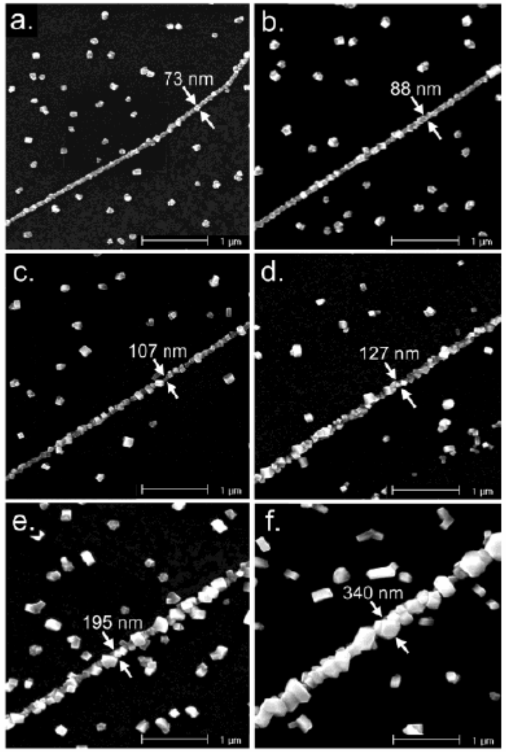


Figure 2. Scanning electron micrographs of copper nanowires. These nanowires were electrodeposited from the solution indicated in Table 1, using $E_{\mathrm{nucl}} = -800\ \mathrm{mV_{SCE}}$ and $E_{\mathrm{grow}} = -5\ \mathrm{mV_{SCE}}$. The growth times employed in each experiment were (a) 120 s, (b) 180 s, (c) 300 s, (d) 600 s, (e) 900 s, (f) 2700 s.

R.M. Penner, J. Phys. Chem. B106 (2002) 3339.

Synthesis of Nano Materials- 1D from Liquid

- **Template-based** (electrochemical deposition)

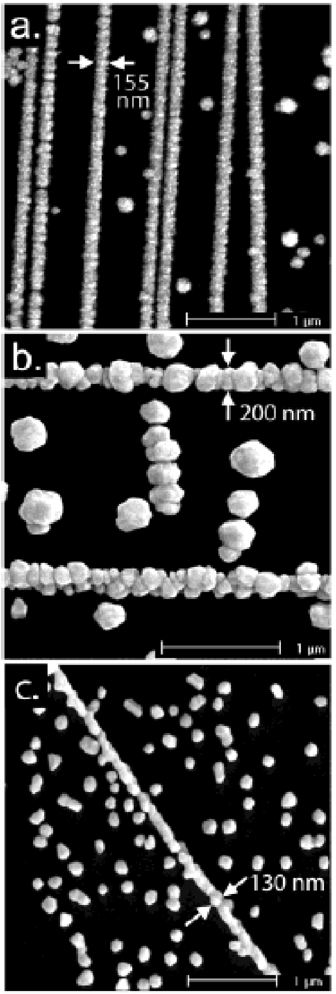


Figure 7. Representative scanning electron micrographs of (a) nickel, (b) silver, and (c) gold nanowires prepared by the potentiostatic double pulse method.

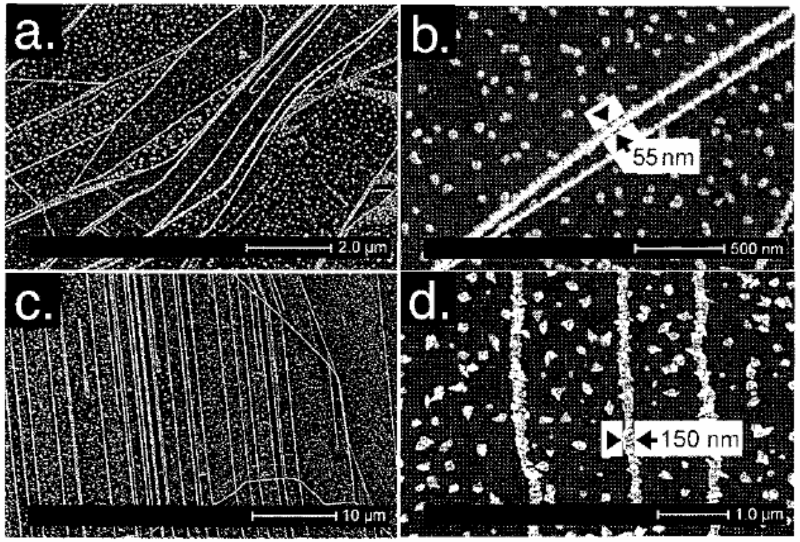


Figure 19. (a and b) Scanning electron micrographs (SEMs) of Pd mesowires prepared by electrodeposition from aqueous 2.0 mM $PdCl_2$, 0.1 M HCl, $E_{dep} = 0.3$ V, $t_{dep} = 900$ s; (c and d) from aqueous 2.0 mM $Pd(NO_3)_2$, 0.1 M $HClO_4$, $E_{dep} = 0.3$ V, $t_{dep} = 150$ s.

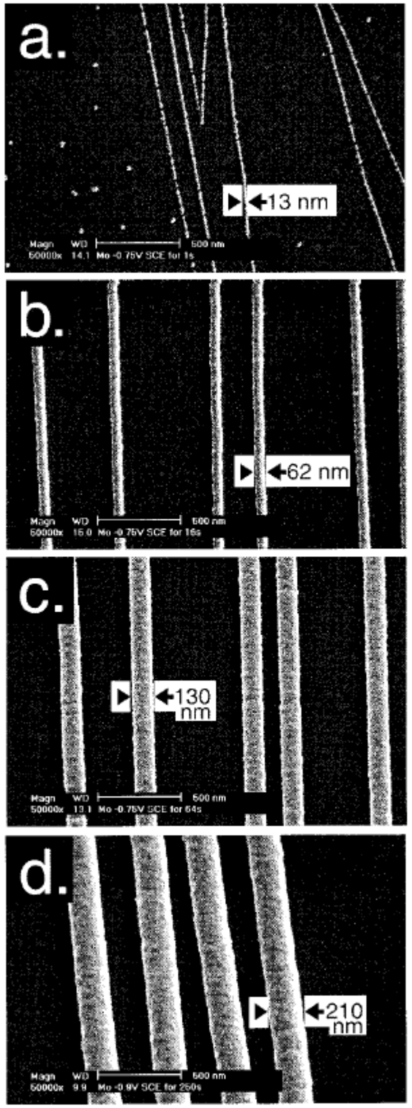


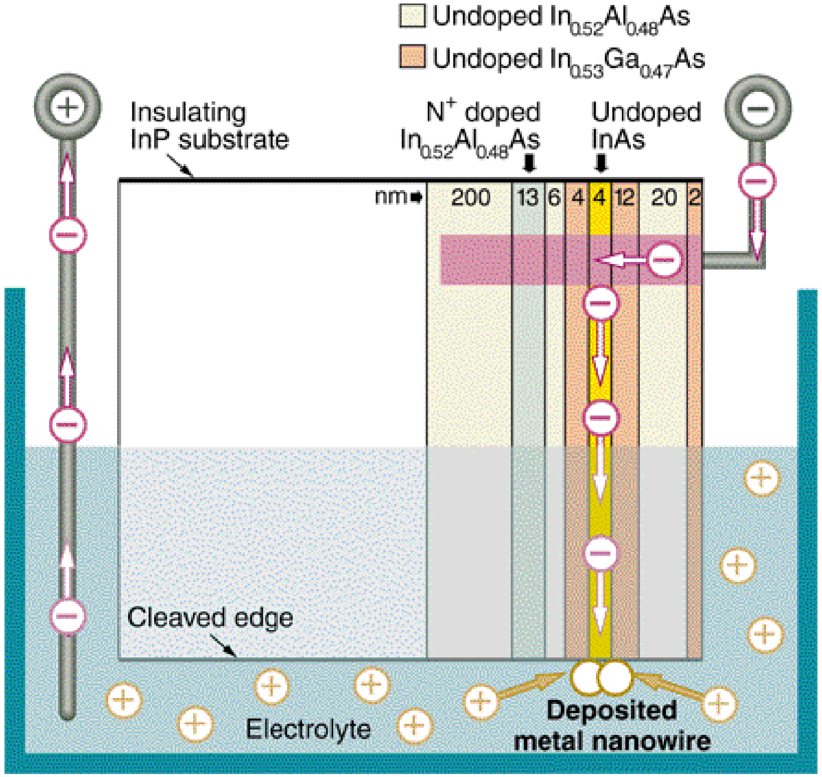
Figure 15. SEMs of graphite surfaces following the electrodeposition of MoO_2 nanowires at −0.75 V vs SCE from a plating solution containing 1.0 mM MoO_4^{2-}. Nanowires obtained using a deposition duration, (a) $t_{dep} = 1.0$ s; (b) $t_{dep} = 4.0$ s; (c) $t_{dep} = 16.0$ s; (d) $t_{dep} = 256$ s.

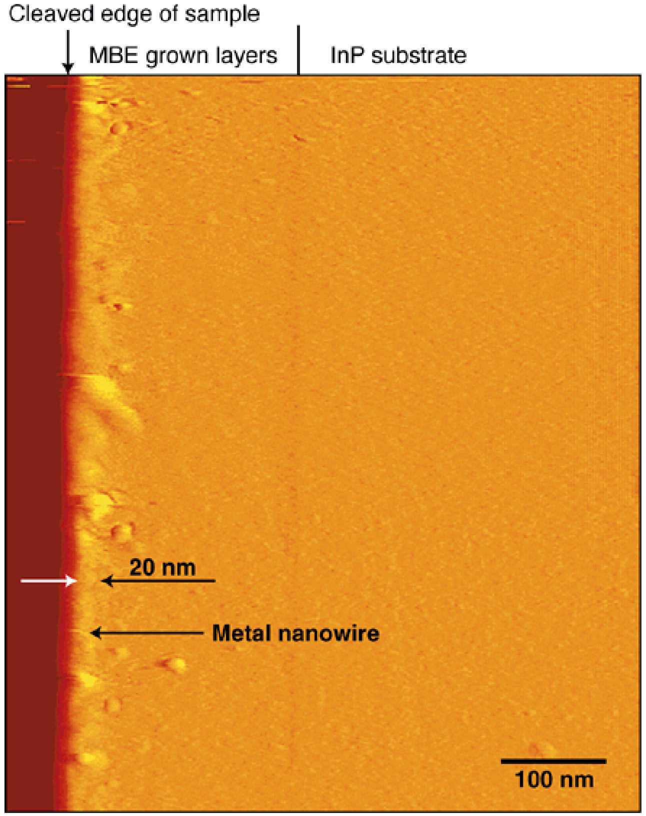
E.C.Walter, J. Phys. Chem. B106 (2002) 11407

Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (electrochemical deposition)

- cleavage-edge overgrowth (CEO)
- multilayer structure by MBE+ cleavage
- electroplating in citrate-complexed nickel-iron electrolyte





G. Fasol. Appl. Phys. Lett. 70 (1997) 2467.

Synthesis of Nano Materials- 1D from Liquid

☐ Electrokinetic Phenomena

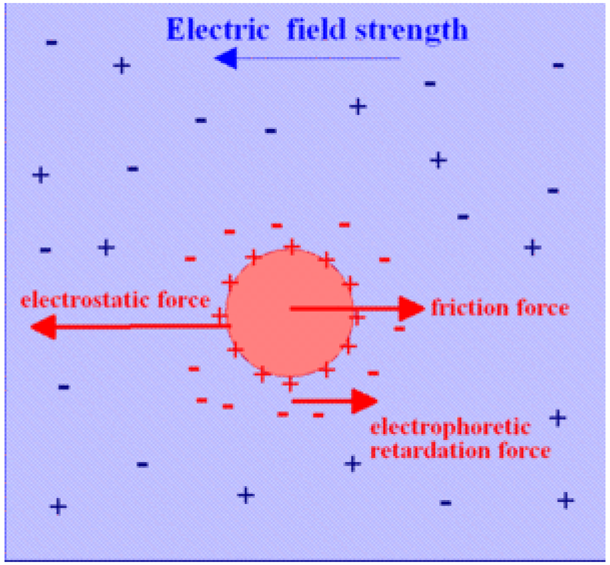
Name of Procedure	Property Measured	Mobile Phase	Example
Electrophoresis	Particle Mobility	Particle	Microelectrophoresis Moving boundary Electrophoretic transfer
Sedimentation Potential	Potential	Liquid	Sedimentation Potential
Streaming Potential	Potential	Liquid	Streaming Potential
Electroosmosis	Pressure Velocity	None Liquid	Electroosmosis

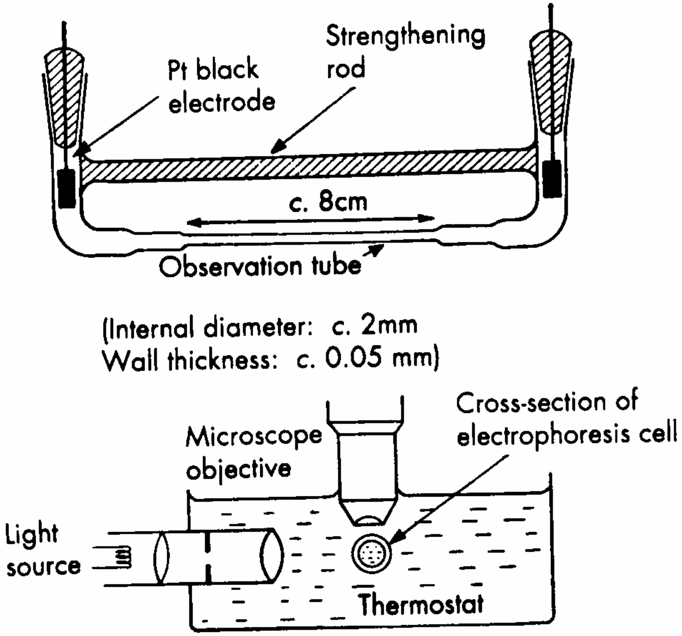
http://en.wikipedia.org/wiki/Electrophoresis

Synthesis of Nano Materials- 1D from Liquid

❑ Electrophoresis

electrophoresis is a motion of dispersed particles relative to a fluid under influence of electric field that is space uniform. Alternatively, similar motion in space non-uniform electric field is called dielectrophoresis.

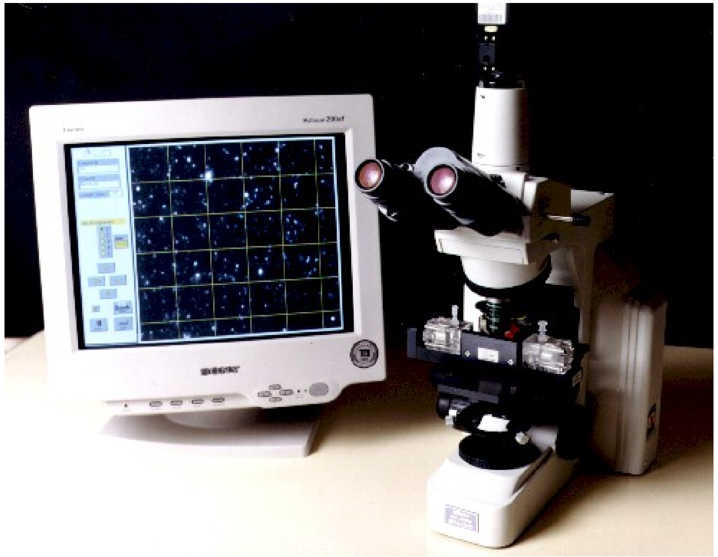


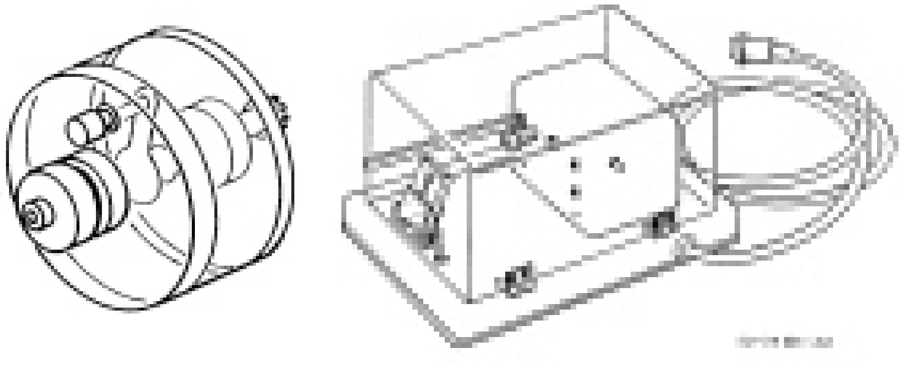


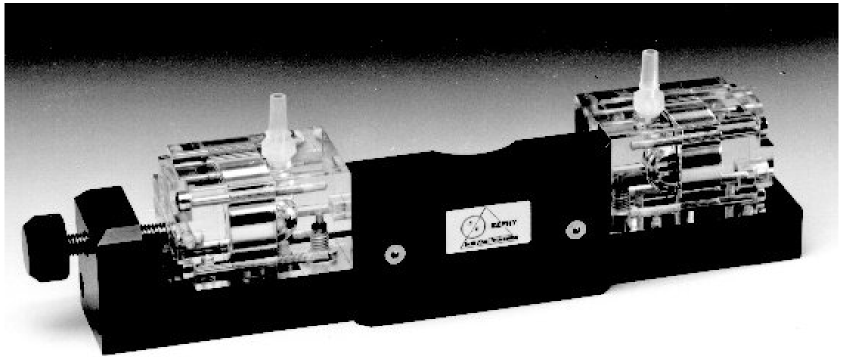
http://en.wikipedia.org/wiki/Electrophoresis

Synthesis of Nano Materials- 1D from Liquid

❑ Electrophoresis







http://www.micromeritics.com/

http://www.lavallab.com/eng/zeta-eng/zeta-meter.htm

Synthesis of Nano Materials- 1D from Liquid

☐ **Template-based** (electrophoretic deposition)

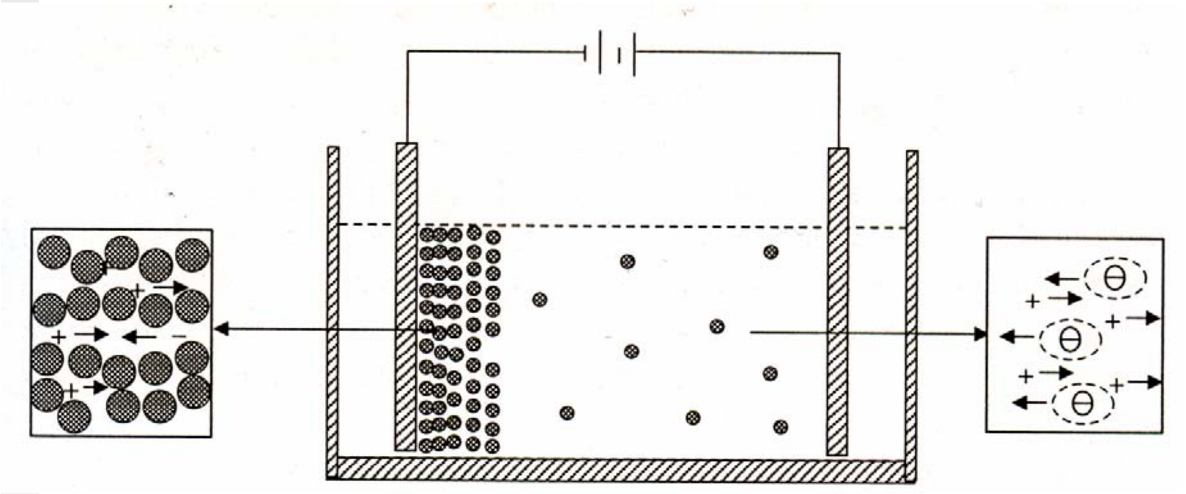
- A characteristic feature of this process is that colloidal particles suspended in a liquid medium migrate under the influence of an electric field (electrophoresis) and are deposited onto an electrode. All colloidal particles that can be used to form stable suspensions and that can carry a charge can be used in electrophoretic deposition. This includes material classes such as polymers, pigments, dyes, ceramics and metals.

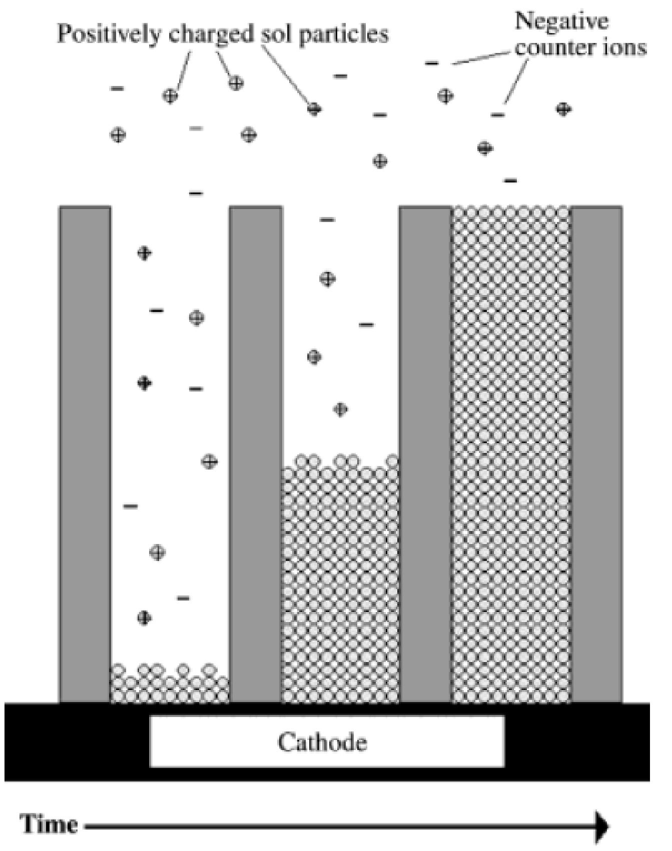
- The process is useful for applying materials to any electrically conductive surface. The materials which are being deposited are the major determining factor in the actual processing conditions and equipment which may be used.

http://en.wikipedia.org/wiki/Electrophoretic_deposition

Synthesis of Nano Materials- 1D from Liquid

- ☐ **Template-based** (electrophoretic deposition)

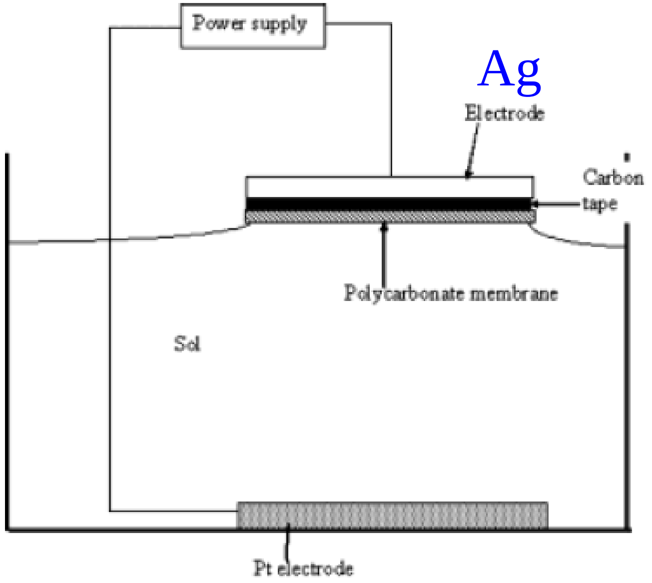




S.J. Limmer, Adv. Func Mater. 12 59 (2002).

Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (electrophoretic deposition)



	Precursors	Solvents / Other chemicals	pH
TiO_2	Titanium (IV) isopropoxide	Glacial acetic acid, water, lactic acid, glycerol, ethylene glycol	~2
$BaTiO_3$	Titanium (IV) isopropoxide, barium acetate	Glacial acetic acid, ethylene glycol	~5
SiO_2	Tetraethyl orthosilicate	Ethanol, water, hydrochloric acid	~3
$SrNb_2O_6$	Strontium nitrate, niobium chloride	Ethylene glycol, ethanol, citric acid, water	~1
$Pb(Zr,Ti)O_3$	Lead (II) acetate, titanium isopropoxide, zirconium *n*-propoxide	Glacial acetic acid, water, lactic acid, glycerol, ethylene glycol	~4

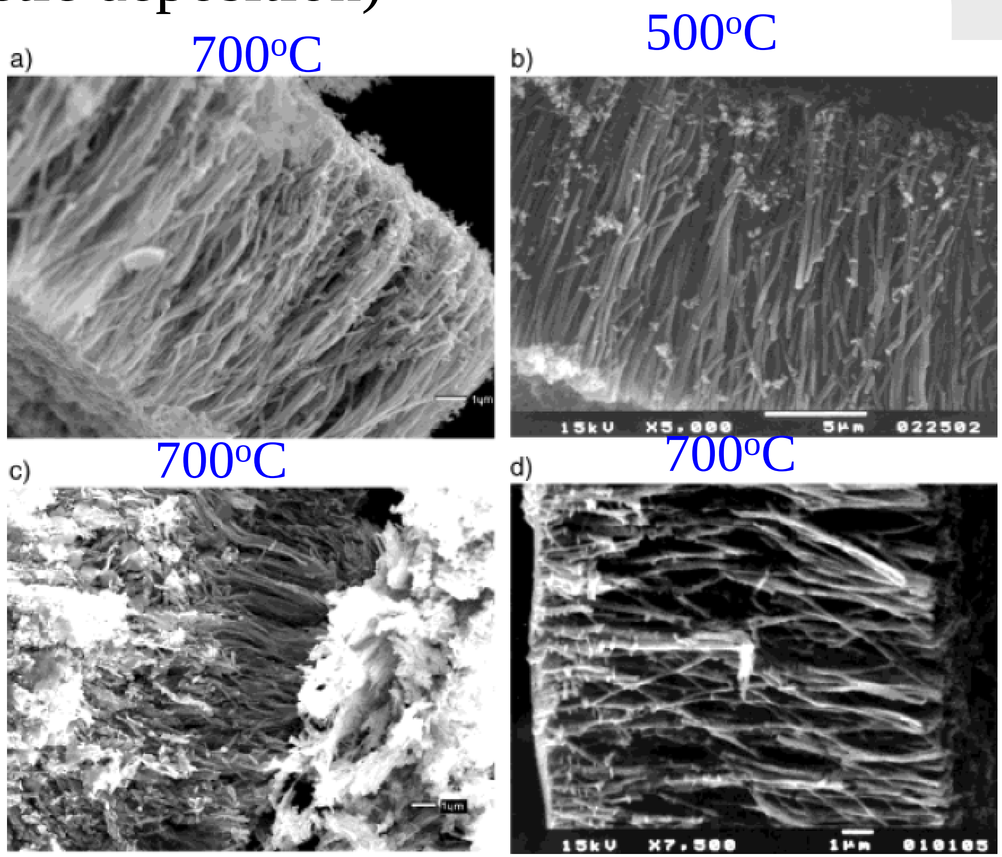


Fig. 3. SEM images of a) $BaTiO_3$, b) SiO_2, c) Sr_2-Nb_2O_7, and d) PZT nanorods grown in a PC membrane with 200 nm diameter pores by sol–gel electrophoresis.

S.J. Limmer, Adv. Func Mater. 12 59 (2002).

Synthesis of Nano Materials- 1D from Liquid

- **Template-based** (electrophoretic deposition)

ex) $Pb(Zr,Ti)O_3$

- track-etched hydrophilic PC

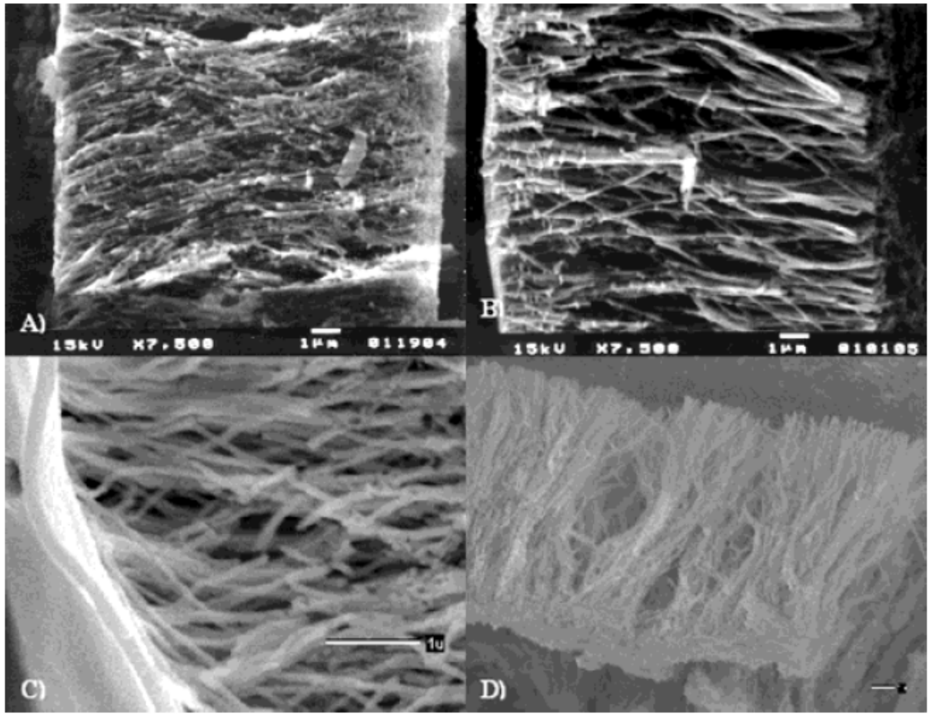
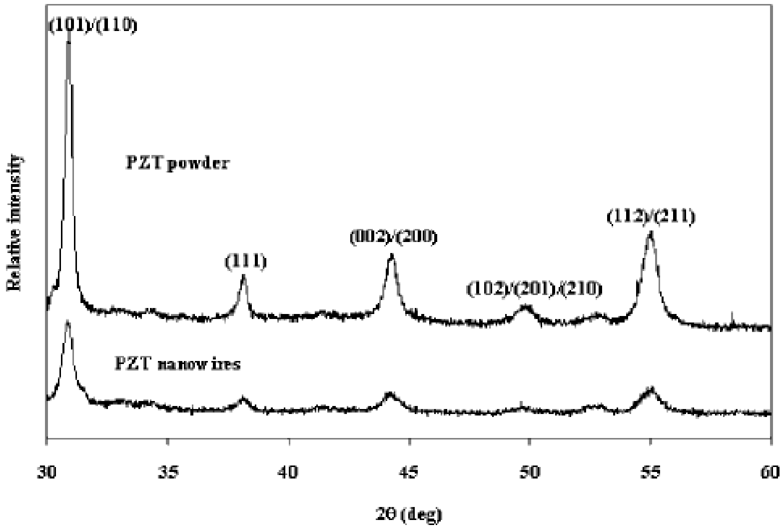


Fig. 1. a) PZT nanowires grown in a 100 nm diameter membrane. b) PZT nanowires grown in a 200 nm diameter membrane. c) Close up showing the films to which the nanowires are attached. d) Image showing the large area over which the wires are grown. The scale bar on all four images is 1 μm.



no preferred orientation

S.J. Limmer, Adv. Mater. 13 1269 (2001).

Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (electrophoretic deposition)

ex) ZnO

ZnO colloidal sol, AAO template

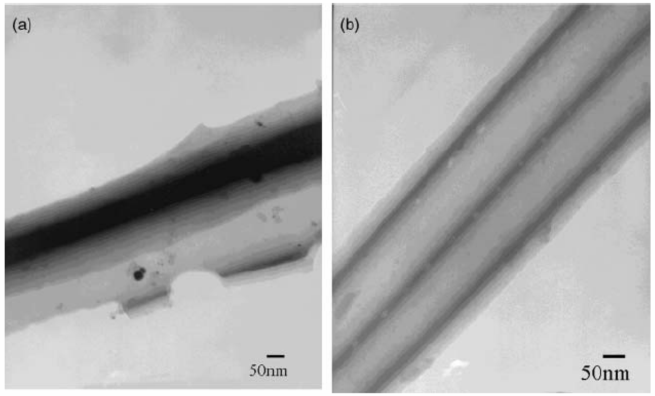
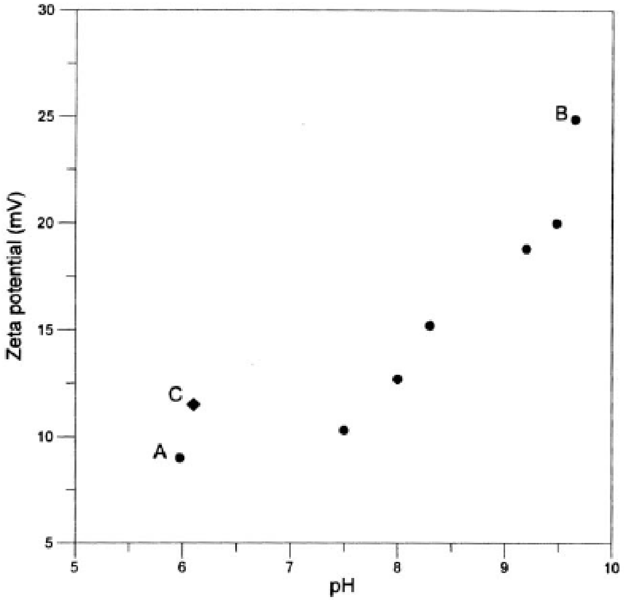


Fig. 6 Typical TEM images for ZnO arrays showing (a) a nanofibril and (b) a nanotubule.



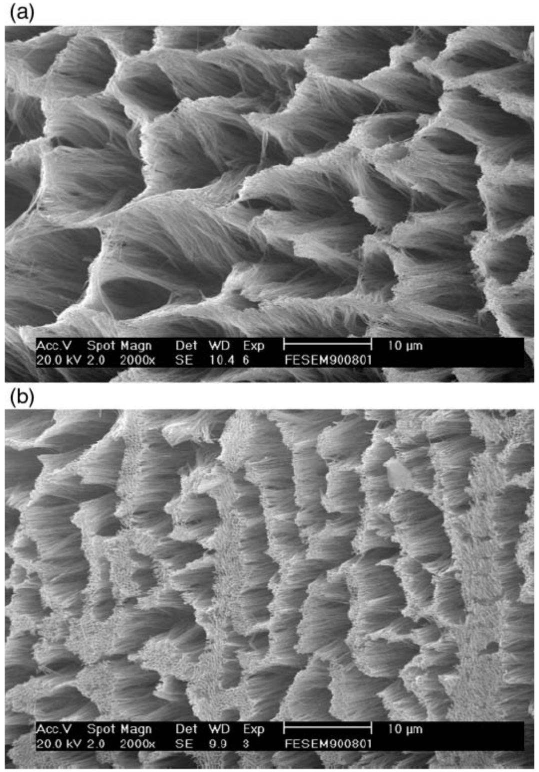
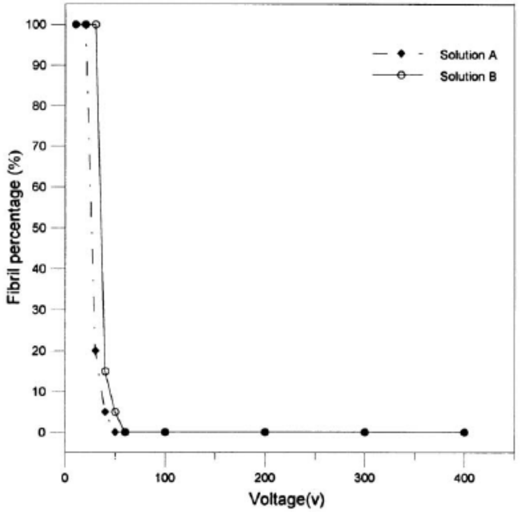


Fig. 3 SEM micrographs of the deposited ZnO nanowire arrays obtained at (a) 20 and (b) 200 V.



Y.C. Wang, J. Mater. Chem. 12 (2002) 2439.

Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (coating+dissolution)

- polyelectrolyte (PDADMAC/PSS)-layer by layer deposition
- PDADMAC/TALH(titanium bis9ammonium lactato) dihydroxide)

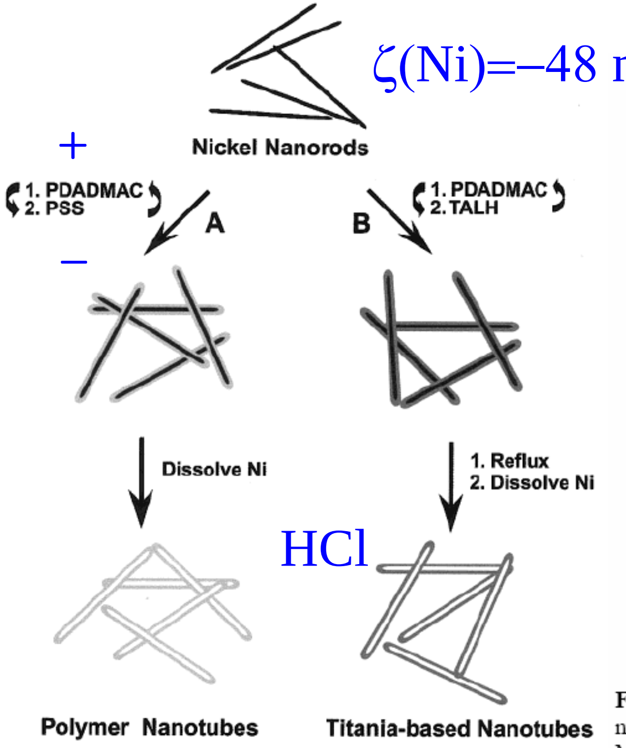


Figure 1. Schematic illustration of the preparation of polymer and inorganic–organic composite nanotubes by the LbL-CT strategy.

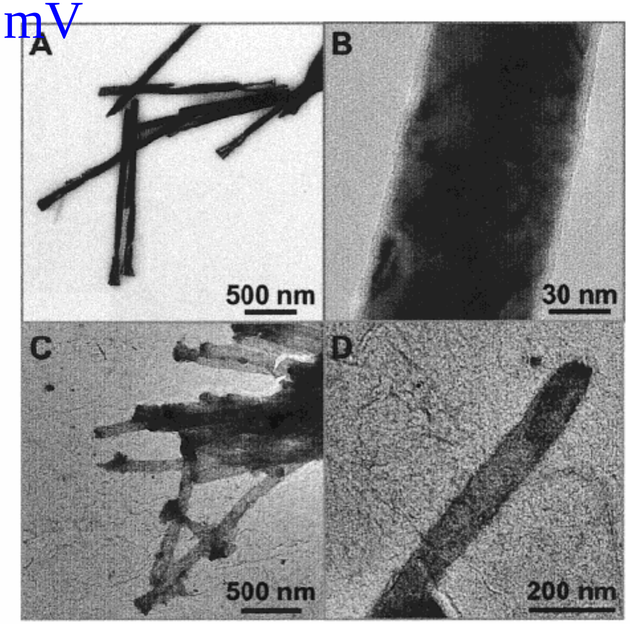


Figure 2. TEM images of (A) uncoated nickel nanorods, (B) a nickel nanorod coated with eight layers of polyelectrolyte [(PDADMAC/PSS)$_4$], (C) polymer nanotubes obtained upon dissolution o the sacrificial nickel nanorod, and (D) a higher magnification image of a polymer nanotube.

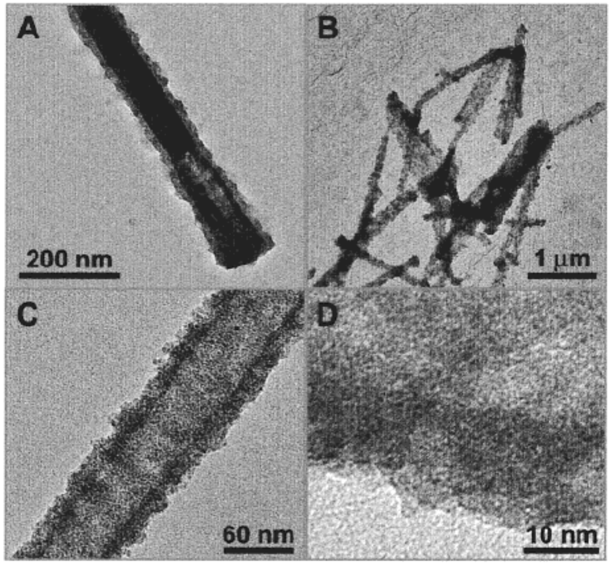


Figure 3. TEM images of (A) a nickel nanorod coated with titania/PDADMAC coating, (B) titania-based nanotubes obtaine on dissolution of coated nickel nanorods, (C) a higher magnificatio image of a nanotube, and (D) a high-resolution image of a composite (titania/PDADMAC) nanotube showing the titania nanoparticles.

K. Subramanya, Nano Lett. 1 (2001) 727.

Synthesis of Nano Materials- 1D from Liquid

☐ **Template-based** (coating+burn-out)

- suction filtering unit
- Zr(OnPr)$_4$ in C_2H_5OH, Al(O^{sec}Bu)$_3$ in CCl_4, $SiCl_4$ in CCl_4
- calcine at 1023 K

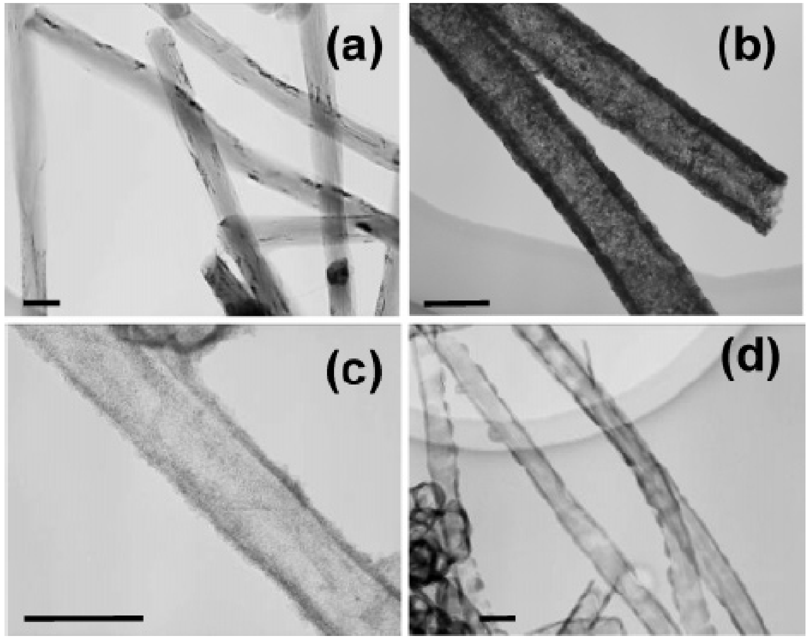


Figure 1. TEM images of (a) VGCF, (b) ZrO_2 nanotubes, (c) Al_2O_3 nanotubes, and (d) SiO_2 nanotubes. The number of coating processes is 20. The scale bars represent 200 nm.

108 ***Nanomaterials***

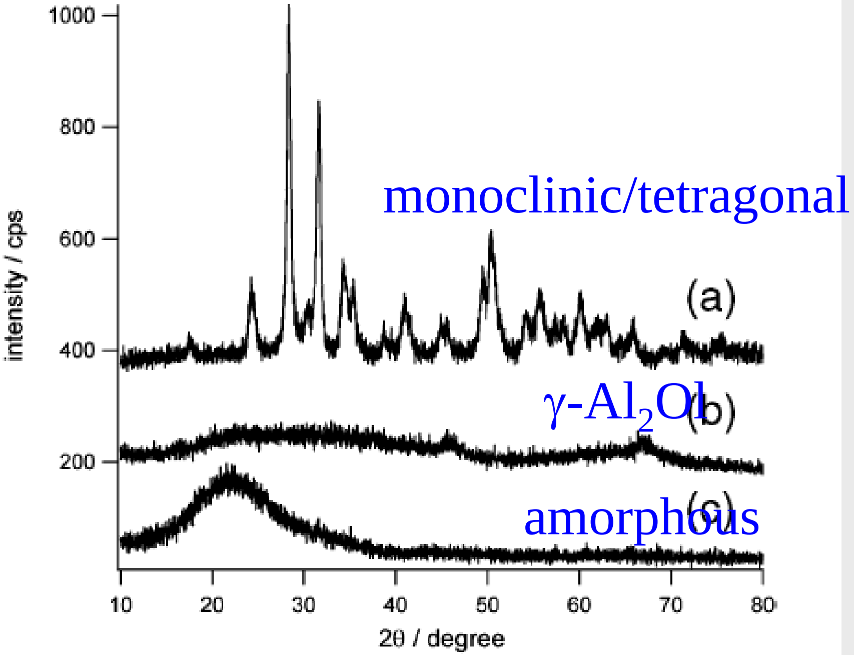


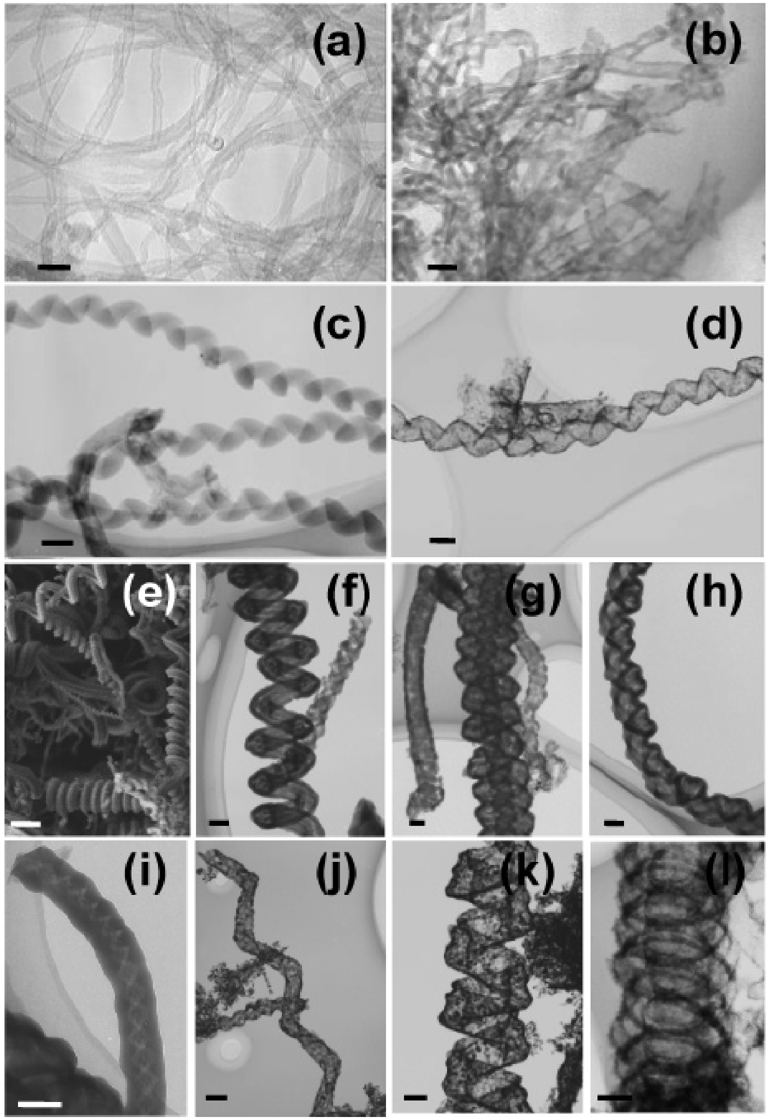
Figure 2. XRD patterns of (a) ZrO_2, (b) Al_2O_3, and (c) SiO_2 nanotubes.

VGCF (vapor grown carbon fiber)

H. Ogihara, Chem. Mater. 18, 21 (2006).

Synthesis of Nano Materials- 1D from Liquid

- **Template-based** (coating+burn-out)



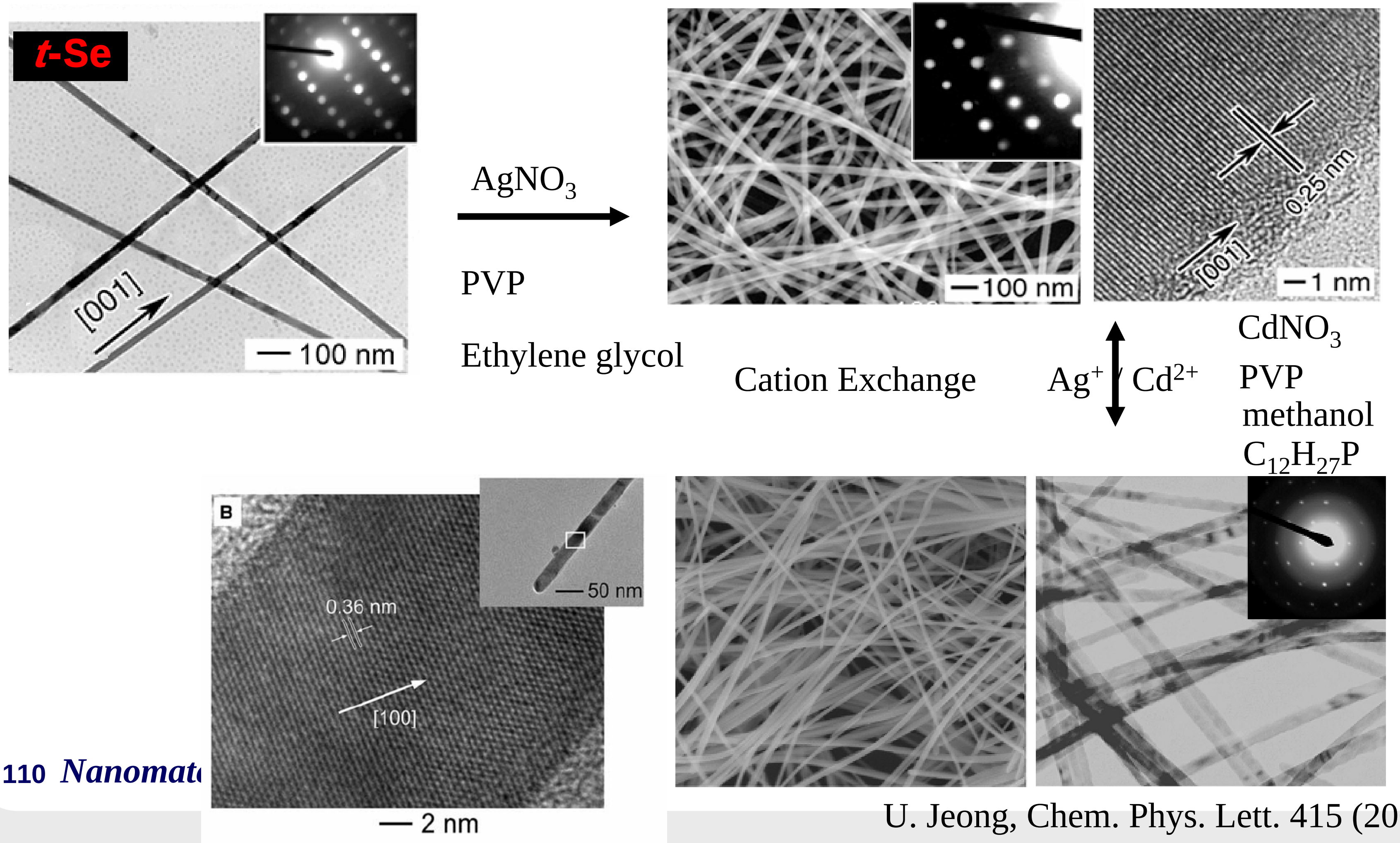
CNC1: carbon nanocoil
CNC2: carbon nanotube

Figure 3. TEM and SEM images of (a) CNT, (b) ZrO_2 nanotubes synthesized using CNT (the number of coating processes is 40), (c) CNC1, (d) ZrO_2 nanotubes synthesized using CNC1 (the number of coating processes is 40), (e) CNC2, (f−i) SiO_2 nanotubes synthesized using CNC2 (the number of coating processes is 20), (j and k) ZrO_2 nanotubes synthesized using CNC2 (the number of coating processes is 10), and (l) Al_2O_3 nanotubes synthesized using CNC2 (the number of coating processes is 20). The scale bars shown in panels a and b; e; and c, d, and f−l represent 30 nm, 1 μm, and 200 nm, respectively.

H. Ogihara, Chem. Mater. 18, 21 (2006).

Synthesis of Nano Materials- 1D from Liquid

- ❑ **Template-based** (chemical templating)



$\xrightarrow{AgNO_3}$

PVP

Ethylene glycol

Cation Exchange

Ag^+ / Cd^{2+}

$CdNO_3$

PVP

methanol

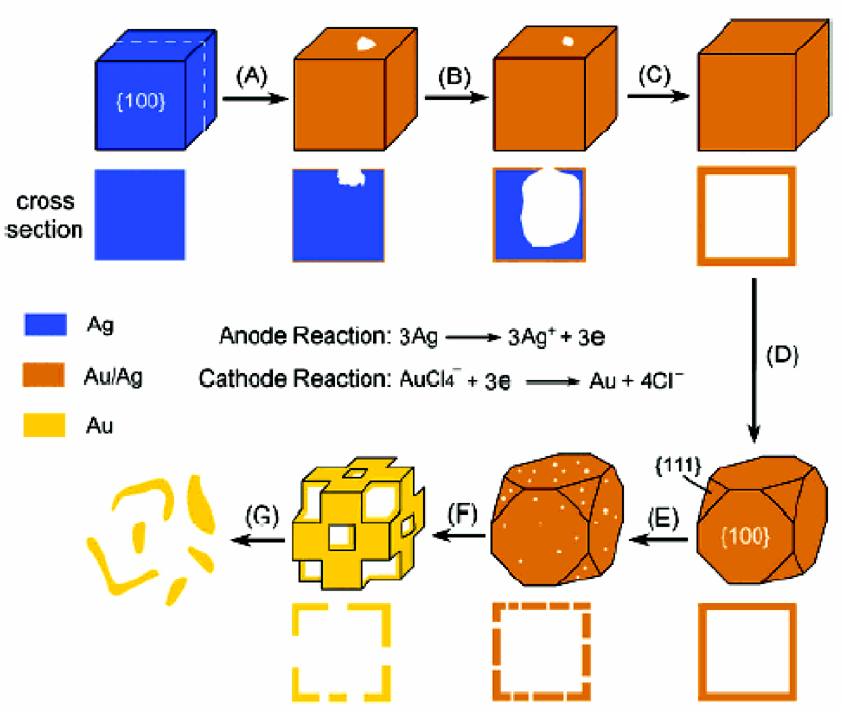
$C_{12}H_{27}P$

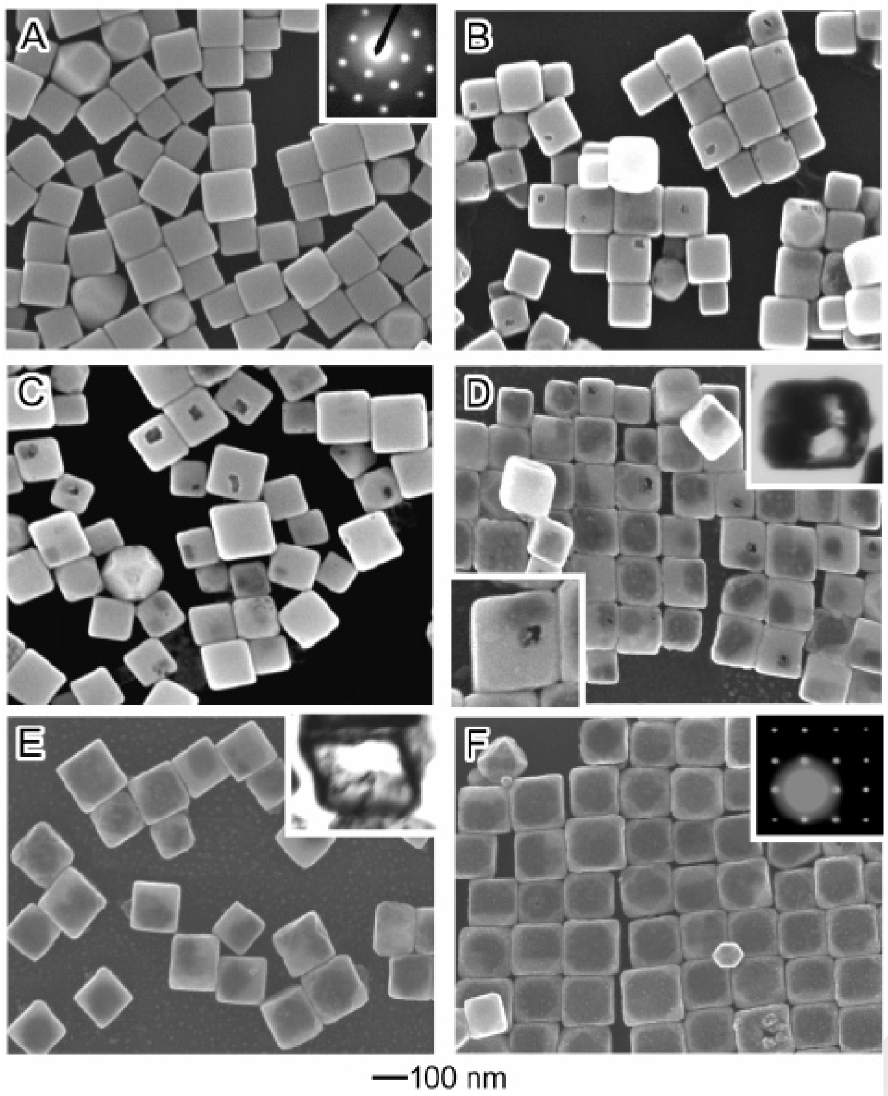
U. Jeong, Chem. Phys. Lett. 415 (2005) 246

Synthesis of Nano Materials- 1D from Liquid

Template-based (galvanic replacement)

Galvanic Replacement Reaction
1. Alloy formation
2. Hollow structures
Ex) Ag+$HAuCl_4$
3. dealloying

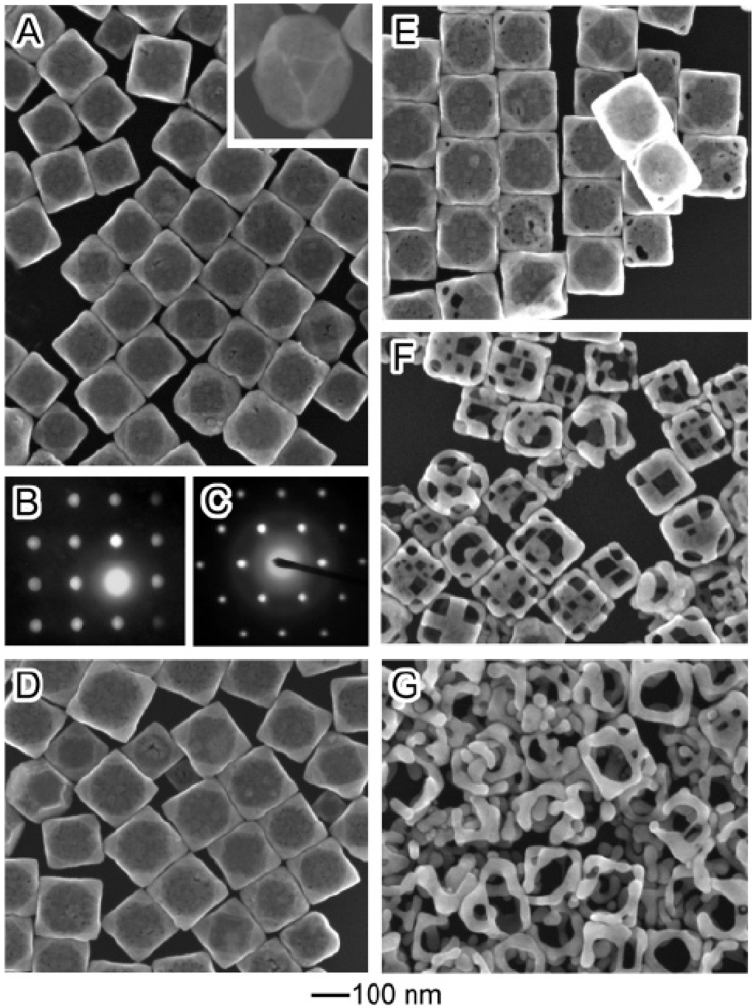




Y. Sun, J. Am. Chem. Soc. 126 (2004) 3892.

Synthesis of Nano Materials- 1D from Liquid

❑ Template-based (galvanic replacement)



Y. Sun, J. Am. Chem. Soc. 126 (2004) 3892.

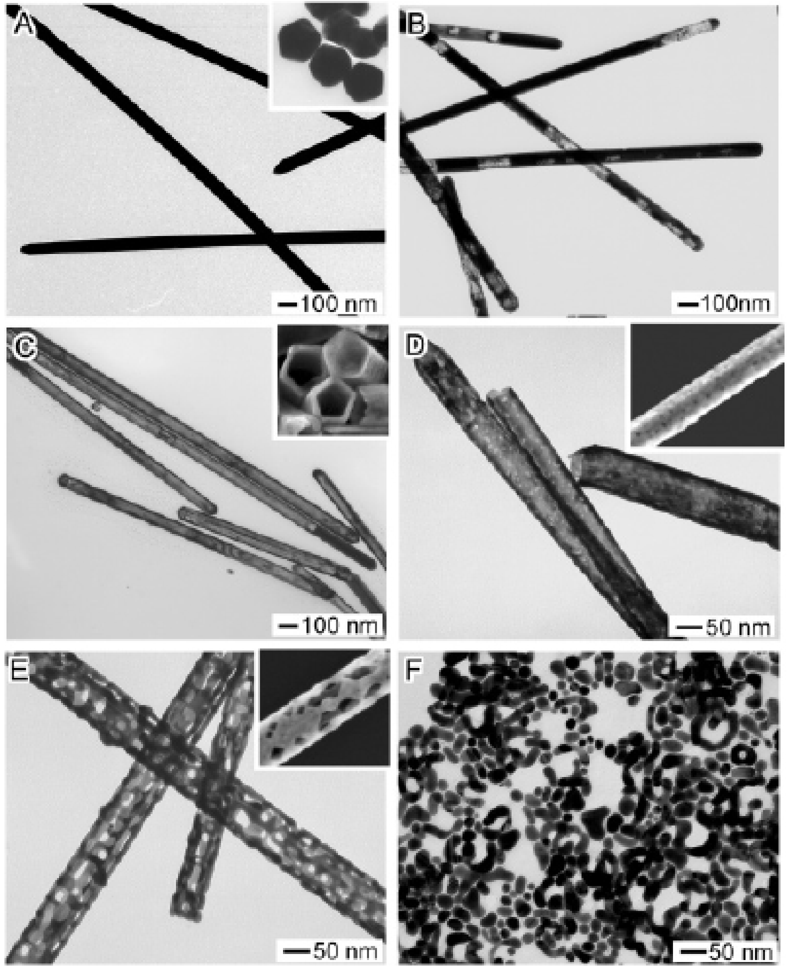


Figure 7. TEM images taken from silver nanowires (A) before and (B−F) after they had reacted with different volumes of 1 mM $HAuCl_4$ solution: (B) 0.3, (C) 0.6, (D) 1.5, (E) 2.3, and (F) 3.0 mL. The inset of A shows TEM image taken from the microtomed sample of silver nanowires. The insets of C−E are SEM images of the corresponding products.

Synthesis of Nano Materials- 1D from Liquid

- ☐ **Template-based (**galvanic replacement**)**

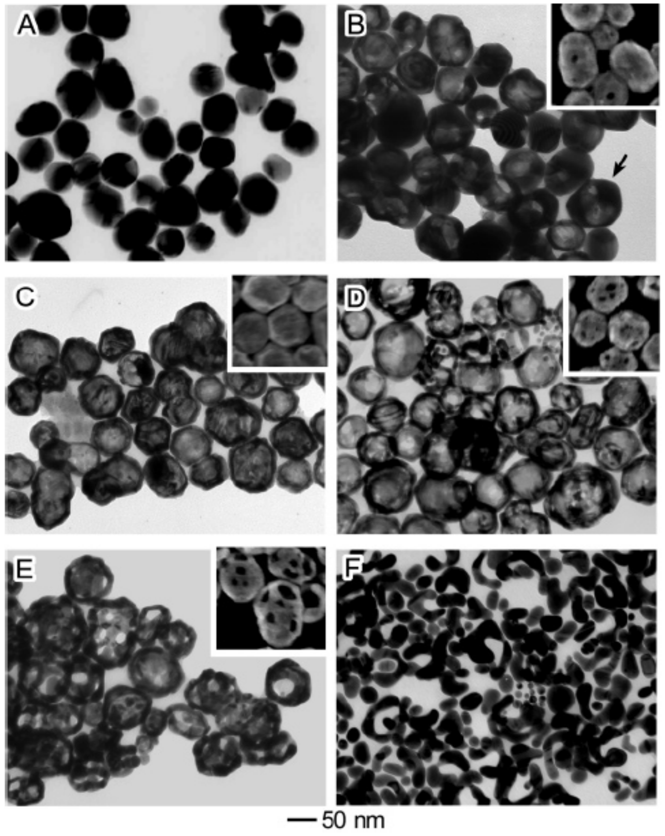


Figure 10. Photographs of aqueous dispersions of silver nanoparticles with spherical shape (see Figure 9A for a TEM image) before and after they had reacted with different volumes of 1 mM $HAuCl_4$ solution (from left to right): 0, 0.15, 0.25, 0.4, 0.6, 0.8, 1.0, 1.15, and 1.2 mL. Their major extinction peaks were located at 425, 451, 665, 705, 751, 793, 885, 990, and 1030 nm, respectively.

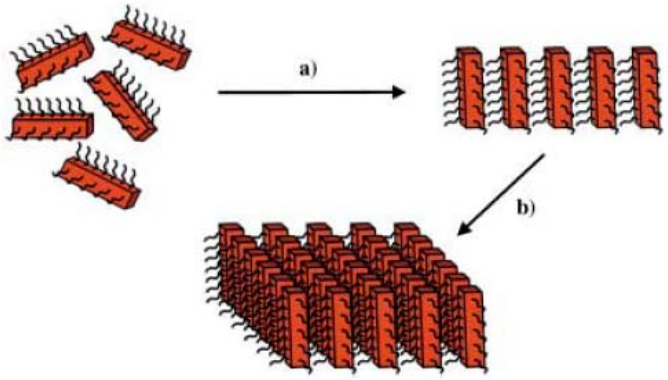
Y. Sun, J. Am. Chem. Soc. 126 (2004) 3892.

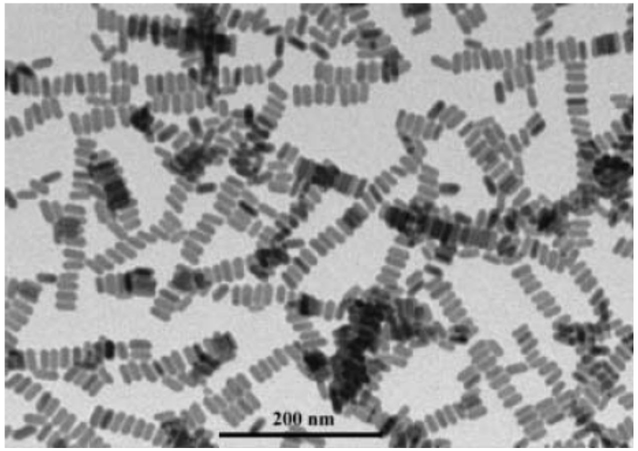
Synthesis of Nano Materials- 1D from Liquid

☐ **Template-based (**self assembly, surfactant**)**

Ex) $BaCrO_4$

- aqueous solution of sodium AOT (sodium bis (ethylhexylsulfosuccinate)+ $BaCl_2$
  → $Ba(AOT)_2$
- $Ba(AOT)_2$ in isooctane → Na_2CrO_4-containing NaAOT microemulsion
- Surfactant induced self assembly of nanoparticle chains and superlattices



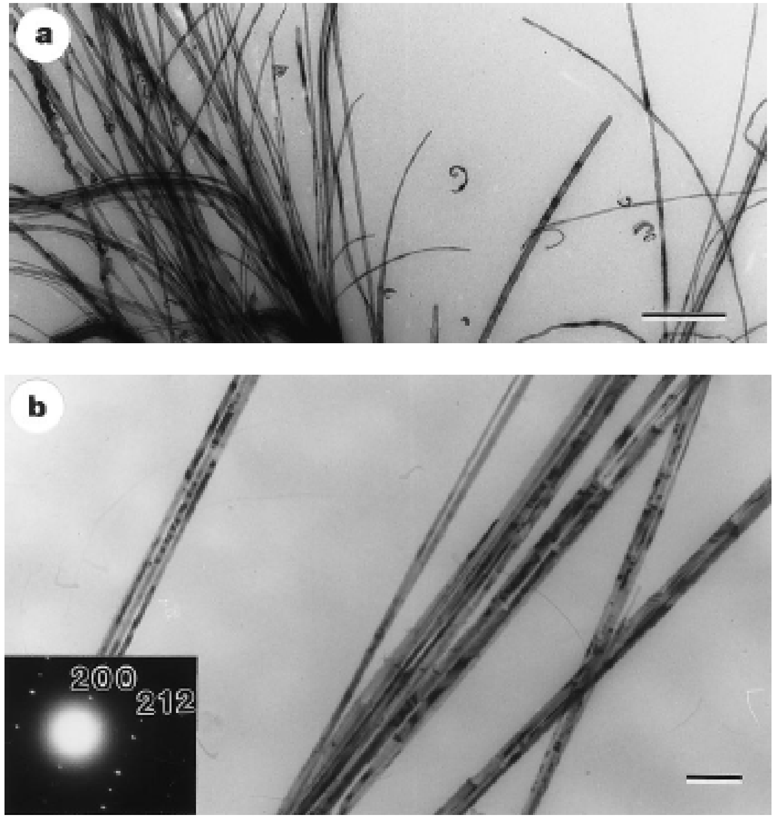


H. Colfen, Angew. Chem. Int. Ed. 42 (2003) 2350.

Synthesis of Nano Materials- 1D from Liquid

❑ Template-based (self assembly, surfactant)

Ex) $BaCrO_4$



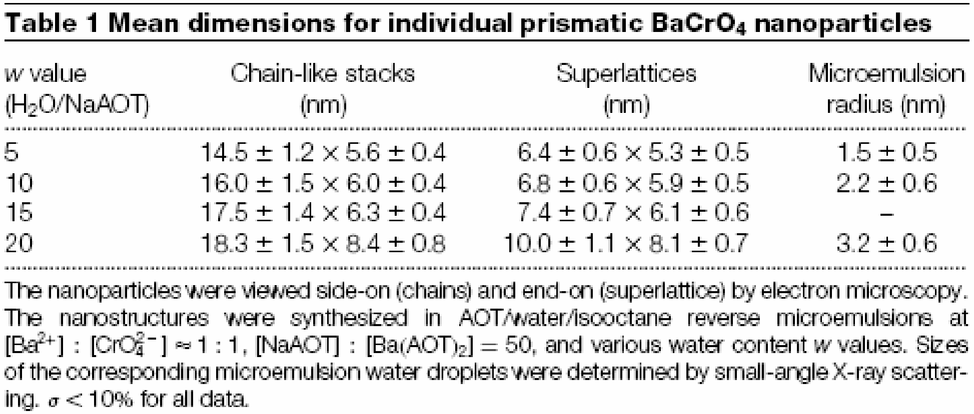
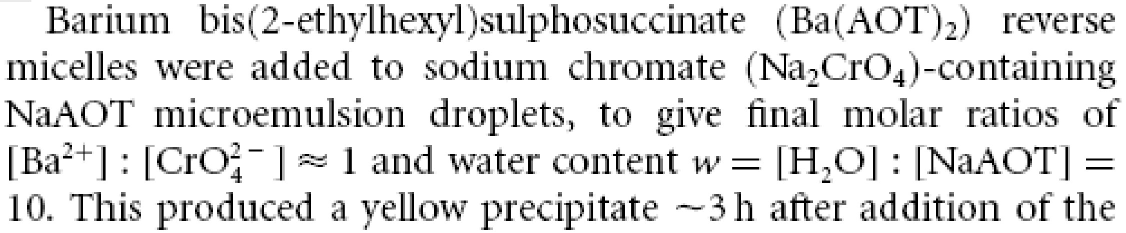


Table 1 Mean dimensions for individual prismatic $BaCrO_4$ nanoparticles

w value (H_2O/NaAOT)	Chain-like stacks (nm)	Superlattices (nm)	Microemulsion radius (nm)
5	14.5 ± 1.2 × 5.6 ± 0.4	6.4 ± 0.6 × 5.3 ± 0.5	1.5 ± 0.5
10	16.0 ± 1.5 × 6.0 ± 0.4	6.8 ± 0.6 × 5.9 ± 0.5	2.2 ± 0.6
15	17.5 ± 1.4 × 6.3 ± 0.4	7.4 ± 0.7 × 6.1 ± 0.6	–
20	18.3 ± 1.5 × 8.4 ± 0.8	10.0 ± 1.1 × 8.1 ± 0.7	3.2 ± 0.6

The nanoparticles were viewed side-on (chains) and end-on (superlattice) by electron microscopy. The nanostructures were synthesized in AOT/water/isooctane reverse microemulsions at $[Ba^{2+}] : [CrO_4^{2-}] \approx 1:1$, [NaAOT] : $[Ba(AOT)_2] = 50$, and various water content *w* values. Sizes of the corresponding microemulsion water droplets were determined by small-angle X-ray scattering. $\sigma < 10\%$ for all data.


Barium bis(2-ethylhexyl)sulphosuccinate ($Ba(AOT)_2$) reverse micelles were added to sodium chromate (Na_2CrO_4)-containing NaAOT microemulsion droplets, to give final molar ratios of $[Ba^{2+}] : [CrO_4^{2-}] \approx 1$ and water content $w = [H_2O] : [NaAOT] = 10$. This produced a yellow precipitate ~3 h after addition of the

M. Li, Nature 402 (1999) 393.

Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based (**self assembly, surfactant**)**

- electrochemical synthesis (Au: anode, Pt: cathode
  C_{16}TAB-cationic surfactant, TC8AB-rod-inducing cosurfactant)

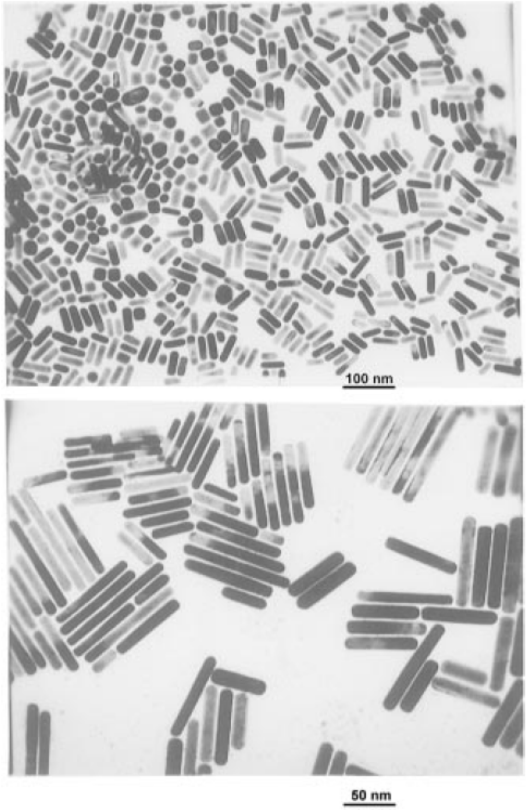
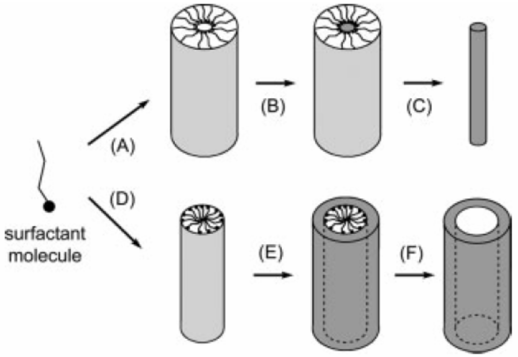


Figure 1. TEM images of Au nanorods with different mean aspect ratios: 2.6 (top) and 7.6 (bottom).



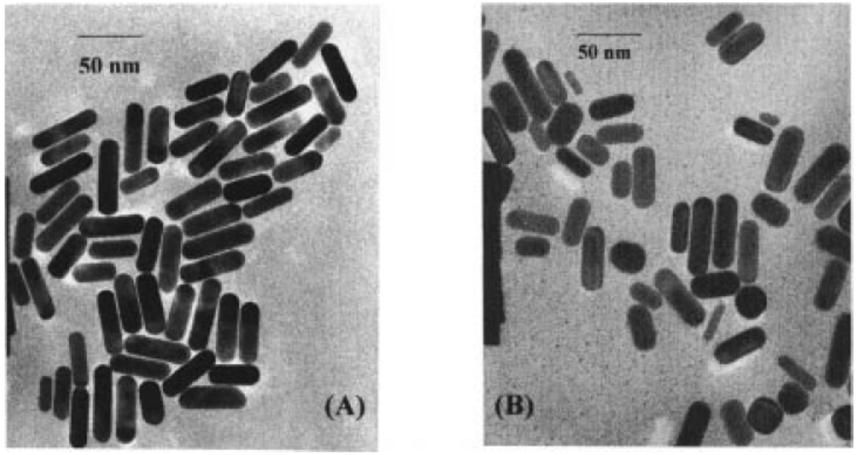


Figure 2. TEM images of gold nanorods taken from solution (A) at room temperature (B) after heating the solution sample to 100 °C.

temp ↑ aspect ratio ↓

Y.Y. Yu, J. Phys. Chem. B101 (1997) 6661.

M.B. Mohamed, J. Phys. Chem. B102 (1998) 9370.

Synthesis of Nano Materials- 1D from Liquid

☐ **Template-based** (block copolymer)

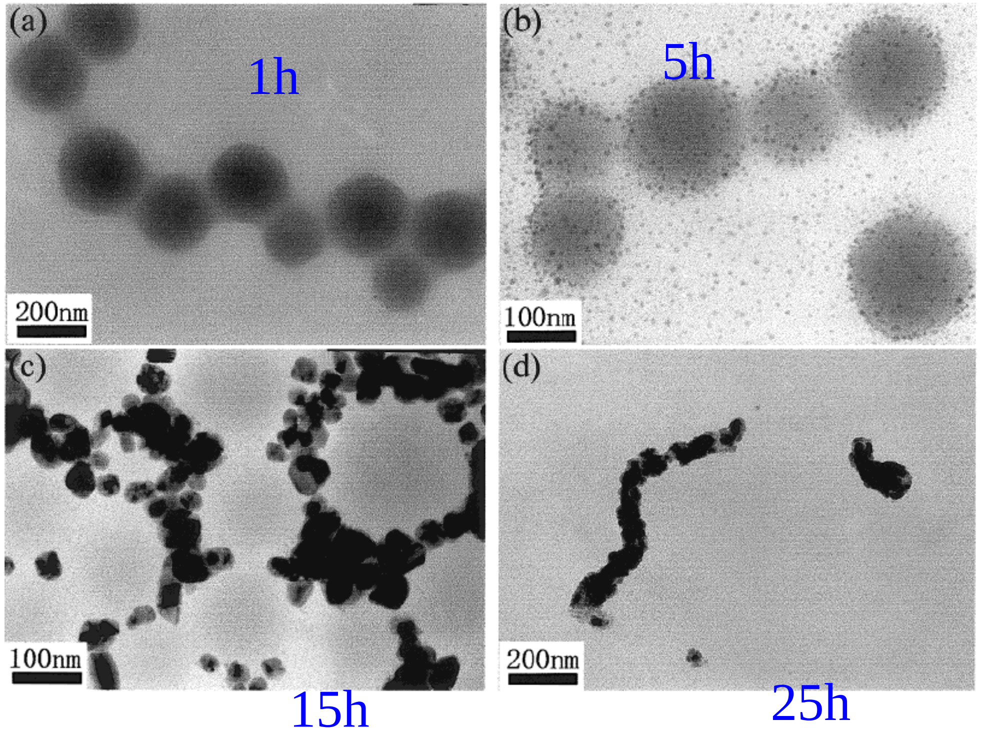
Ex) Ag nanowire

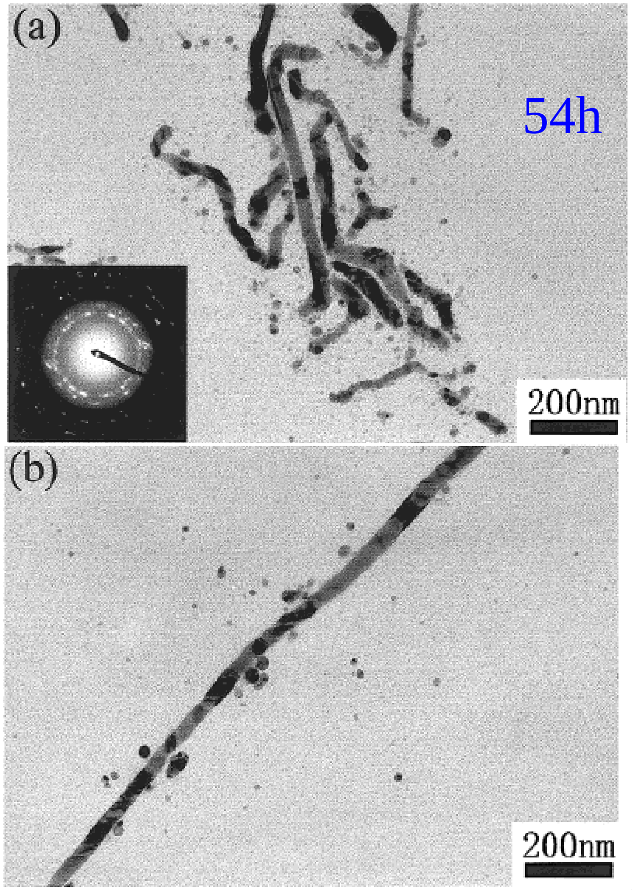
carboxylic acid group- interact with Ag^+

double hydrophilic block copolymer

poly(ethylene oxide)-*block*-poly(methacrylic acid) (PEO-*b*-PMAA)

$AgNO_3$



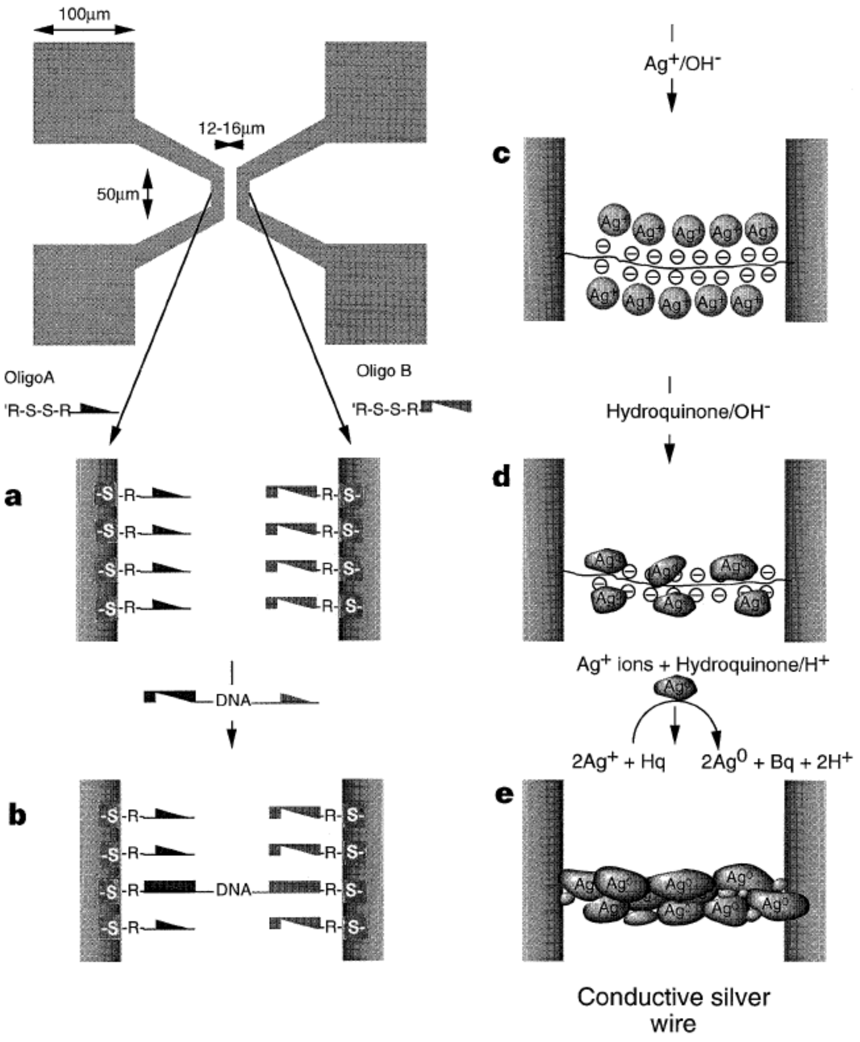


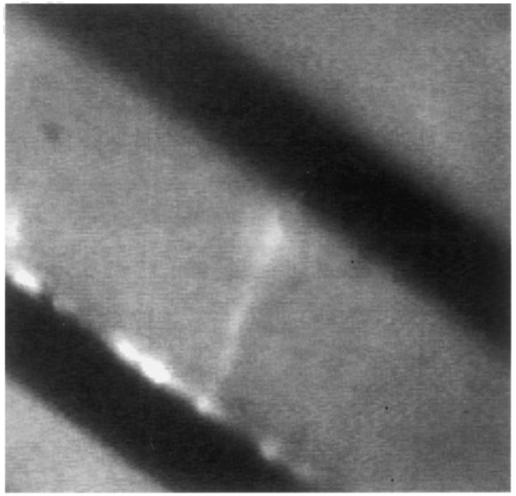
D. Zhang, Chem. Mater. 13 (2001) 2753.

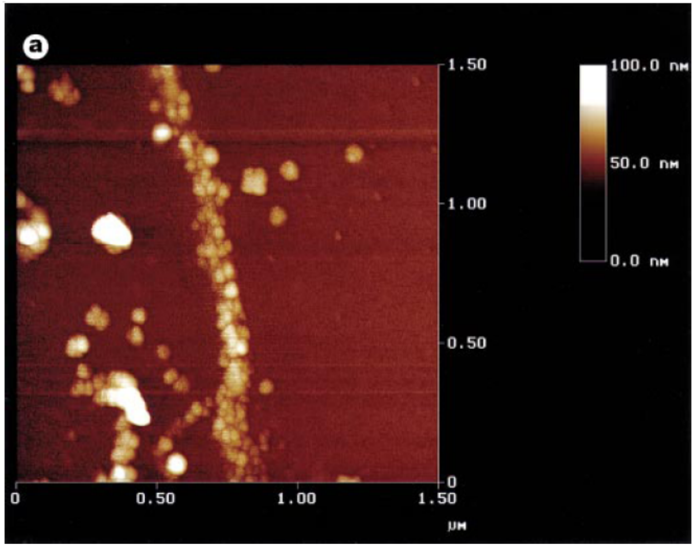
Synthesis of Nano Materials- 1D from Liquid

❑ **Template-based** (DNA-templated assembly)

Ex) Ag wire (Ag^+/Na^+ ion exchange)



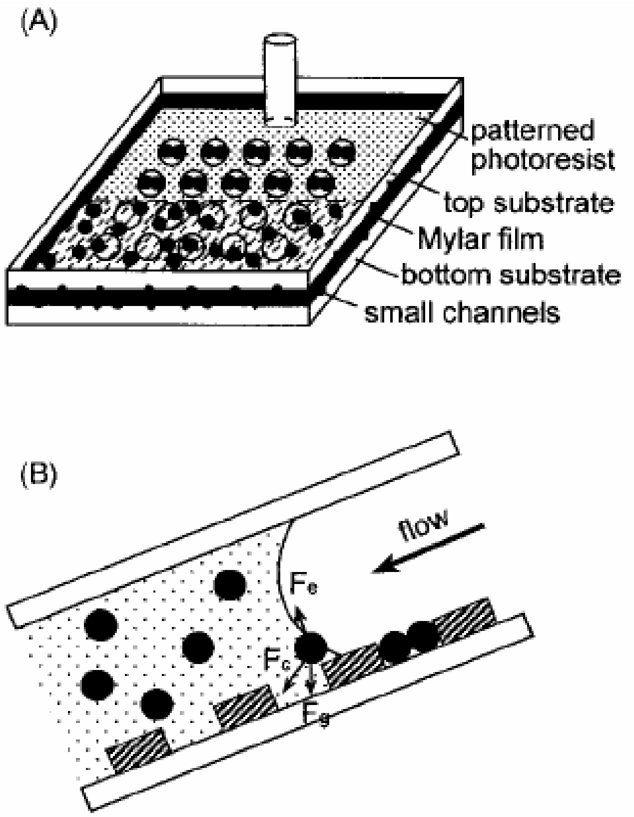




E. Braun, Nature, 391 (1998) 775.

Synthesis of Nano Materials- 1D from Liquid

❑ Nanowires from Self-Assembly



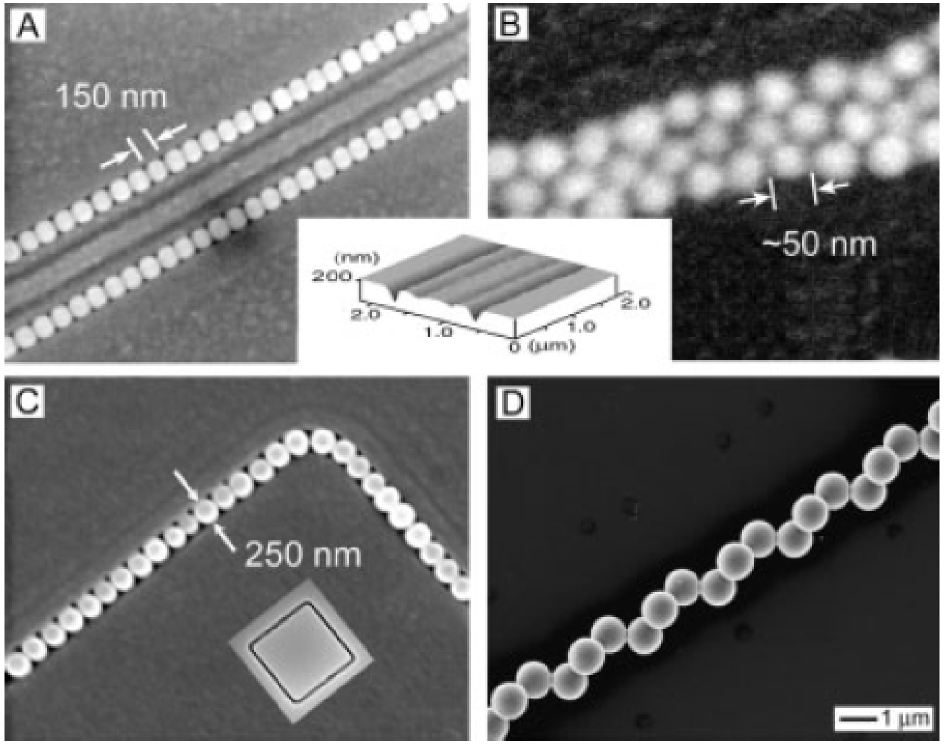


Fig. 21. A,B) Structures that were assembled from 150 nm polystyrene beads (A), and 50 nm Au colloids (B), by templating against 120 nm-wide channels patterned in a thin photoresist film (see the inset) [161a]. C) An L-shaped chain of Au@SiO$_2$ spheres assembled against a template (see the inset) patterned in a thin photoresist film [161c]. D) A spiral chain of polystyrene beads that were assembled by templating against a V-groove etched in the surface of a Si(100) wafer [161d].

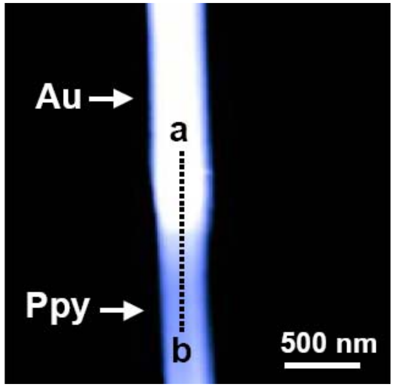
Y. Xia, J. Am. Chem.Soc. 123 (2001)8718.

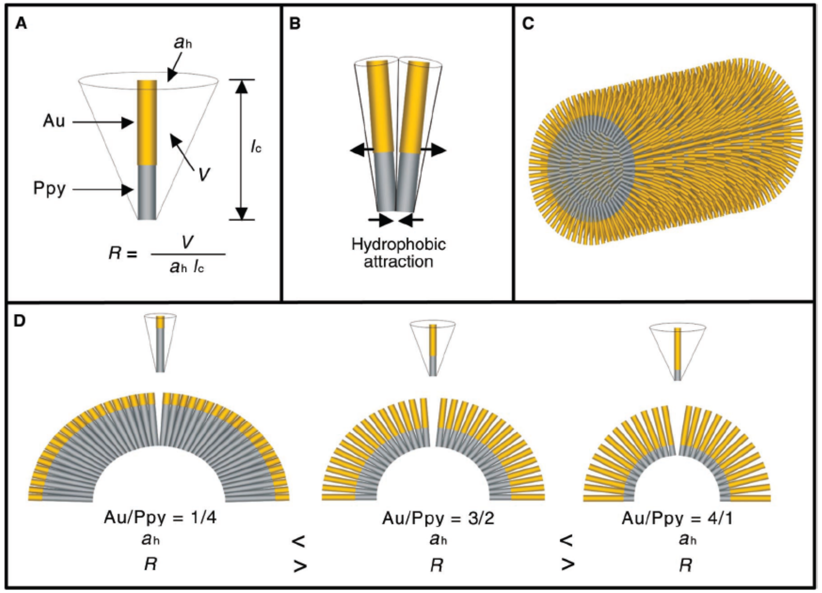
Y. Xia, Adv. Mater. 15, 353 (2003)

Synthesis of Nano Materials- 1D from Liquid

❑ Self-Assembly

metal-polymer amphiphile
(AAO+electrodeposition)

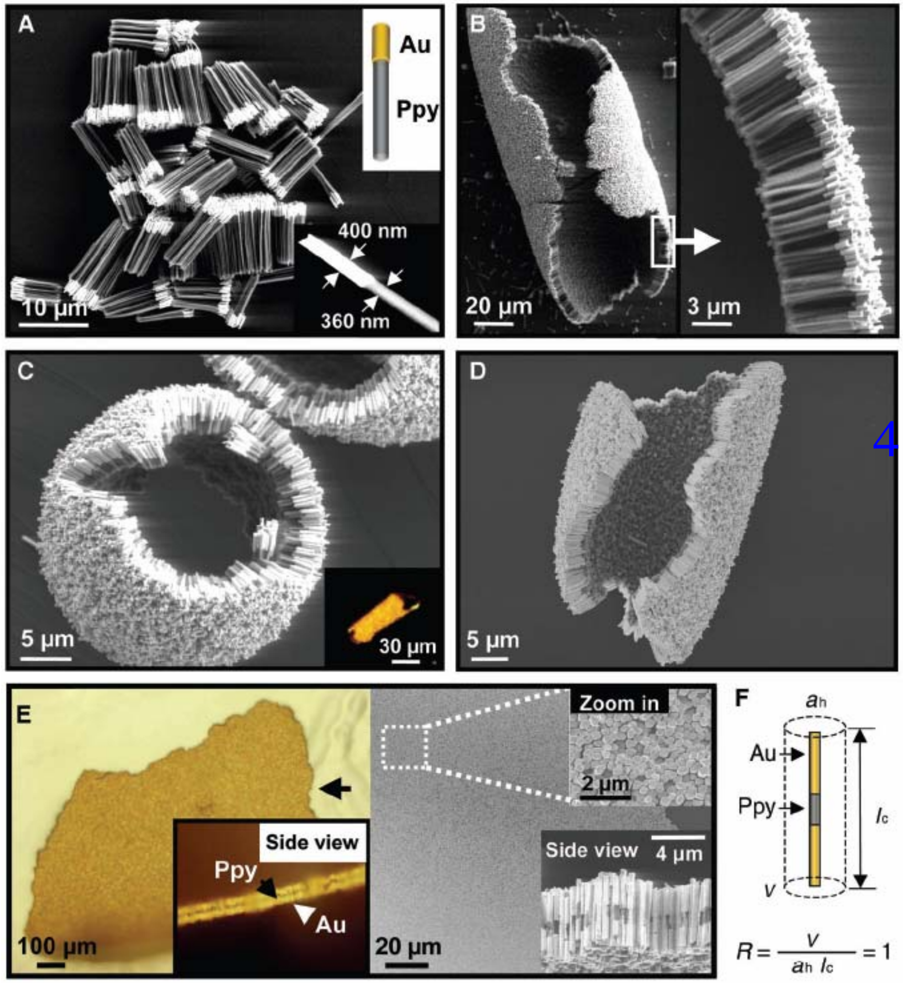




strong interaction between organic polymer ends

bundle

tube (1:4)



2:3

4:1

S. Park, Science 303 (2004) 348.

Synthesis of Nano Materials- 1D from Liquid

❑ Nanofibers from Electrospinning

High viscoelastic solutions under Electric Field

- Viscous polymer solutions
- Sol-gel processable metal oxides

1~30 kV

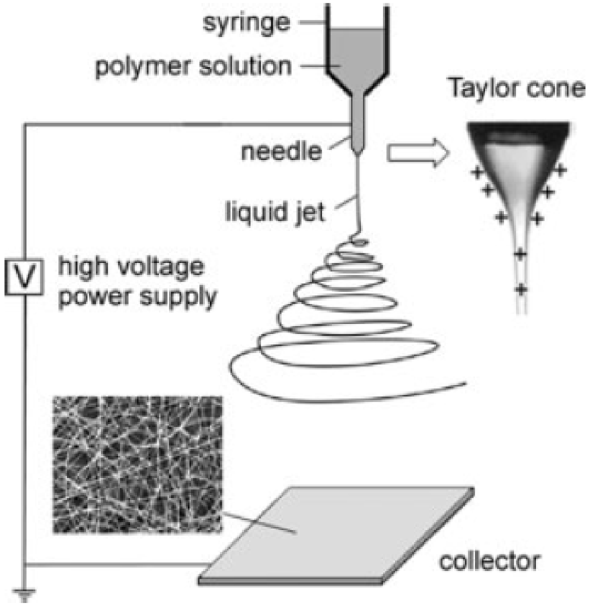


Figure 2. Schematic illustration of the basic setup for electrospinning. The insets show a drawing of the electrified Taylor cone and a typical SEM image of the nonwoven mat of poly(vinyl pyrrolidone) (PVP) nanofibers deposited on the collector.

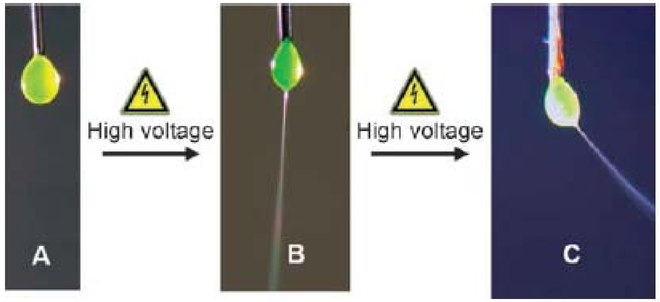


Figure 5. A droplet of a 5% solution of poly(ethylene oxide) (PEO) in water, dyed with fluorescein: A) in the absence of an applied voltage; B) at an applied voltage of 20 kV, with a jet perpendicular to the counter electrode; C) at an applied voltage of 20 kV, with a jet diagonal to the counter electrode.

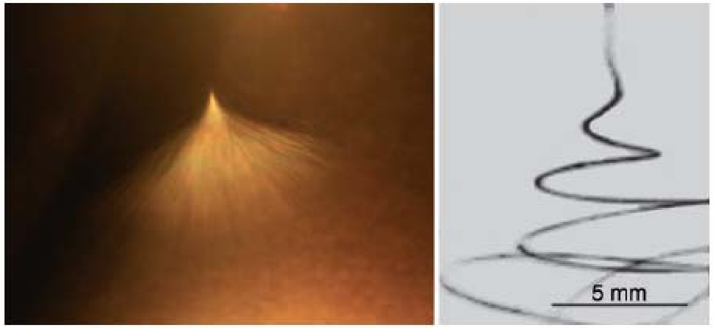


Figure 7. Left: Photograph of a jet of PEO solution during electrospinning. Right: High-speed photograph of jet instabilities.[37]

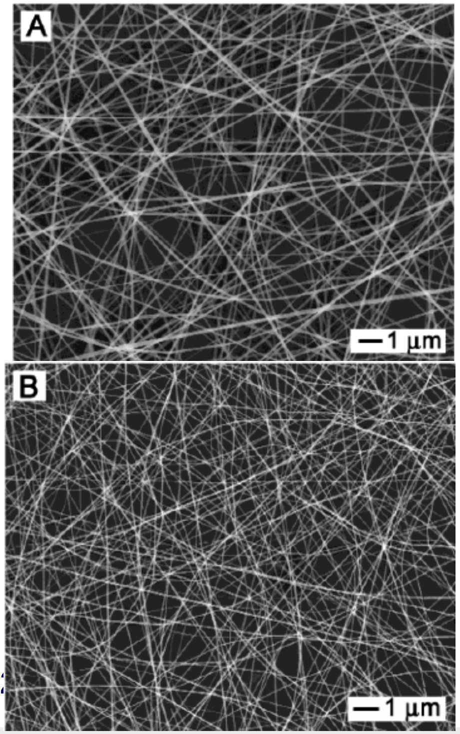
D. Li, Adv. Mater. 16 1151 (2004)

A. Greiner, Angew. Chem In. Ed. 46 5670 (2007)

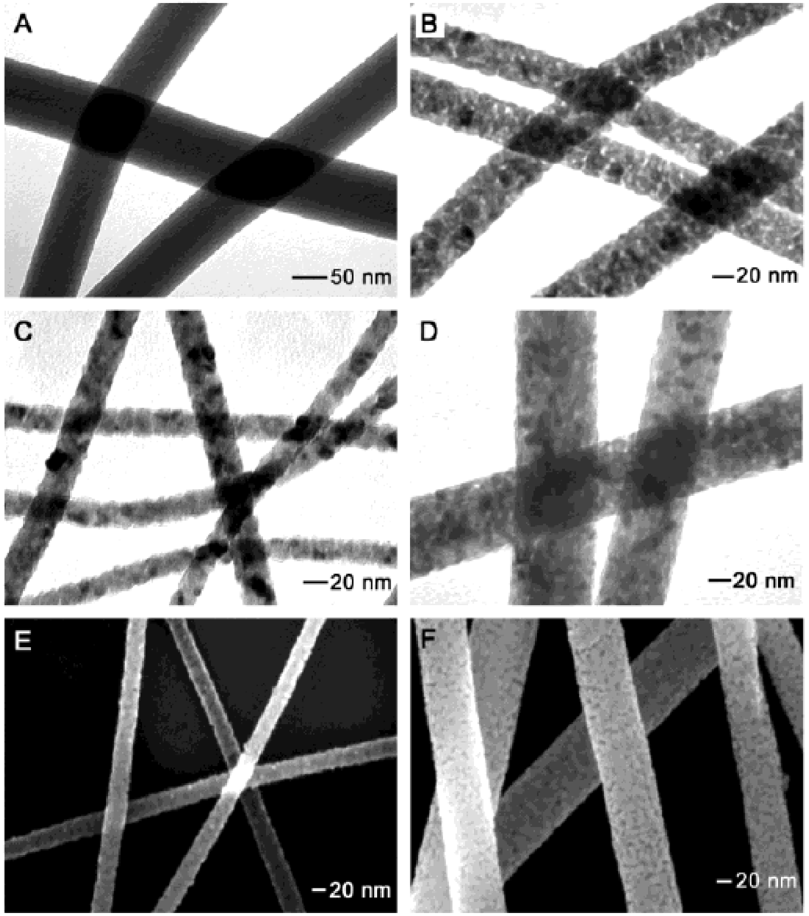
Synthesis of Nano Materials- 1D from Liquid

❑ Nanofibers from Electrospinning

- TiO_2/PVP composite nanofiber
- $Ti(O\textit{i}Pr)_4$ in (acetic acid+ethanol)
  + PVP in ethanol
- electrospinning



500°C
anatase



500°C

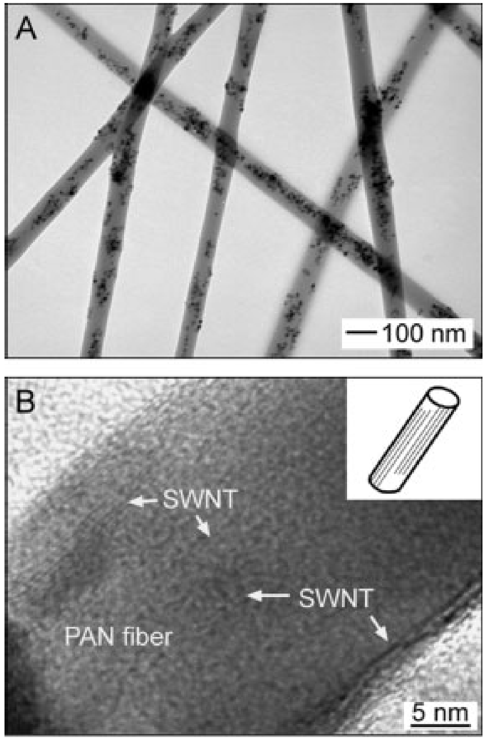
Figure 3. (A) TEM image of TiO_2/PVP composite nanofibers fabricated by electrospinning an ethanol solution that contained 0.03 g/mL PVP and 0.1 g/mL $Ti(O\textit{i}Pr)_4$. (B) TEM image of the same sample after it had been calcined in air at 500 °C for 3 h. (C, D) TEM images of nanofibers made of anatase that were prepared under the same conditions except that the precursor solution contained (C) 0.025 g/mL and (D) 0.15 g/mL $Ti(O\textit{i}Pr)_4$, respectively. (E, F) High-magnification SEM images taken from the samples shown in C and D, respectively. No gold coatings were applied to the samples for all SEM studies.

D. Li, Nano Letters 3, 555 (2003).

Synthesis of Nano Materials- 1D from Liquid

❑ Nanofibers from Electrospinning

Composite fibers



PVP+iron oxide

Figure 6. A) TEM image of poly(vinyl pyrrolidone) (PVP) nanofibers whose interiors had been encapsulated with iron oxide nanoparticles by directly adding this material to the electrospinning solution. B) High-resolution TEM image showing the alignment of CNTs in a poly(acrylonitrile) fiber with the diameter of about 50 nm. The inset shows a schematic illustration of the orientation of CNTs in a fiber. This figure was adapted from [44a].

Surface coating

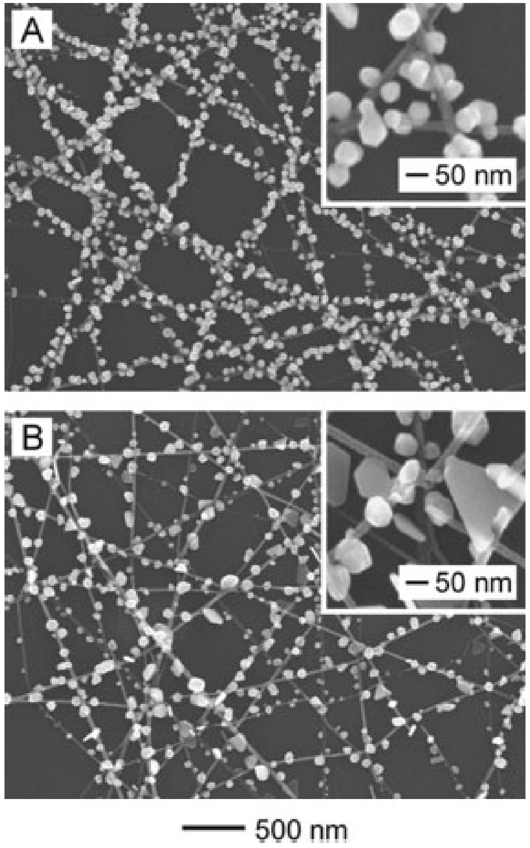


Figure 7. SEM images of anatase nanofibers whose surfaces had been decorated with gold (A) and silver (B) nanoparticles via photocatalytic reduction of $HAuCl_4$ and $AgNO_3$ in aqueous solutions, respectively.

D. Li, Adv. Mater. 16 1151 (2004)

Synthesis of Nano Materials- 1D from Liquid

❑ Nanofibers from Electrospinning

Hollow fibers

Porous

mineral oil

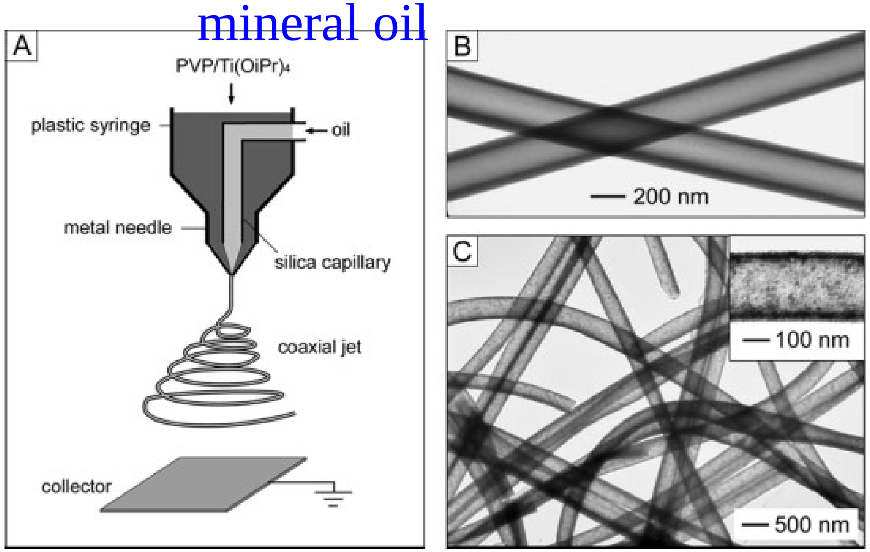


Figure 8. A) Schematic illustration of the setup used for direct fabrication of hollow nanofibers by electrospinning. It involves the use of a spinneret consisting of two coaxial capillaries, through which mineral oil and an ethanol solution containing poly(vinyl pyrrolidone) (PVP) and titanium tetraisopropoxide were simultaneously ejected to form a compound jet. B) TEM image of the as-spun hollow nanofibers whose walls were made of a composite of PVP and amorphous TiO_2. The oil cores had been extracted with octane. C) TEM image of anatase hollow nanofibers that were obtained by calcining the composite nanotubes at 500 °C in air. These figures were adapted from [21b] with permission. Copyright American Chemical Society, 2004.

500^{o}C

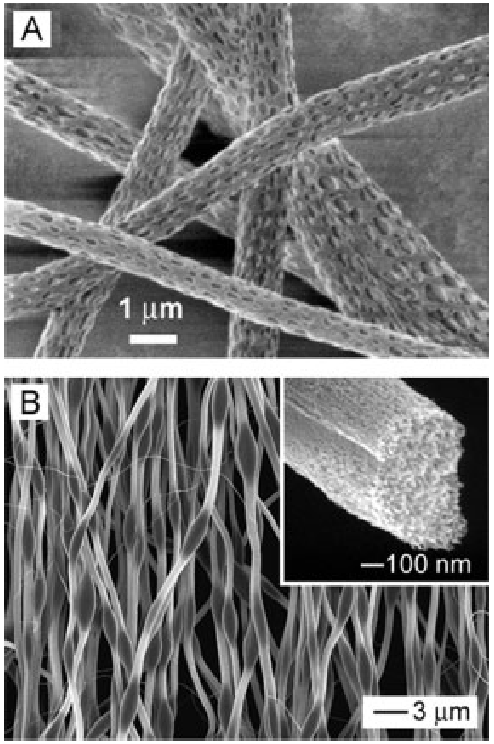


Figure 9. A) SEM image of porous poly(L-lactide) (PLA) fibers fabricated by electrospinning a solution of PLA in dichloromethane (adapted from [60]). B) SEM images of porous anatase nanofibers fabricated by co-electrospinning an ethanol solution of $Ti(OiPr)_4$/PVP and a poly(styrene) (PS) solution in a mixture of *N*,*N*-dimethyl formamide (DMF) and tetrahydrofuran (THF) (1:1 by volume) through a coaxial, two-capillary spinneret. The sample had been calcined in air to remove both PS and PVP. The inset shows a cross-sectional SEM image of the nanofiber, clearly indicating the formation of a mesoporous structure. This figure was adapted from [21b] with permission. Copyright American Chemical Society, 2004.

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D. Li, Adv. Mater. 16 1151 (2004)

Synthesis of Nano Materials- 1D from Liquid

❑ Nanofibers from Electrospinning

Alignment

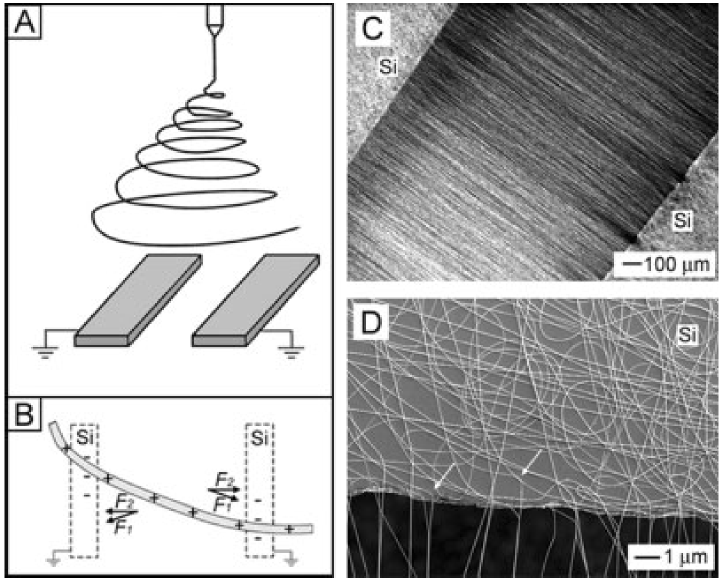


Figure 10. A) Schematic illustration of the setup used for electrospinning nanofibers as uniaxially aligned arrays. The collector was constructed from two conductive substrates separated by a void gap. B) The electrostatic force analysis of a charged nanofiber spanning across the gap. The fiber experiences a strong stretching force (*F*) due to the Coulombic interactions between the positive charges on the fiber and the negative, image charges on the two grounded electrodes. C) Dark-field optical micrograph of poly(vinyl pyrrolidone) (PVP) nanofibers collected across the void gap between two silicon strips. D) SEM image of another sample taken from the region close to the edge of a void gap. As indicated by arrows, some nanofibers near the gap took sharp turns to position them perpendicular to the edge of the silicon strip. These figures were adapted from [40b] with permission. Copyright American Chemical Society, 2003.

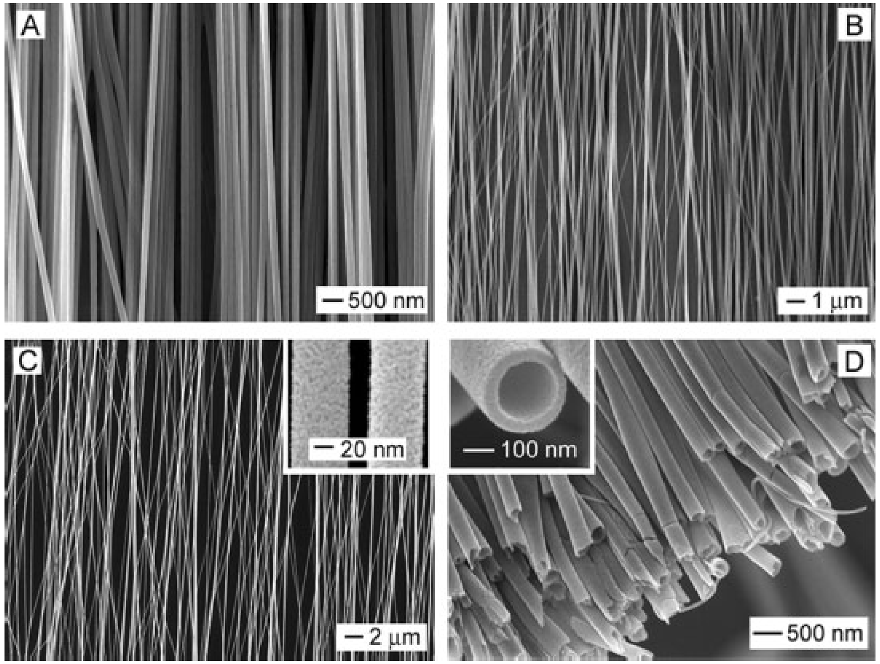


Figure 11. SEM images of uniaxially aligned nanofibers (A–C) and nanotubes (D) made of various materials: A) carbon; B) TiO_2/PVP composite; C) Sb-doped SnO_2; and D) anatase. These figures were adapted from [21b,40b] with permission. Copyright American Chemical Society, 2003, 2004.

D. Li, Adv. Mater. 16 1151 (2004)

Synthesis of Nano Materials- 1D from Liquid

❑ Nanofibers from Electrospinning- conducting fiber

Polyaniline doped with *d,l* camphorsulfonic acid (Pan.HCSA)
Polyethylene oxide (PEO)

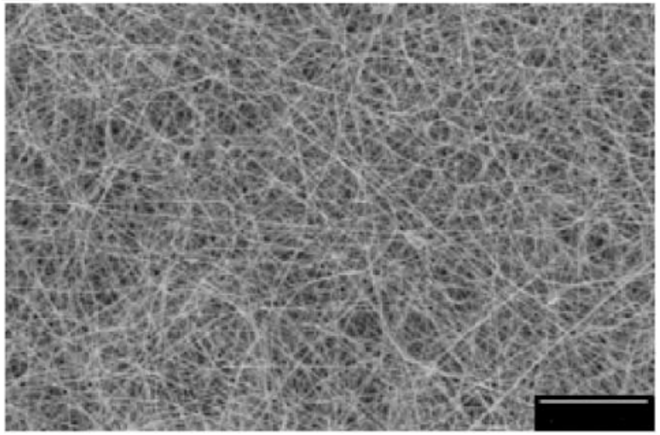


Figure 1. 50 wt% Nanofiber blend of PAn.HCSA fabricated from 2 wt% PAn.HCSA and 2 wt% PEO from chloroform solution at 25,000 V (anode/cathode separation, 25 cm). Scale bar: 100,000 nm. [6]

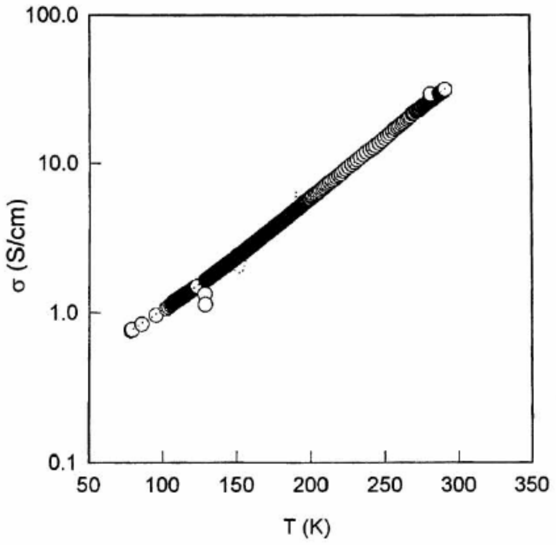


Figure 6. Conductivity/temperature relationship for a 72 wt% blend fiber of PAn.HCSA in PEO (see text).

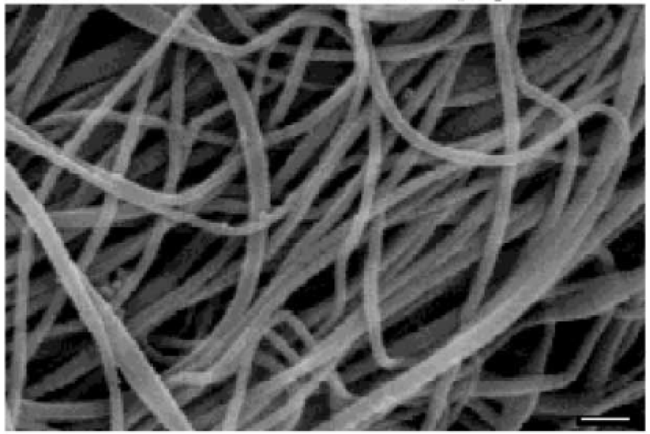


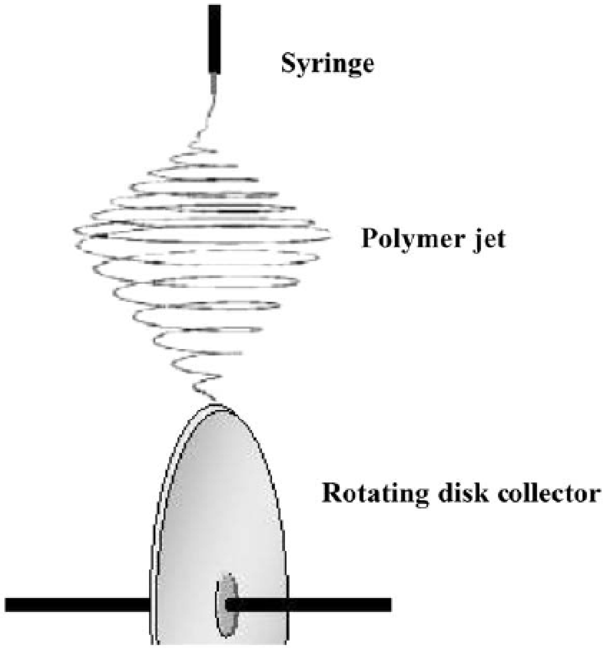
Figure 7. Conducting polypyrrole coated polyacrylonitrile nanofibers. Scale bar: 1000 nm.

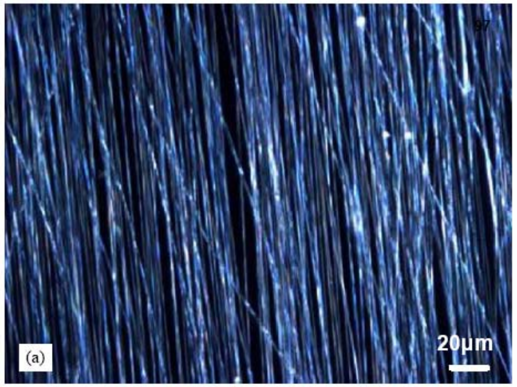
A.G. MacDiarmid, Synthetic Metals 119 (2001) 27.

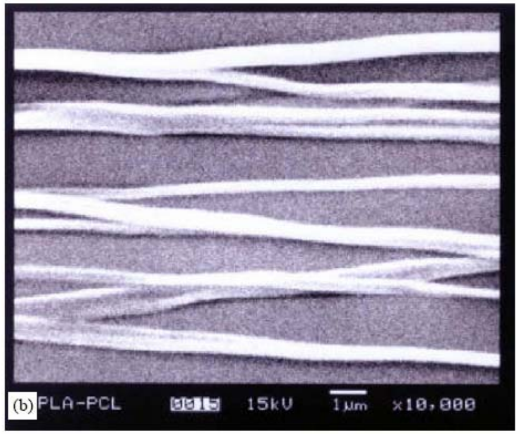
Synthesis of Nano Materials- 1D from Liquid

❑ Nanofibers from Electrospinning - Biopolymer Fibers

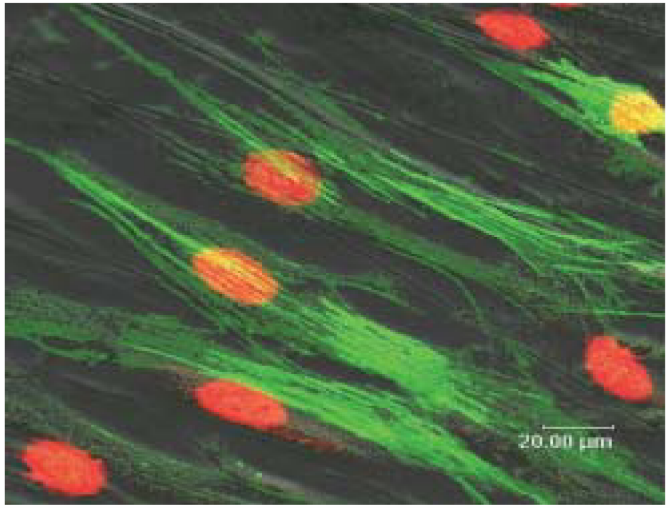
poly(L-lactid-*co*-ε-caprolactone) [P(LLA-CL)]







scaffolds for tissue engineering



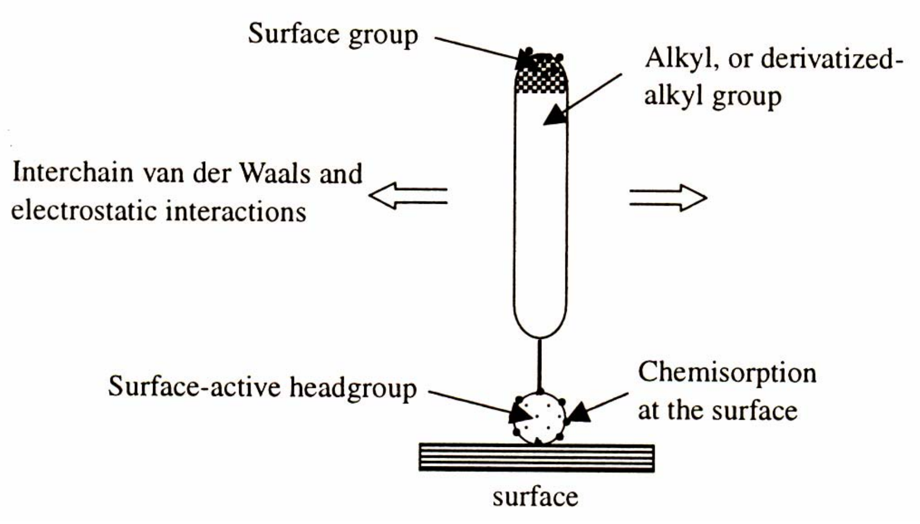
used for cell growth scaffolds

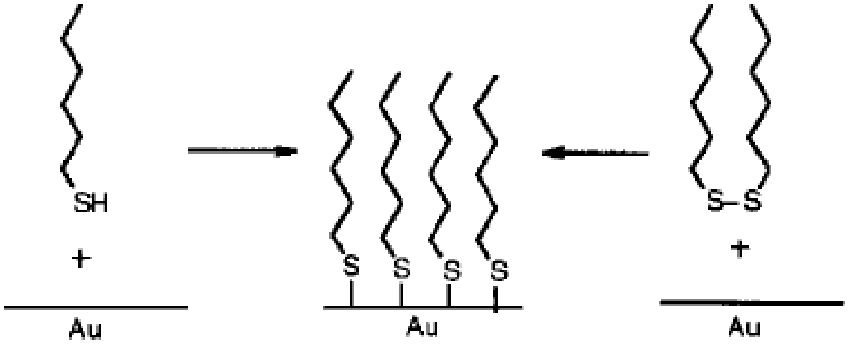
C. Y. Xu, Biomaterials 25 (2004) 877

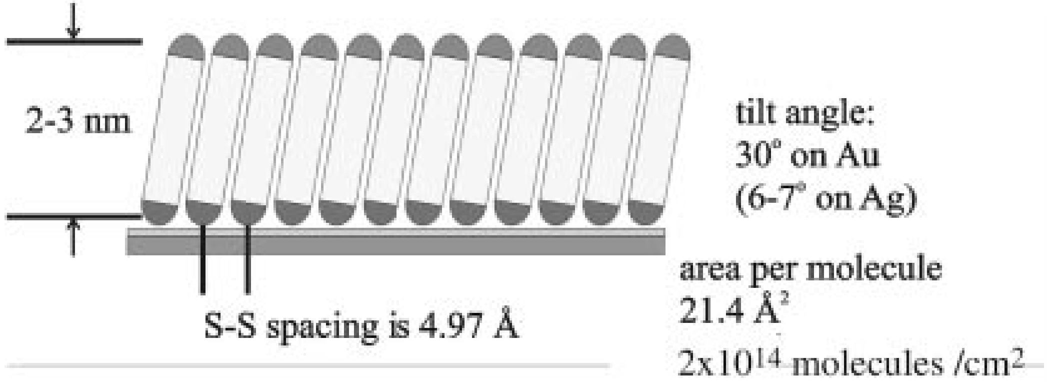
Synthesis of Nano Materials- 2D from Liquid

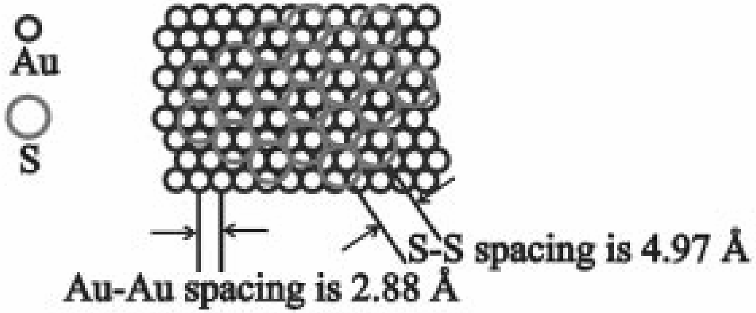
❑ Self Assembly

thiol on gold







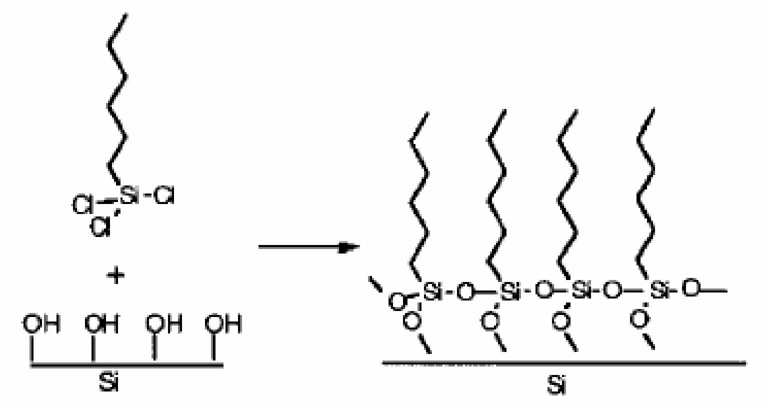


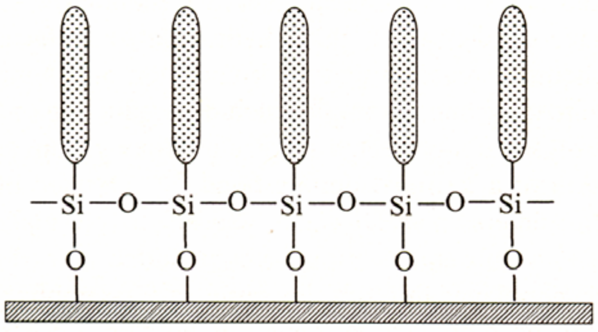
V. Chechik, Adv. Mater. 12 (2000) 1161.

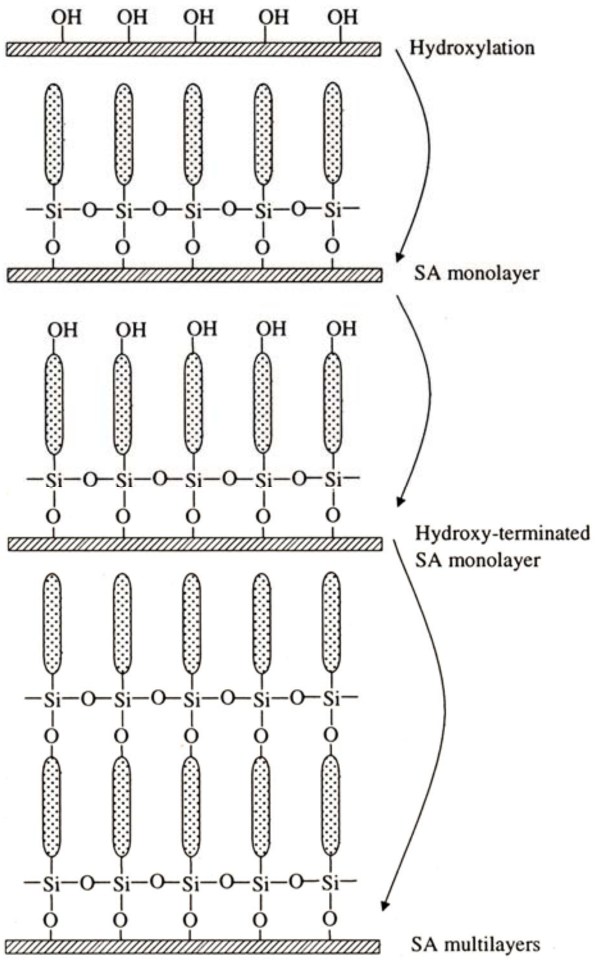
T.P. Sullivan, Eur. J. Org. Chem 17 (2003).

Synthesis of Nano Materials- 2D from Liquid

❑ Self Assembly







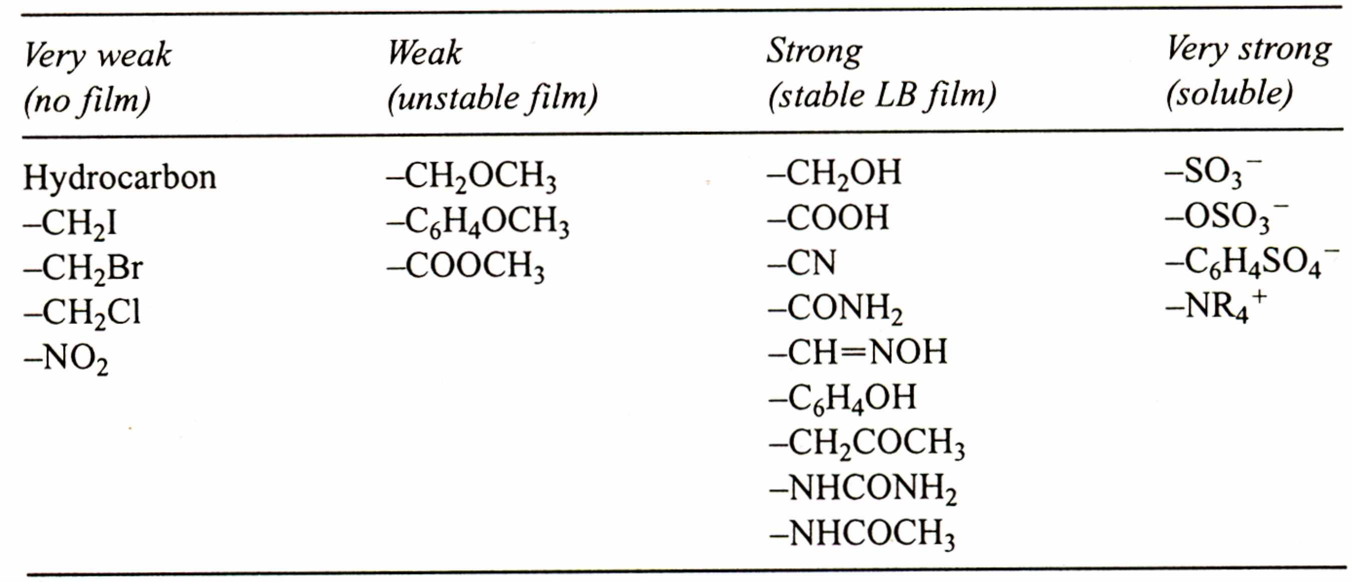
S.J. Limmer, Adv. Mater. 13 1269 (2001).

Synthesis of Nano Materials- 2D from Liquid

❑ Langmuir-Blodgett Films

- Amphiphile

ex) stearic acid $\underbrace{C_{17}H_{35}}_{\text{hydrophobic}}\ \underbrace{CO_2H}_{\text{hydrophilic}}$



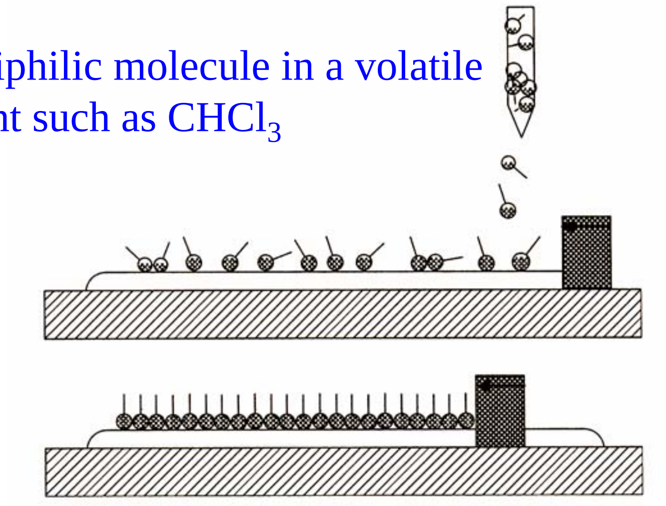
Very weak (no film)	*Weak (unstable film)*	*Strong (stable LB film)*	*Very strong (soluble)*
Hydrocarbon	$-CH_2OCH_3$	$-CH_2OH$	$-SO_3^-$
$-CH_2I$	$-C_6H_4OCH_3$	$-COOH$	$-OSO_3^-$
$-CH_2Br$	$-COOCH_3$	$-CN$	$-C_6H_4SO_4^-$
$-CH_2Cl$		$-CONH_2$	$-NR_4^+$
$-NO_2$		$-CH{=}NOH$	
		$-C_6H_4OH$	
		$-CH_2COCH_3$	
		$-NHCONH_2$	
		$-NHCOCH_3$	

S.J. Limmer, Adv. Mater. 13 1269 (2001).

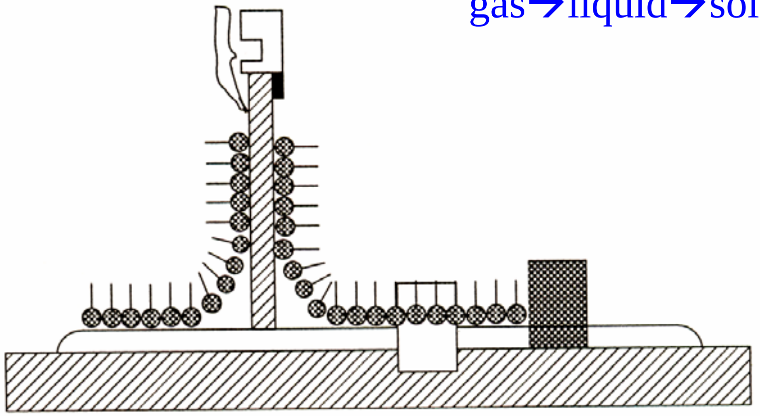
Synthesis of Nano Materials- 2D from Liquid

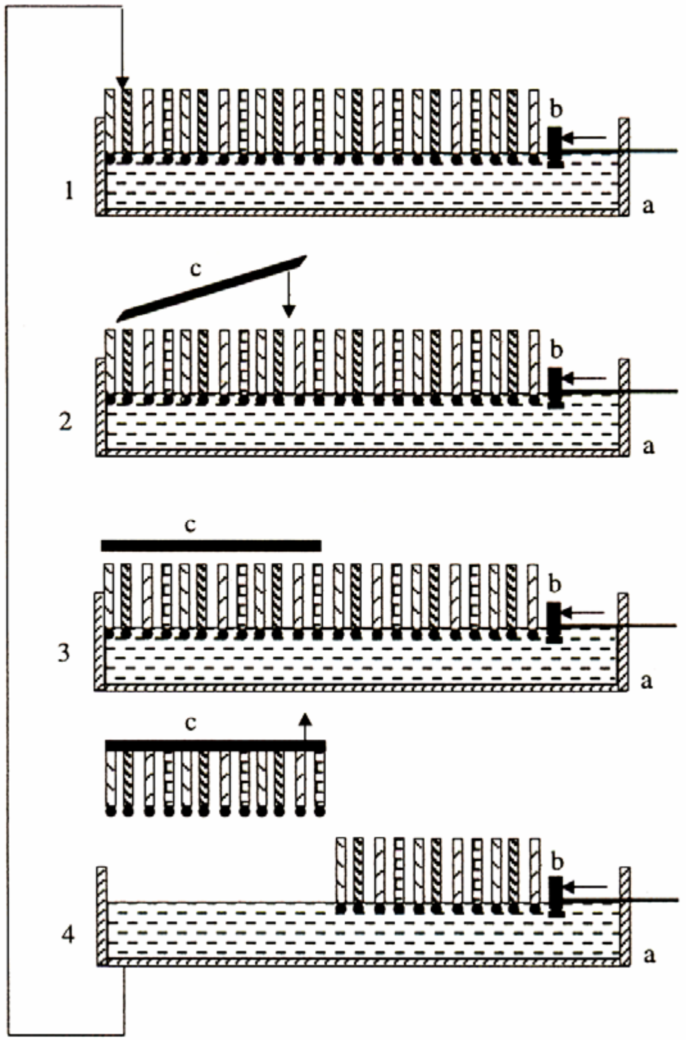
☐ Langmuir-Blodgett Films

amphiphilic molecule in a volatile solvent such as $CHCl_3$



gas→liquid→solid

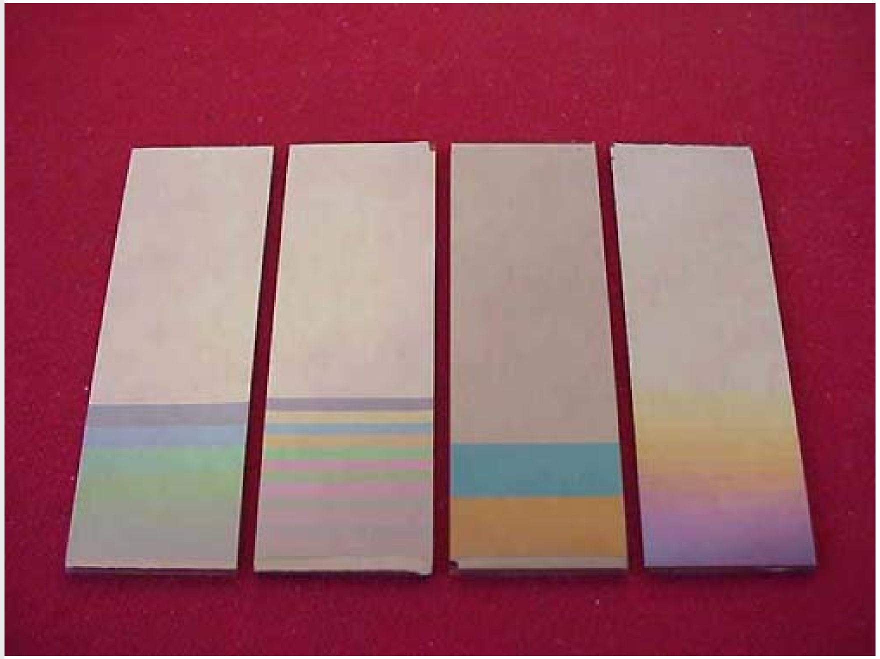




S.J. Limmer, Adv. Mater. 13 1269 (2001).

Synthesis of Nano Materials- 2D from Liquid

❑ Langmuir-Blodgett Films



Soap Films and Blodgett-Langmuir Multilayers

The picture below shows four chromium-plated glass microscope slides on which various thicknesses of barium-copper stearate (soap) were deposited. The layers were built up by repeated immersion into a trough filled with water, the surface of which was covered with a monolayer of the soap film1. Dr. Blodgett made similar slides to serve as gauges to determine thicknesses of various films. For example one could determine the thickness of an oxide film by color comparison.

Consider the slide second from the right. The blue portion has 61 double layers and is 0.00003 cm thick. The yellow portion has 80 double layers and is about 0.00004 cm thick. When a slide travels down into the water it picks up one monomolecular layer. Then, when the slide is brought up again a second layer clings to the slide. Thus, a double layer results after one complete cycle. The thickest film is on the lower end of the second slide from the left. It consists of 247 double layers and is 0.0001 cm thick.

http://www.frognet.net/~ejcov/soapfilms.html

Synthesis of Nano Materials- 2D from Liquid

- ❑ **Electrochemical Deposition**

Synthesis of Nano Materials- 2D from Liquid

❑ Sol-Gel Films (dip-coating)

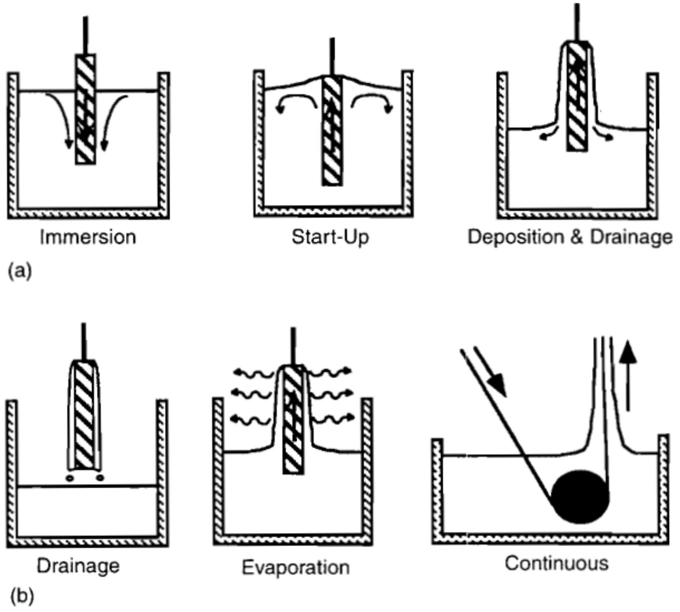


Figure 5: Stages in dip coating processes (after reference 44).

$$h = c_1(\eta U_0/\rho g)^{1/2}$$

L.F. Francis, Mater. Manufac. Proc. 12 (1997) 963

C.J. Brinker, Thin Solid Film, 201(1991)97.

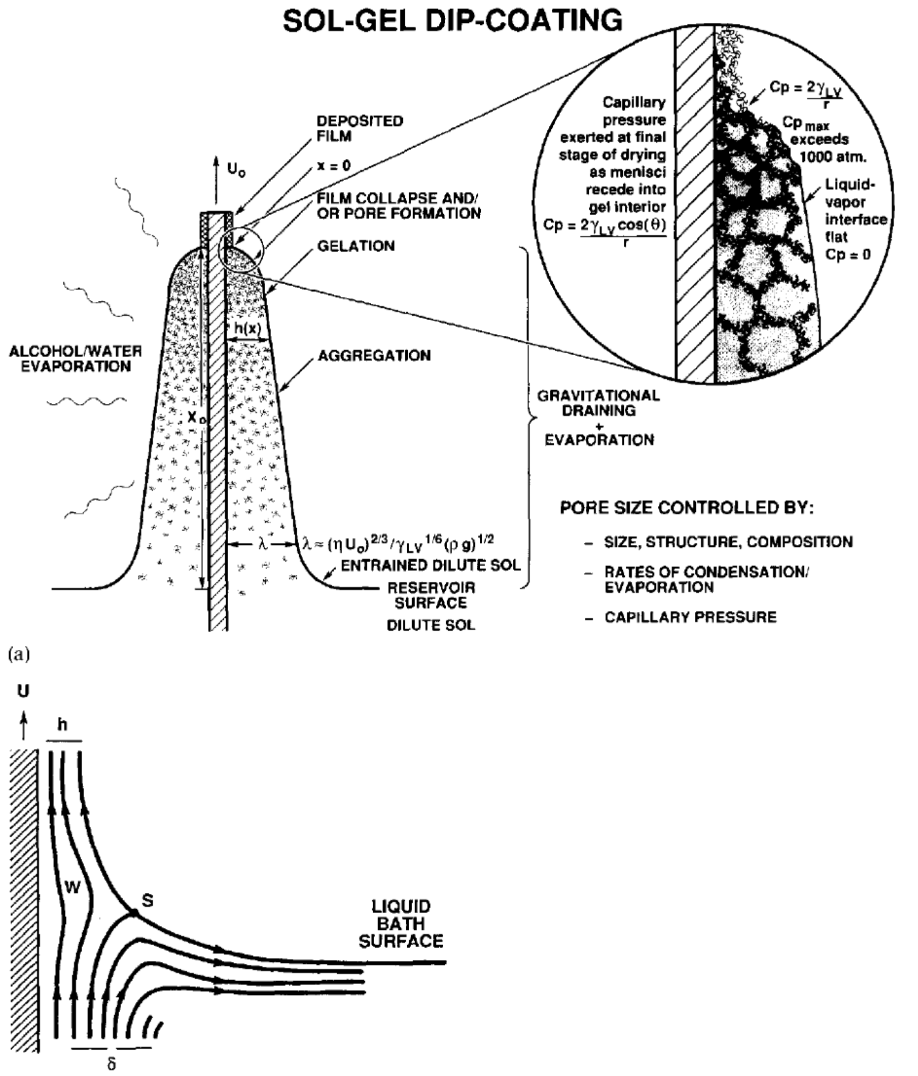


Fig. 1. (a) Schematic diagram of the steady state dip coating process, showing the sequential stages of structure development that result from draining accompanied by solvent evaporation and continued condensation reactions. (b) Detail of liquid flow patterns during dip coating. U is the withdrawal speed, S is the stagnation point, δ is the boundary layer, and h is the thickness of the fluid film.

Synthesis of Nano Materials- 2D from Liquid

❑ Sol-Gel Films (spin coating)

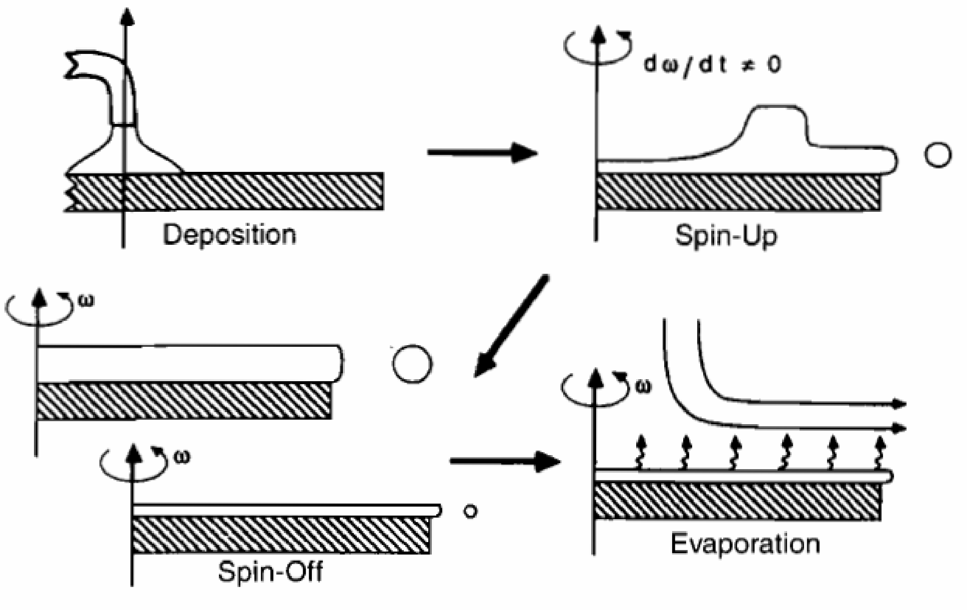


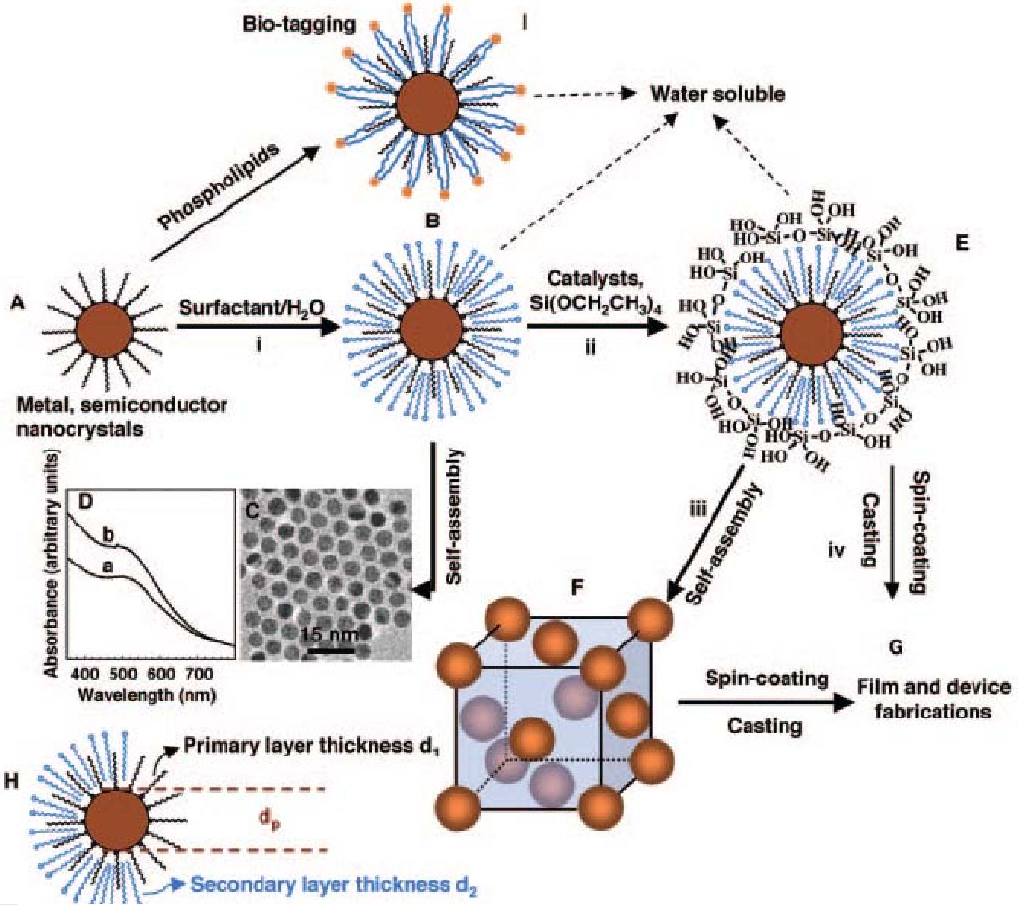
Figure 6: Stages in the spin coating process (after reference 56).

L.F. Francis, Mater. Manufac. Proc. 12 (1997) 963

Synthesis of Nano Materials- 2D from Liquid

☐ Sol-Gel Films (spin coating)

ex) gold/silica array



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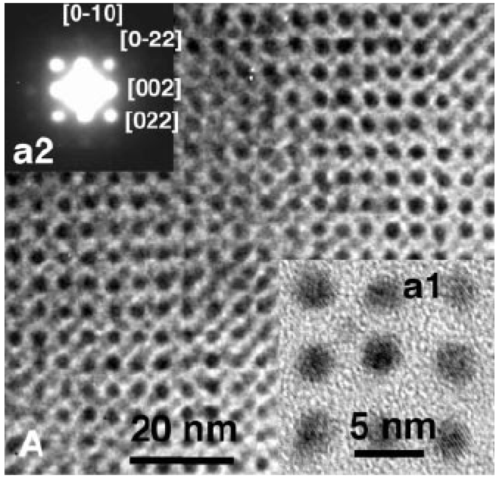

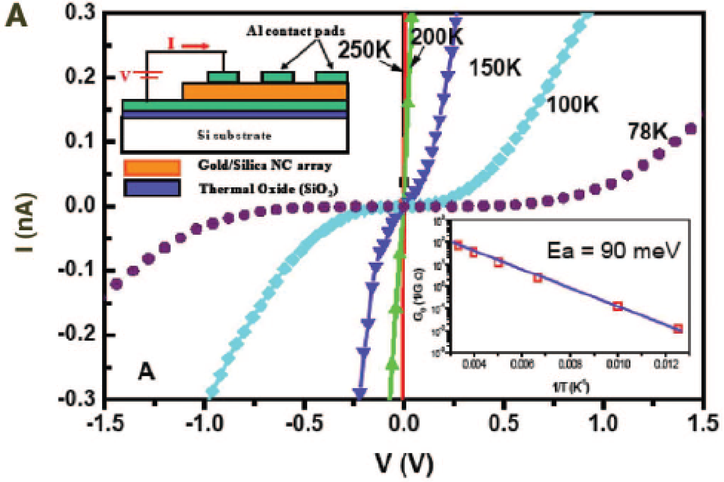

H. Fan, Science, 304 (2004) 567