Self-assembly and Nanotechnology 10.524

Lecture 6. Synthesis and Fabrication of Nanomaterials

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nano manufacturing center at UML

Lecture 6: Synthesis and Fabrication of Nanomaterials

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Section I:

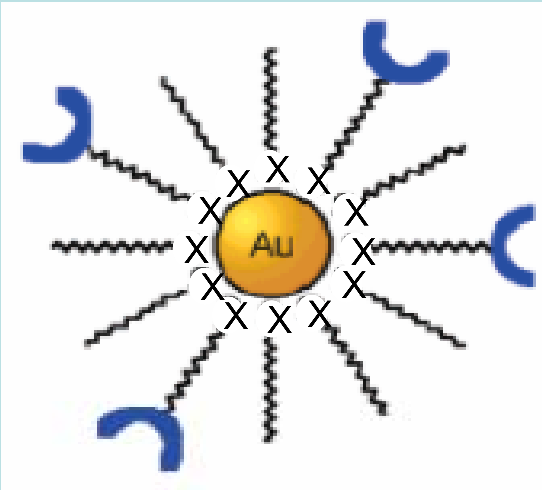
Synthesis of Nanoparticles

Growth of colloidal nanocrystals by reduction in the presence of surfactants

General Strategy

- Metal precursor solution
- Reducing Agent
- Capping (stabilizing agent)
- Solvent (heated)

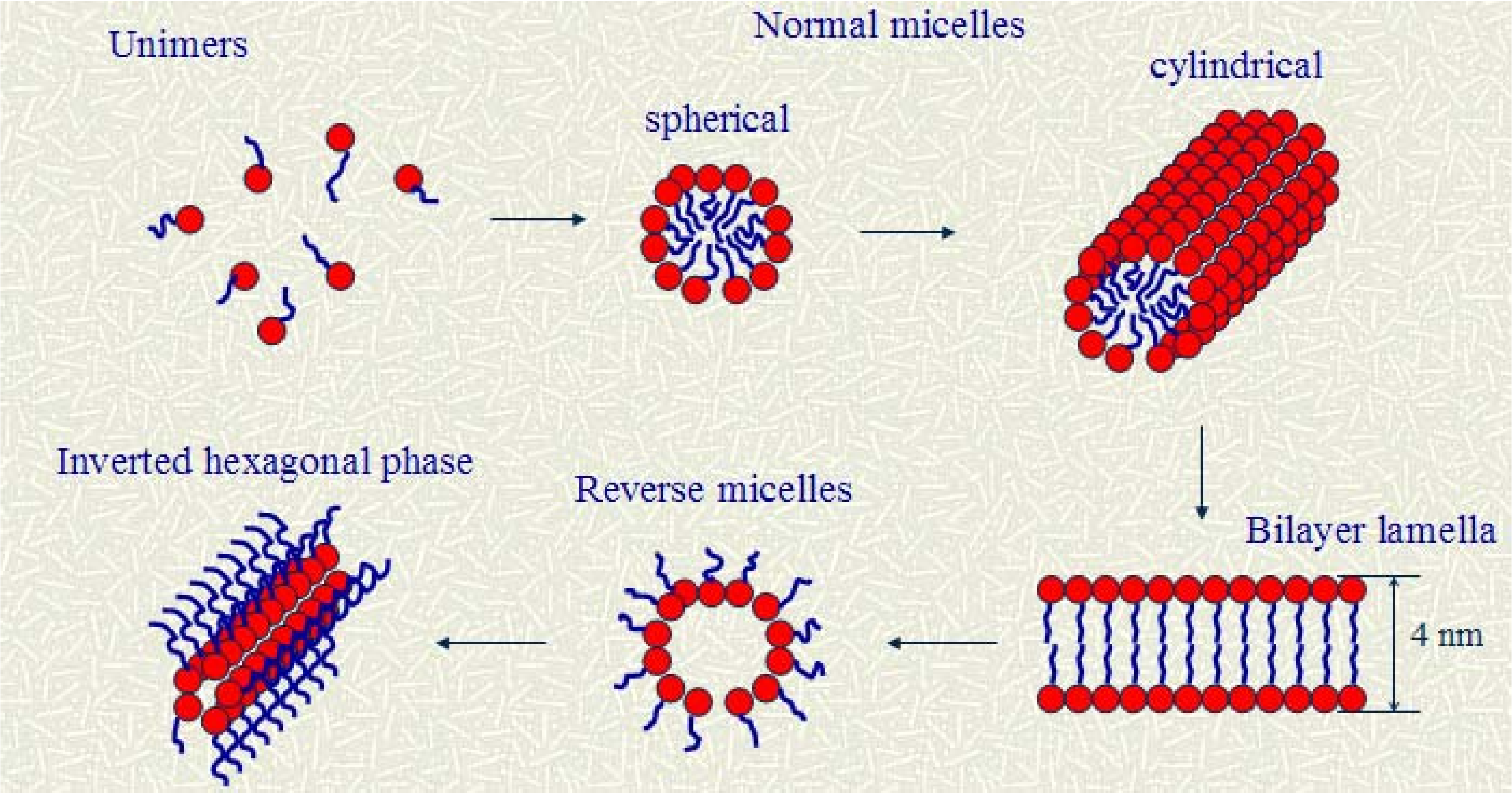
Example: Gold nanocrystals



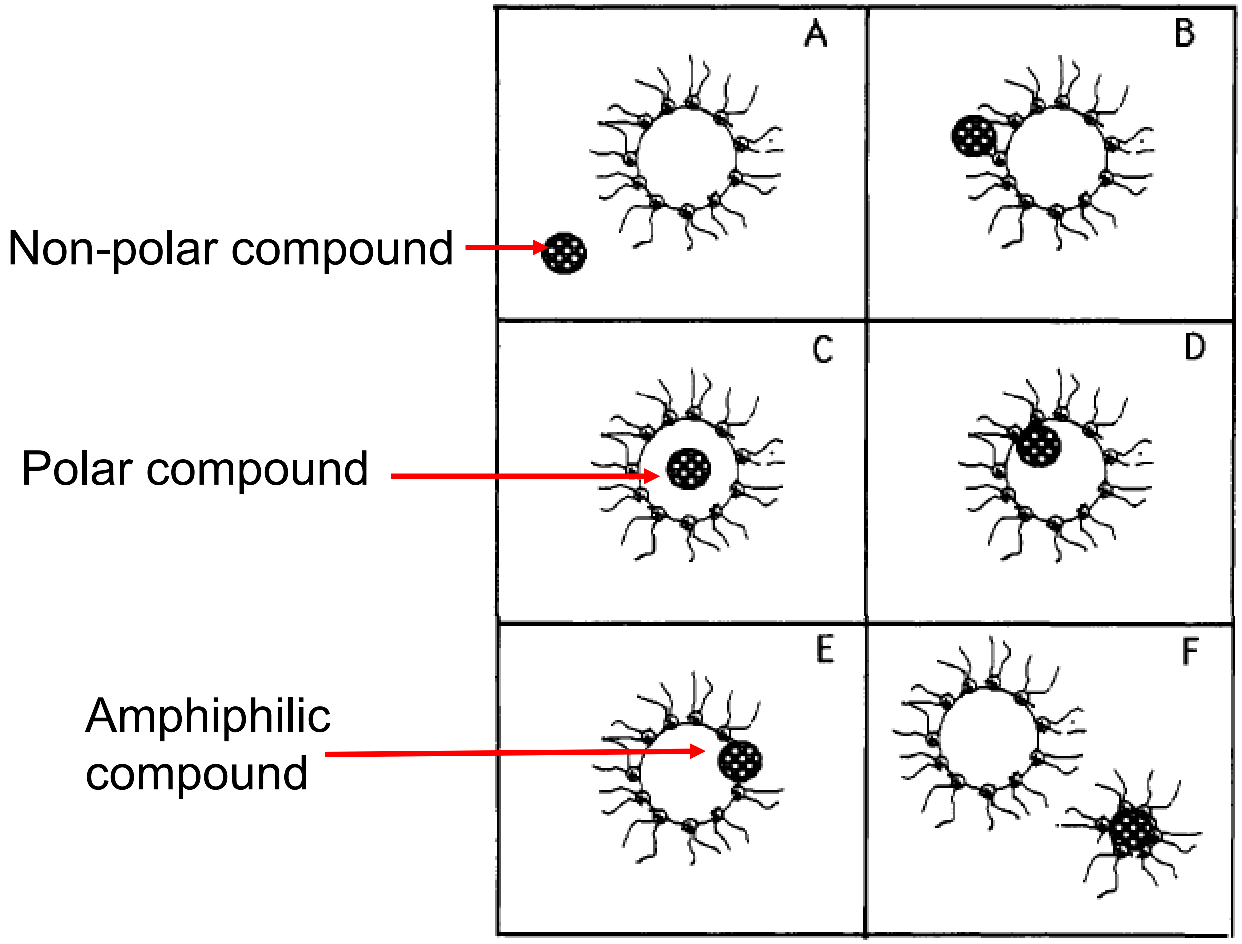
tetrachloroauric acid (HAuCl4)
boil with
Trisodium citrate

Frens, G.. Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions, Nature (1973), 241(105), 20-2. J. Turkevich, et. al. Coagulation of Colloidal Gold. *Discussions Faraday Soc.* No. 11, 58 (1951).

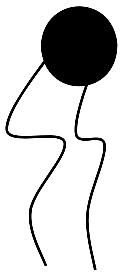
Molecular surfactant templated growth of nanoparticles

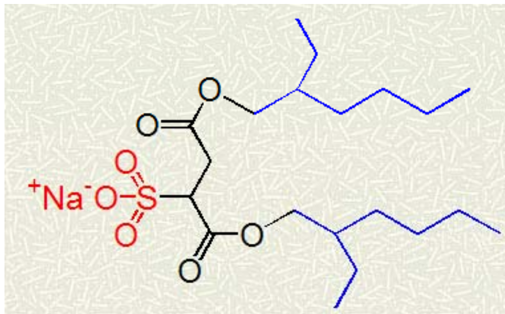


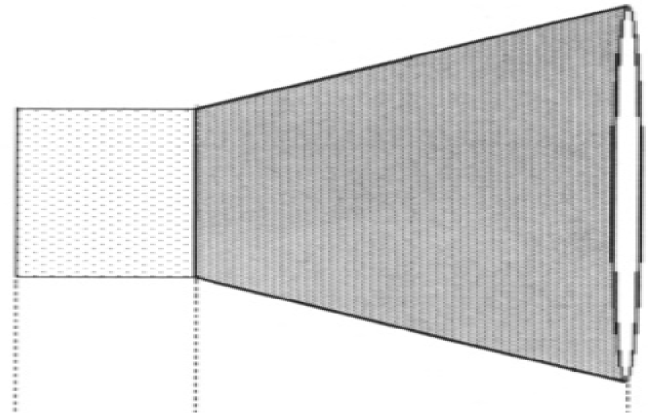
Different solute interaction possibilities can occur



Synthesis of Nanoparticles Using Reverse Micelles







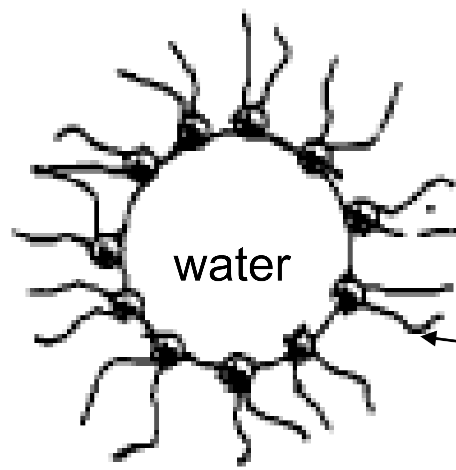
AOT: Sodium
bis (2-ethylhexyl)suflosuccinate)

Radius of micelle (nm) = 0.15 [water] / [AOT]

↑

Molar ratio

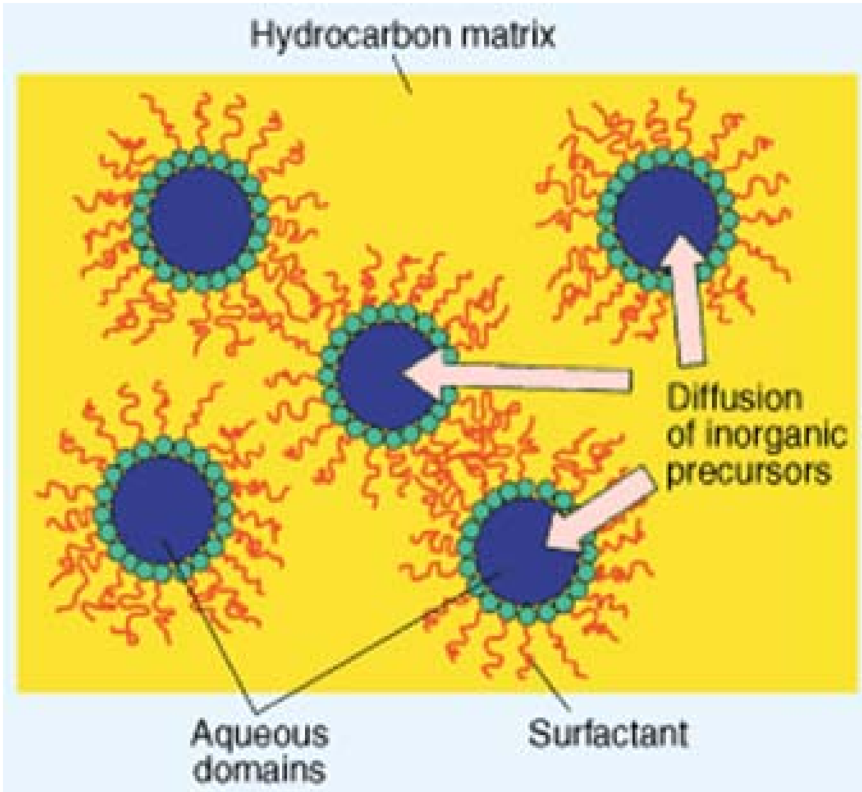
Isooctane

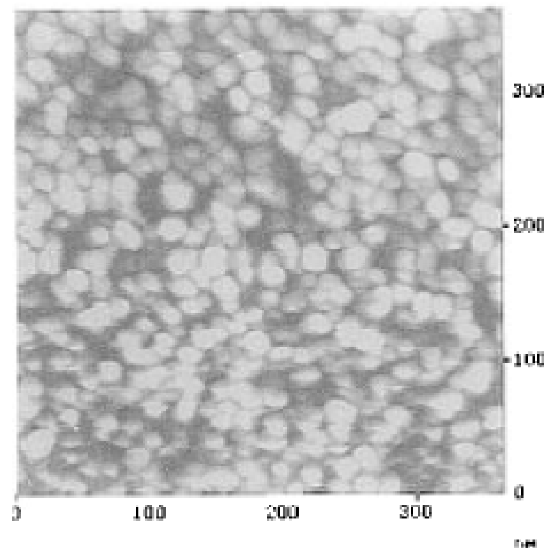


AOT molecules

Shchukin, Dmitry G.; Sukhorukov, Gleb B. Nanoparticle synthesis in engineered organic nanoscale reactors. Advanced Materials (2004), 16(8), 671-682.

Nanoparticle Synthesis in Reverse Micelles



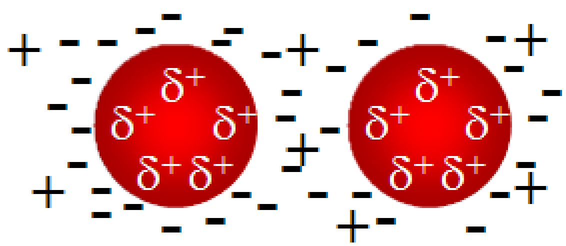


TiO_2 nanoparticle film

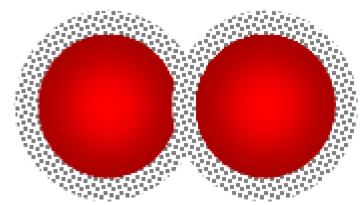
AOT: Reverse micelles (0.2 M AOT + 0.4 M water in cyclohexane)
Titanium isopropoxide $Ti[OCH(CH_3)_2)]_4$ 0.2 M added under vigorous stirring

Langmuir, 13, 16, 1997

Nanoparticles Stabilization against Aggregation (VDW force is high)



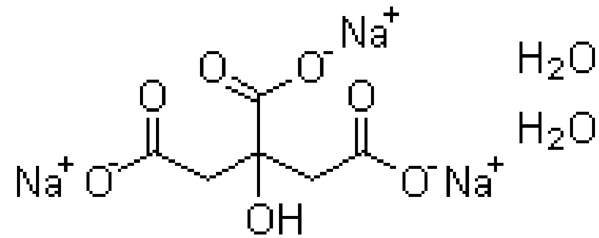
Electrostatic
(adsorption of ions)



Coat particles with
Organic molecules / polymers

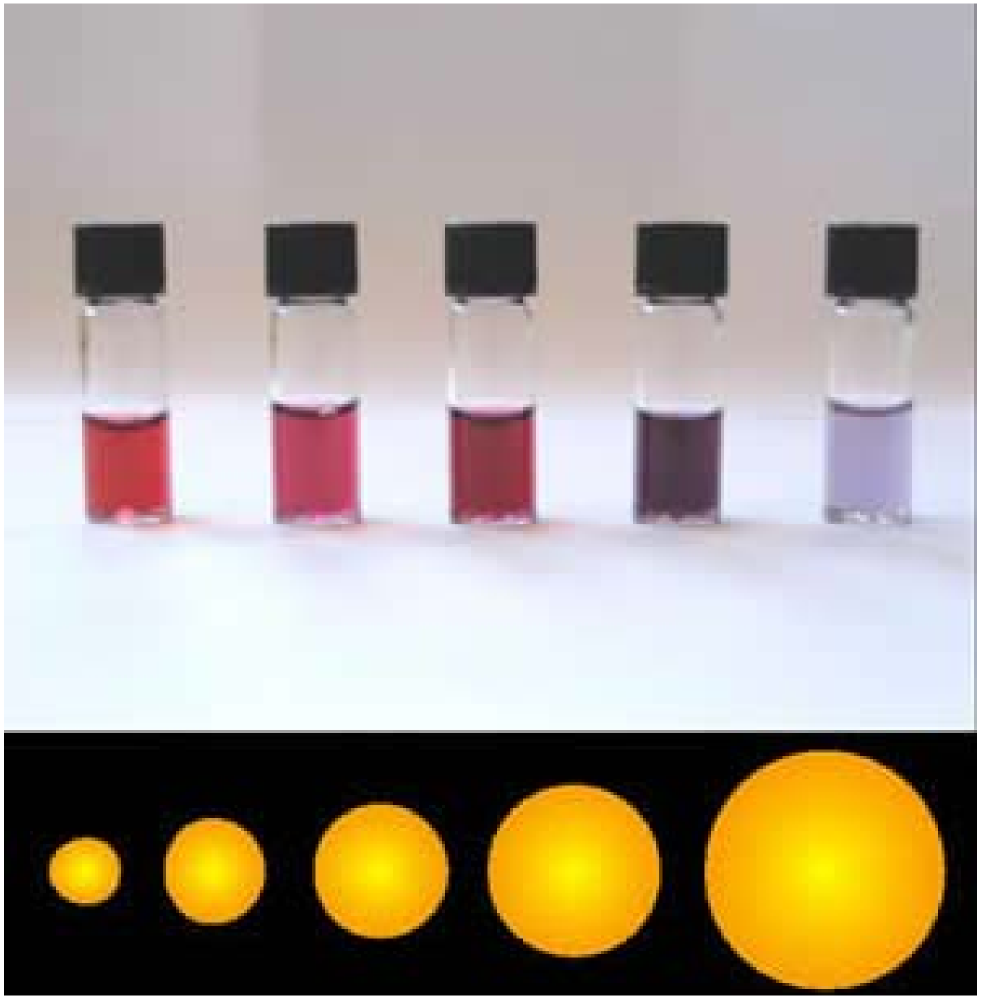
Capping (stabilizing agent)
e.g. Trioctylphosphine oxide (TOPO)

Nanoparticle Size Controlled by Ratio of Au(III) / citrate



Amount of $HAuCl_4$ solution (10 mM, mL)	Amount of trisodium citrate solution (1%, mL)	Color	λ_{max}	Size (nm)
1.25	2.0	Dark red	518	8.0
1.25	1.6	Red	519	10.0
1.25	1.3	Red	520	13.0
1.25	1.0	Red	522	16.0
1.25	0.875	Red	526	20.0
1.25	0.750	Red	528	25.0
1.25	0.625	Pinkish red	529	32.0
1.25	0.500	Pink	532	41.0
1.25	0.400	Pink	534	55.0
1.25	0.300	Orange	545	73.0

Reference: Chemical Physics Letters (2004), 395(4-6), 366-372



The diameter of gold nanoparticles determines the wavelengths of light absorbed. The colors in this diagram illustrate this effect.

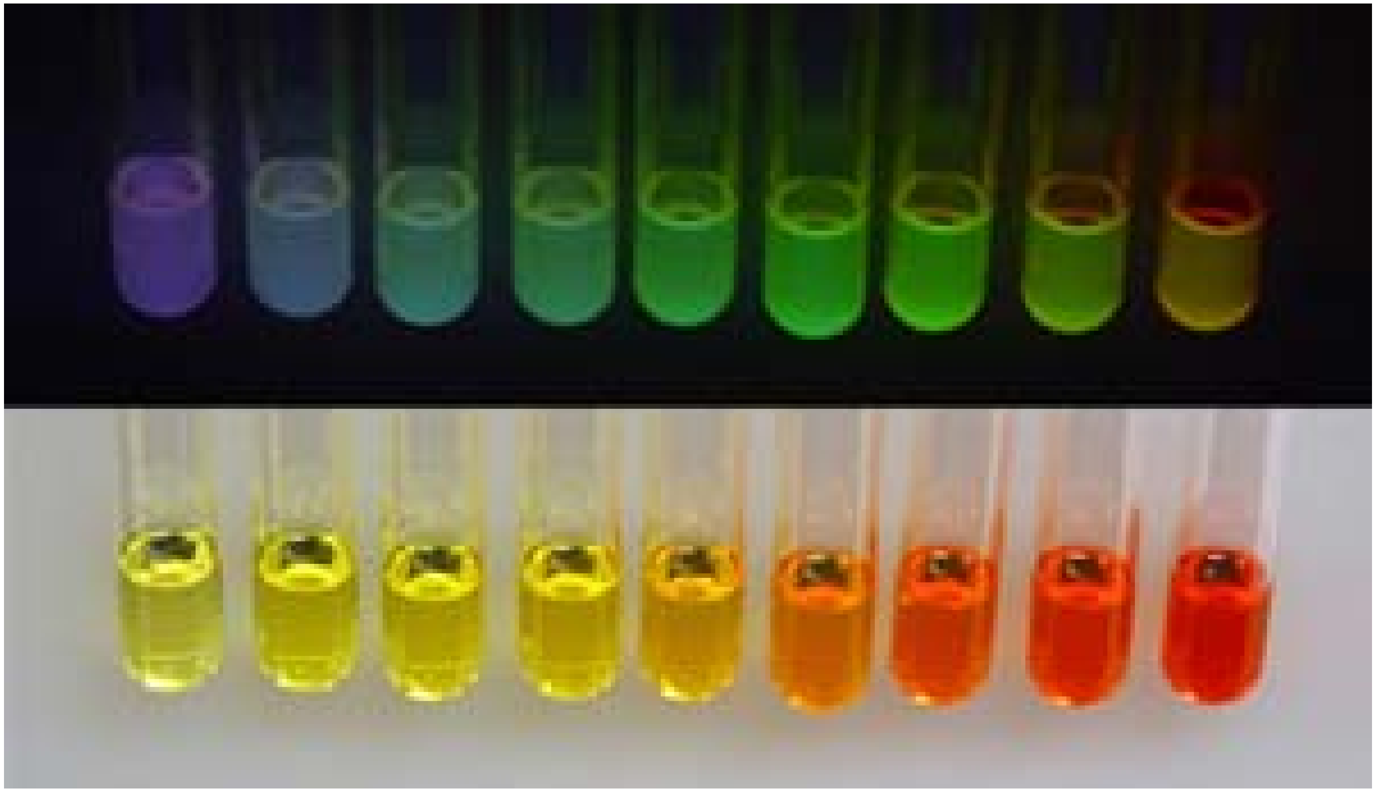
http://www.webexhibits.org/causesofcolor/9.html

Quantum Dots

Fluorescence induced by exposure to ultraviolet light in vials containing various sized Cadmium selenide (CdSe) quantum dots.

A **quantum dot** is a semiconductor nanostructure that confines the motion of conduction band electrons, valence band holes, or excitons (pairs of conduction band electrons and valence band holes) in all three spatial directions.

(Wiki)

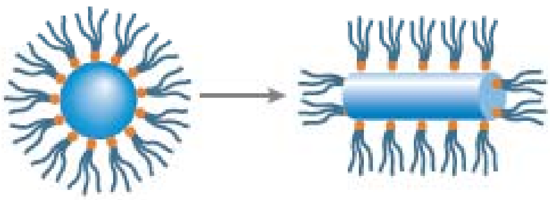


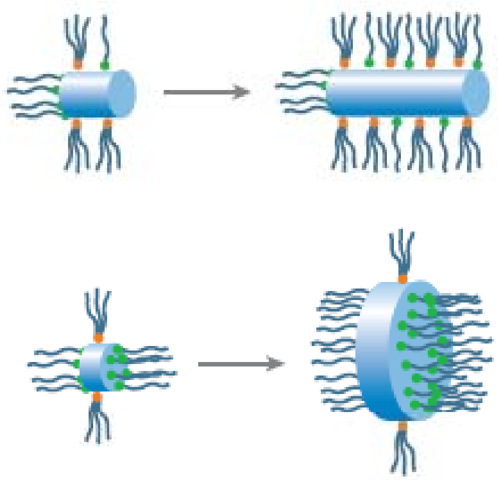
Different sized quantum dot nanoparticles are shown above, first in ultraviolet light and then in ambient light. The length of the synthesis reaction determines particle size for CdSe, increasing from left to right. In colloidal suspension, this semiconductor behaves in the same way as a metal.

http://www.webexhibits.org/causesofcolor/9.html

Shape Control over the Growth of Colloidal Nanocrystals

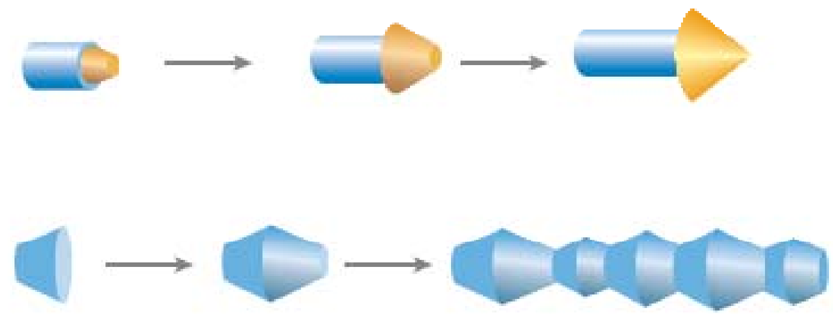
A. Kinetic control: High energy facets grow faster than low energy facets

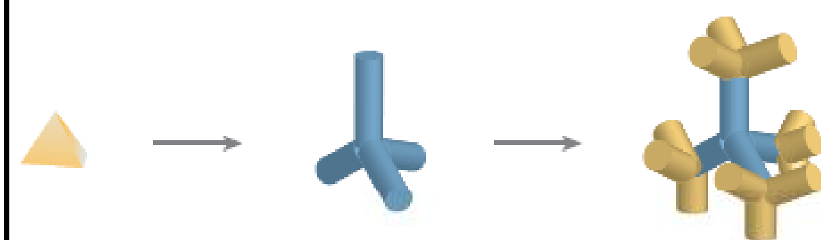




B. Kinetic shape control through selective adhesion

C. Intermediate energy facet eliminates high energy facet.





D. Controlled branching of nanocrystals

Y. Yin and A. P. Alivisatos, Nature, (2005) 664-670

Case Study I:

Shaped Nanoparticles - Nanocubes

Shaped Nanoparticles

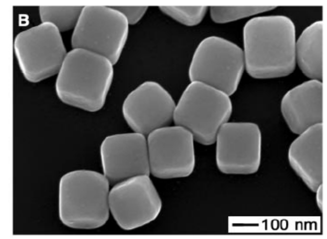
<u>Spherical</u> vs. <u>shaped</u> nanoparticles

Novel properties: size and shape dependent
optical, electrical, etc.

<u>Several examples</u>

- Younan Xia's group, U Washington

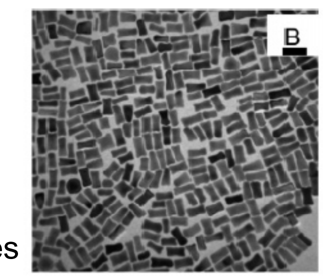
  Nanocubes: *Science*, **2002**, *298*, 2176-2179



Ag nanocubes

- Catherine J. Murphy's group, U South Carolina

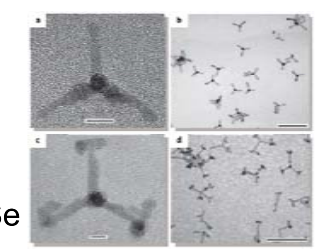
  Nanorods: *J. Phys. Chem. B* **2005,** *109,* 13857-13870



Au nanoparticles

- A Paul Alivisatos's group, UC Berkeley

  Branched nanocrystals: *Nature* **2005,** *437,* 664-670


Tetrapod-shaped CdSe

Shaped Nanoparticles – Polyol Synthesis

Solution-phase synthesis

Including: metal precursor, solvent, reducing agent, capping agent, etc.

Capping agents: surfactants or polymers, modifying the kinetics of atoms assembly/growth to generate shapes

Polyol method: easy and efficient method

Solvent: ethylene glycol

Also as a reducing agent when heated

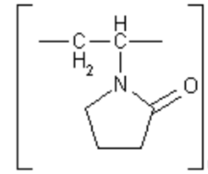
Capping agents: polymers mostly used

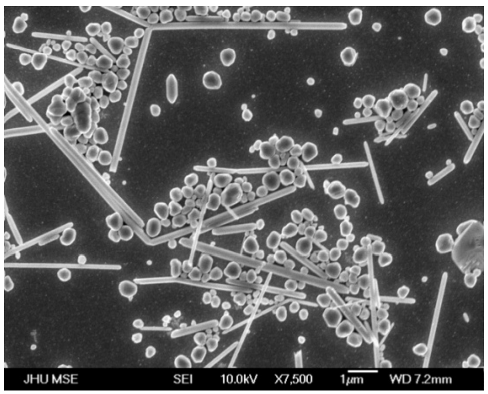
Purposes:

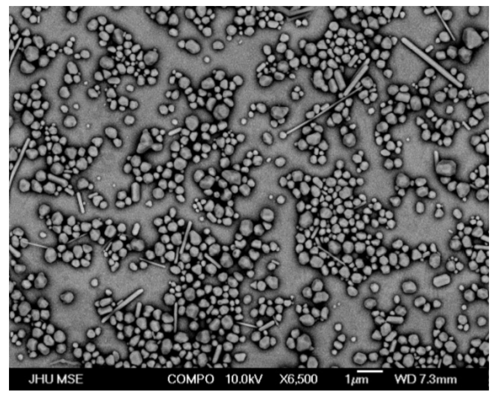
- Self-assembly or directed assembly to create 1D, 2D, and 3D structures
- Self-assembly with polymers or block copolymers to obtain novel nanocomposites

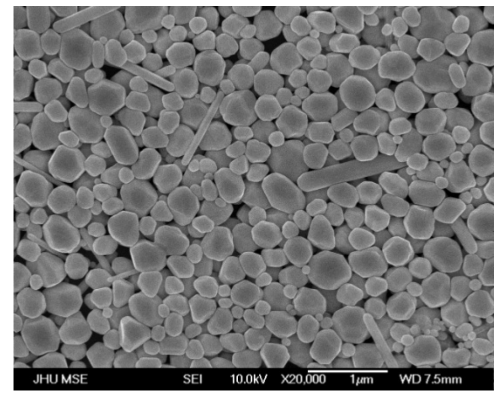
Shaped Nanoparticles – Some Preliminary Results

SEM images of Ag nanoparticles using poly(vinyl pyrrolidone) (PVP)

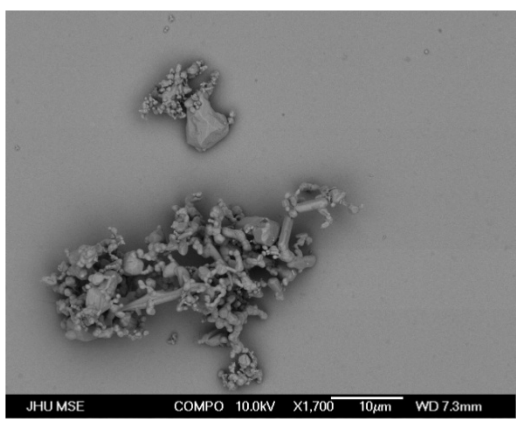


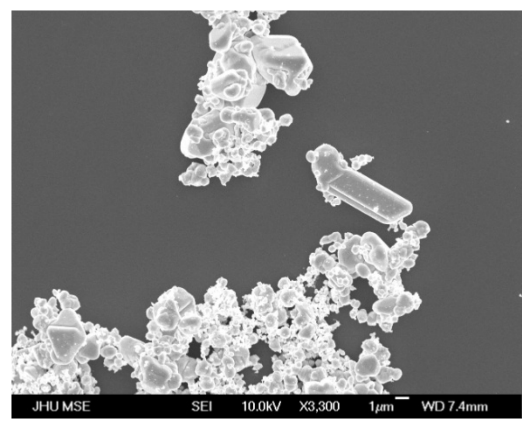






SEM images of Ag nanoparticles using Block copolymers





Pluronic block copolymers PEO-PPO-PEO

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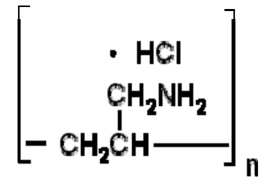
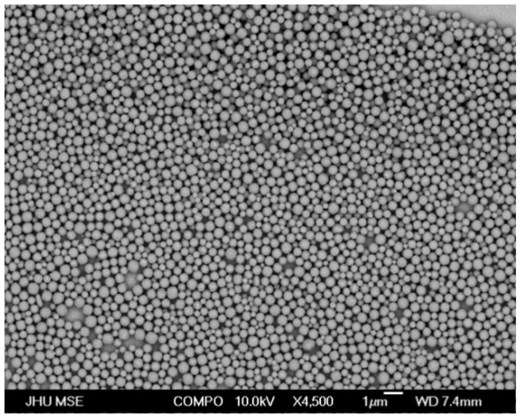
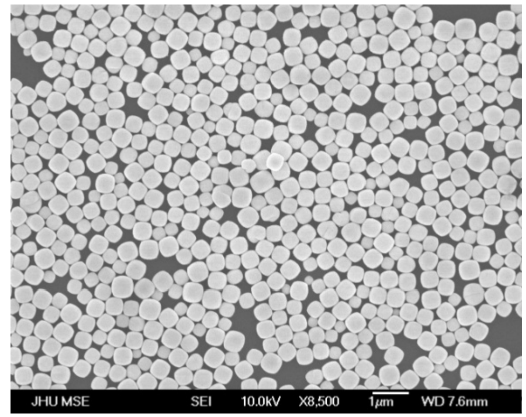
Shaped Nanoparticles – Nanocubes

SEM images of Ag nanoparticles using poly(allylamine hydrochloride) (PAH)

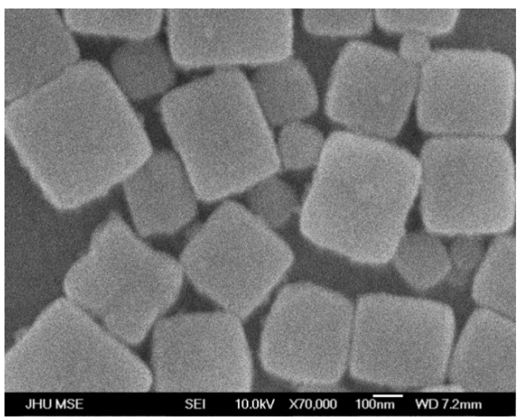




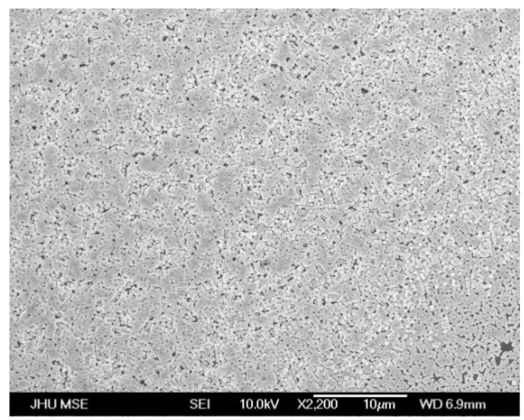
Spherical



Cubes



Zoom in



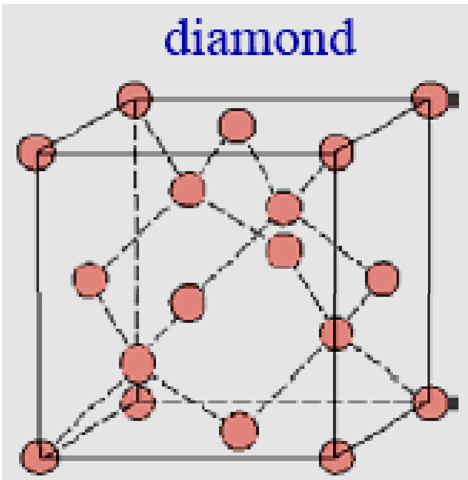
Zoom out

Section II:

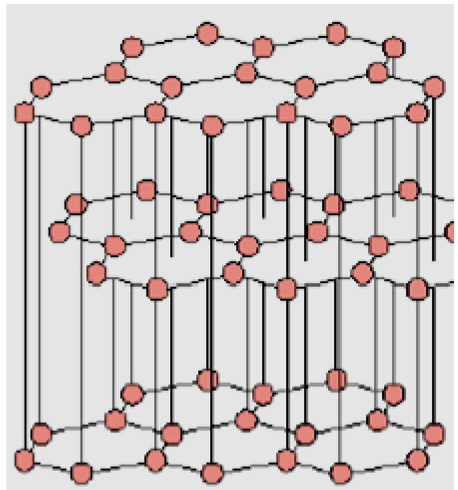
Synthesis of Carbon Nanotubes

Carbon Nanotube: A Form of Carbon

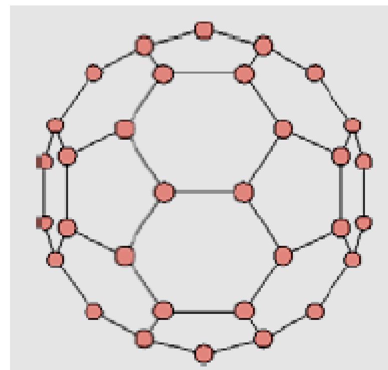
(metastable)



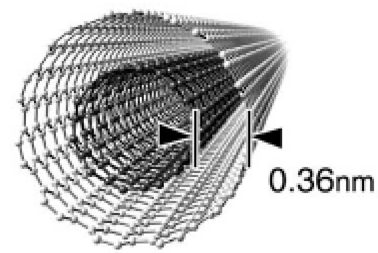
Graphite (stable)



Bucky ball (metastable)



Nanotube = rolled sheet of graphite

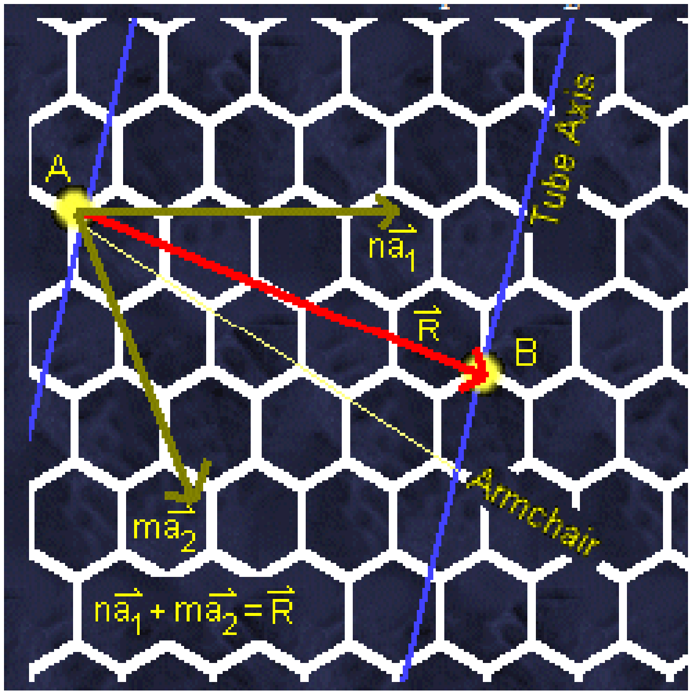


Smalley & Kroto, 1997 Nobel

Helical Microtubules of graphitic Carbon, Ijima, S, Nature, 354 (6348): 56-58 NOV 7 1991
Cited: >4000 times

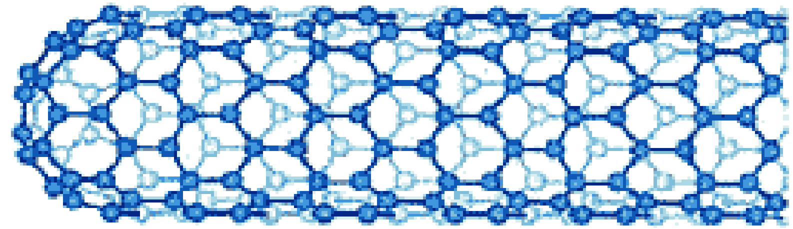
Review on Nanotubes:
Accounts of Chemical Research (2002), 35(12). Entire issue is based on Nanotubes.
Dai, Hongjie. Carbon nanotubes: opportunities and challenges. Surface Science (2002), 500(1-3), 218-241.

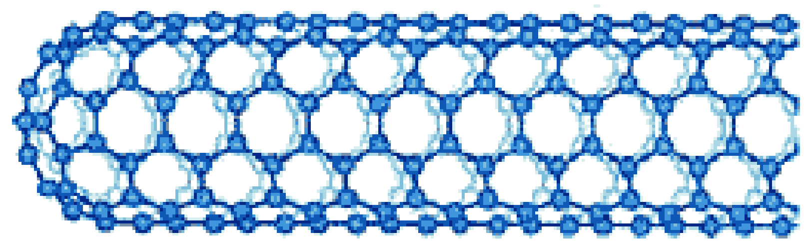
Different Types of Nanotubes



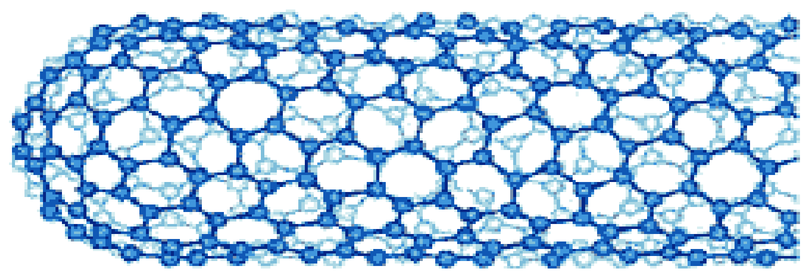
a1 zig zag vector
a2 reflection over armchair line

Zig-Zag



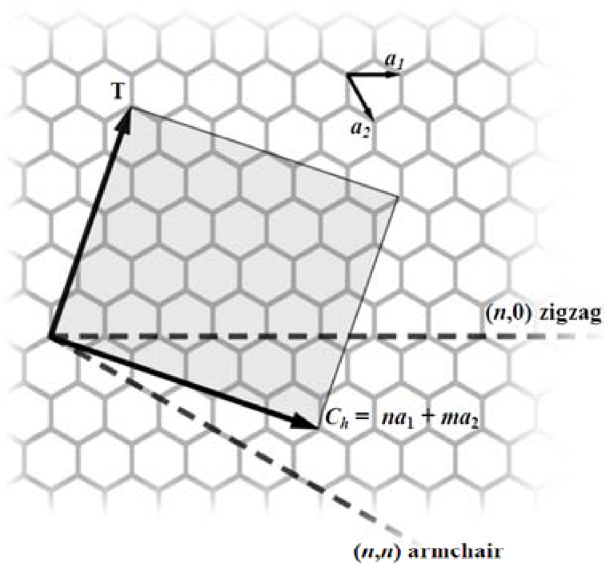


Armchair

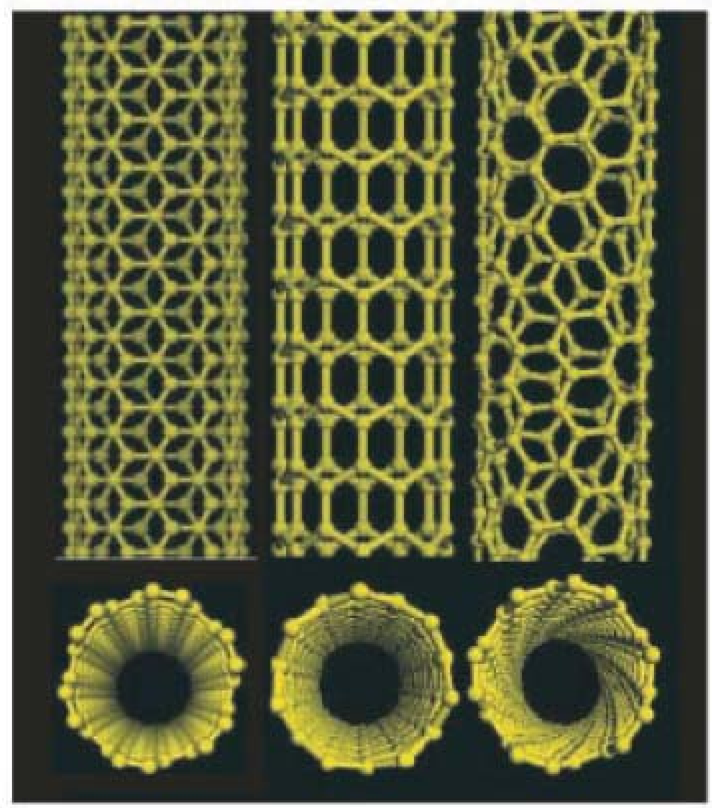


Chiral

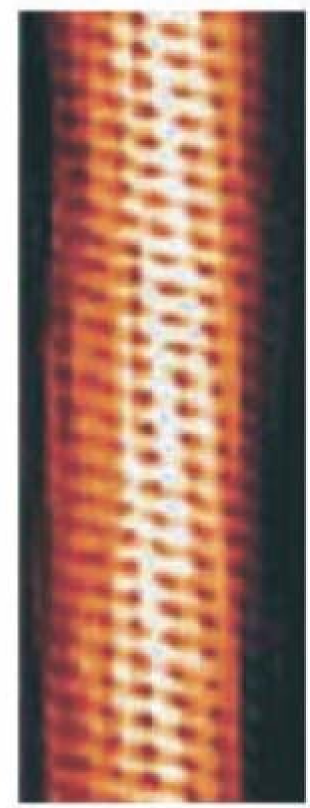
Different Types of Nanotubes



The (n,m) nanotube naming scheme can be thought of as a vector (Ch) in an infinite graphene sheet that describes how to 'roll up' to graphene sheet to make the nanotube. T denotes the tube axis, and a1 and a2 are the unit vectors of graphene in real space. It is based upon similar diagrams found in the literature (for instance, Odom et al. Topics Appl. Phys., 2001, 80, 173).



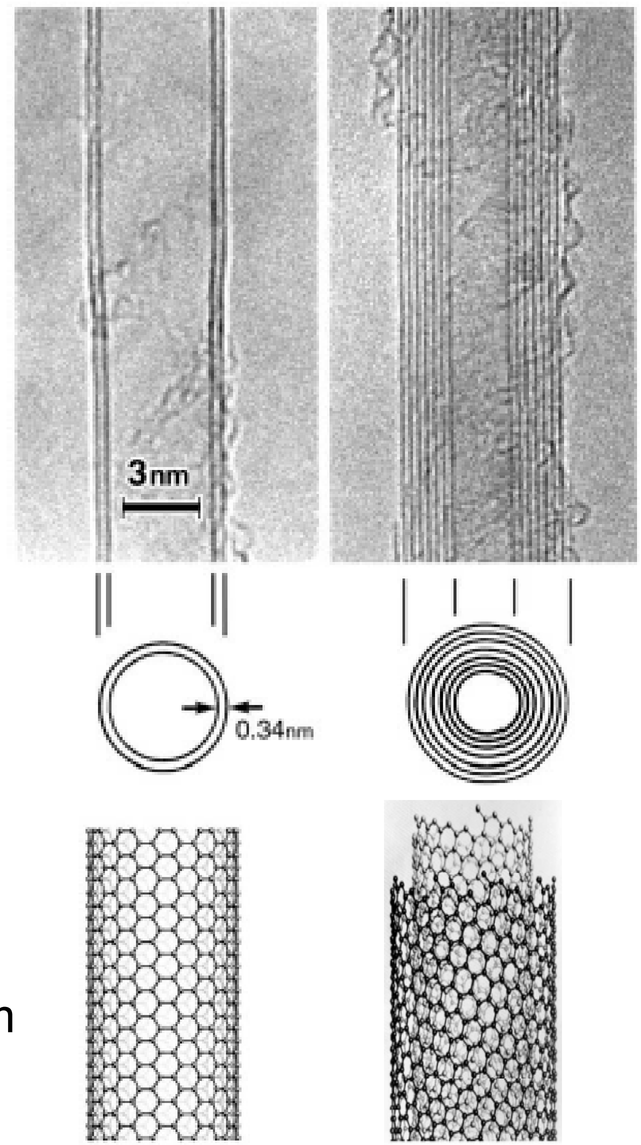
armchair Zig-Zag Chiral



TEM Chiral

Science, 297, 2 Aug 2002

Single Wall and Multi Wall Nanotubes



Up to cm long

SWNT
(single
Wall nanotube)
Diameter ~ 1.4 nm

MWNT
(multiwall)
Diameter 10-20 nm

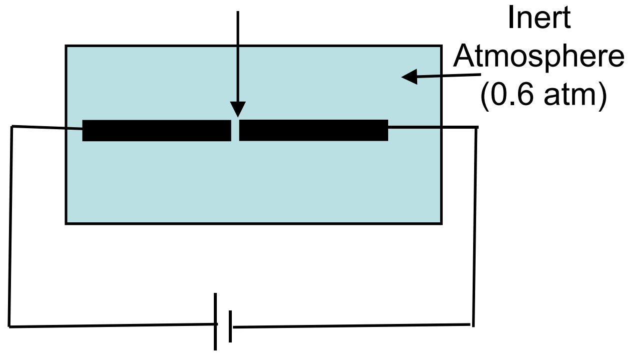
<u>Must read Paper:</u>
Iijima, Sumio. Carbon nanotubes: past, present, and future. Physica B: Condensed Matter (2002), 323, 1-5.

Methods for Fabricating Nanotubes

- Arc Vaporization
- Laser Vaporization
- CVD
- Flame

Arc Discharge

~ 1mm spaced
carbon electrodes



DC (20 V, 100 A)
Generates an arc

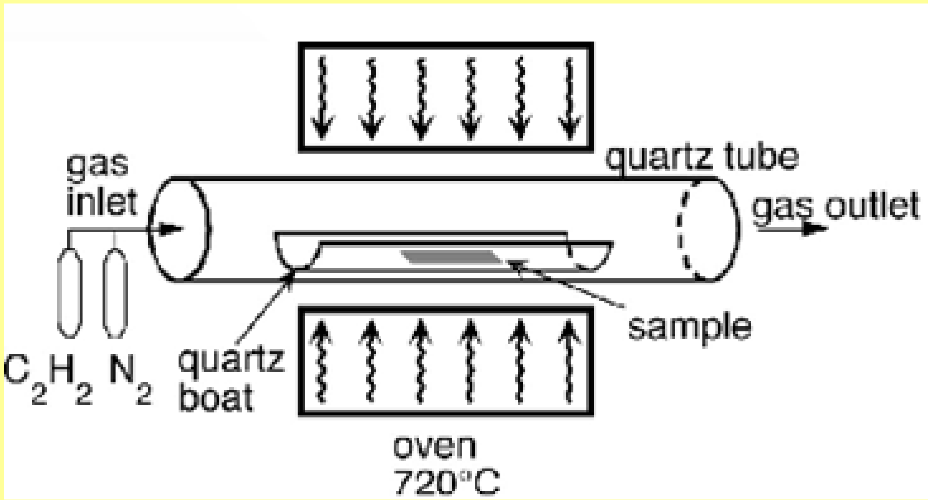
Metal doped electrodes (Fe, Co, Ni, Mo): SWNT

Pure Graphitic electrodes: MWNT (other fullerenes etc)

During this process, the carbon contained in the negative electrode sublimates because of the high temperatures caused by the discharge. Because nanotubes were initially discovered using this technique, it has been the most widely used method of nanotube synthesis.

The yield for this method is up to 30 percent by weight and it produces both single- and multiwall nanotubes, however they are quite short (50 microns)

CVD: Metal Catalysts



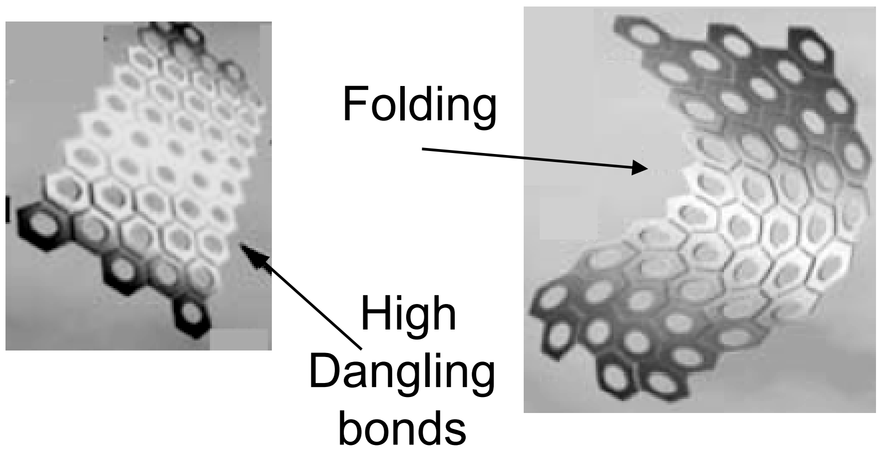
• C based gas
•(acetylene, ethylene, methane)
• Catalyst (Fe, Co, Ni)
• Temperature 700-1000 C

HiPco: CO, $Fe(CO)_5$
Commercial Process
97% Pure, 450 mg /hr

Laser Ablation, pulsed laser, 500 Torr Ar.

Mechanism Ablation, arc discharge: Still Controversial

- Atomize Carbon (Explode or Dissociate on Metal)
- Preclude initial recombination (metal-C bond, high energy)
- Confinement (Prevent over expansion, Background Pressure Key * Note deposition is not in vacuum)
- Cooling (crucial for SWNT, MWNT) (In a metal Dissolution to form a supersaturated solution)
- sp_2 hybridization, sheet bends to reduce dangling bonds (high energy)



In the laser ablation process, a pulsed laser vaporizes a graphite target in a high temperature reactor while an inert gas is bled into the chamber. The nanotubes develop on the cooler surfaces of the reactor, as the vaporized carbon condenses. A water-cooled surface may be included in the system to collect the nanotubes.

Journal of Cluster Science (2003), 14(2), 135-185.

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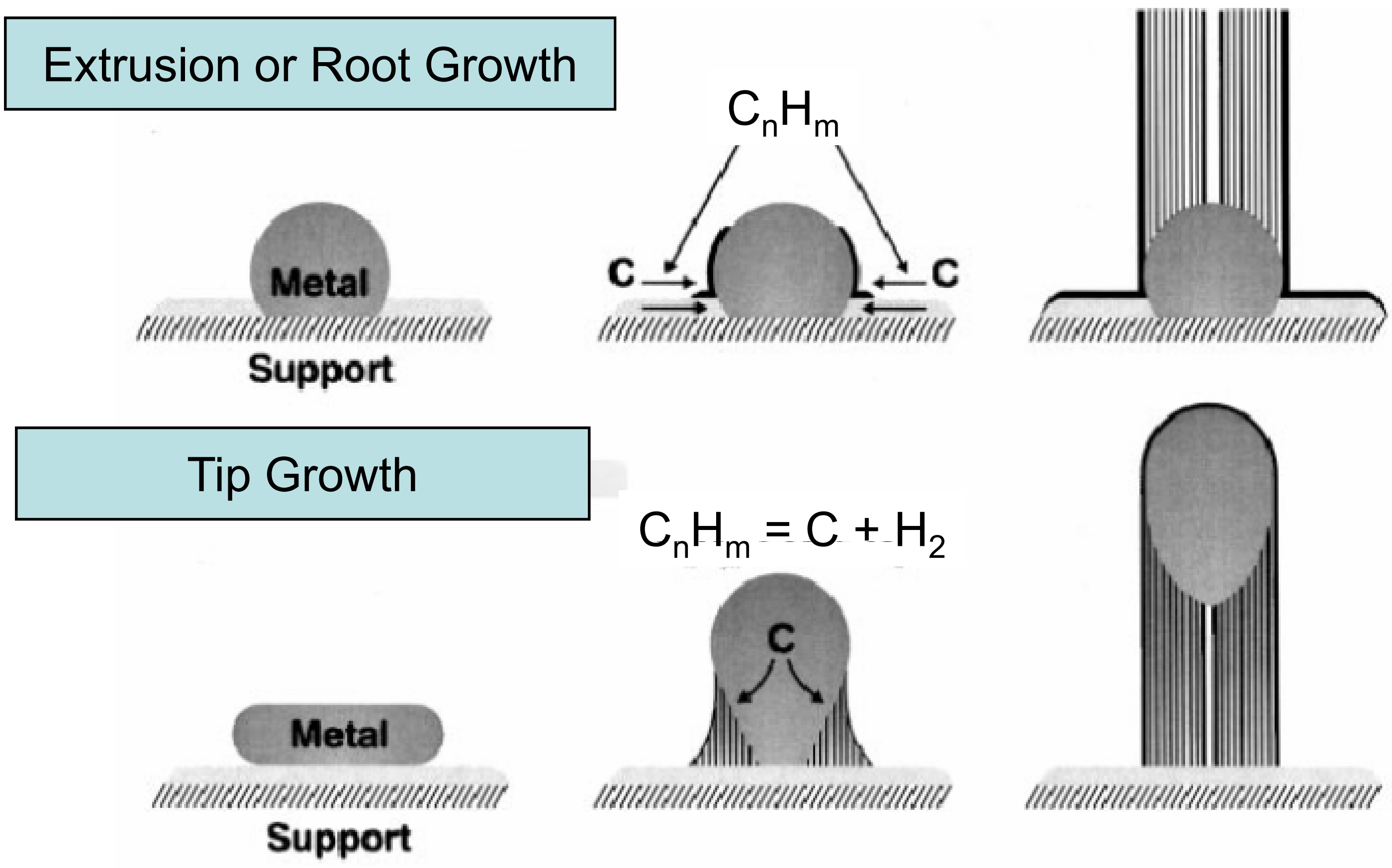
Role of Catalytic Particles in Nanotube Growth



Explains Hollow Tube

Purification to get carbon nanotubes of precise composition and size

- Oxidation: Damage to SWNT (closed structure less reactive) less than other carbon / metal compounds
- Acid treatment, Ultrasonication (Metal removal)
- Magnetic removal of catalysts
- Microfiltration (SNWT trapped), fullerenes solvated in CS2
- Functionalization, Cutting using fluorination and pyrolysis
- Chromatography (HPLC-SEC)

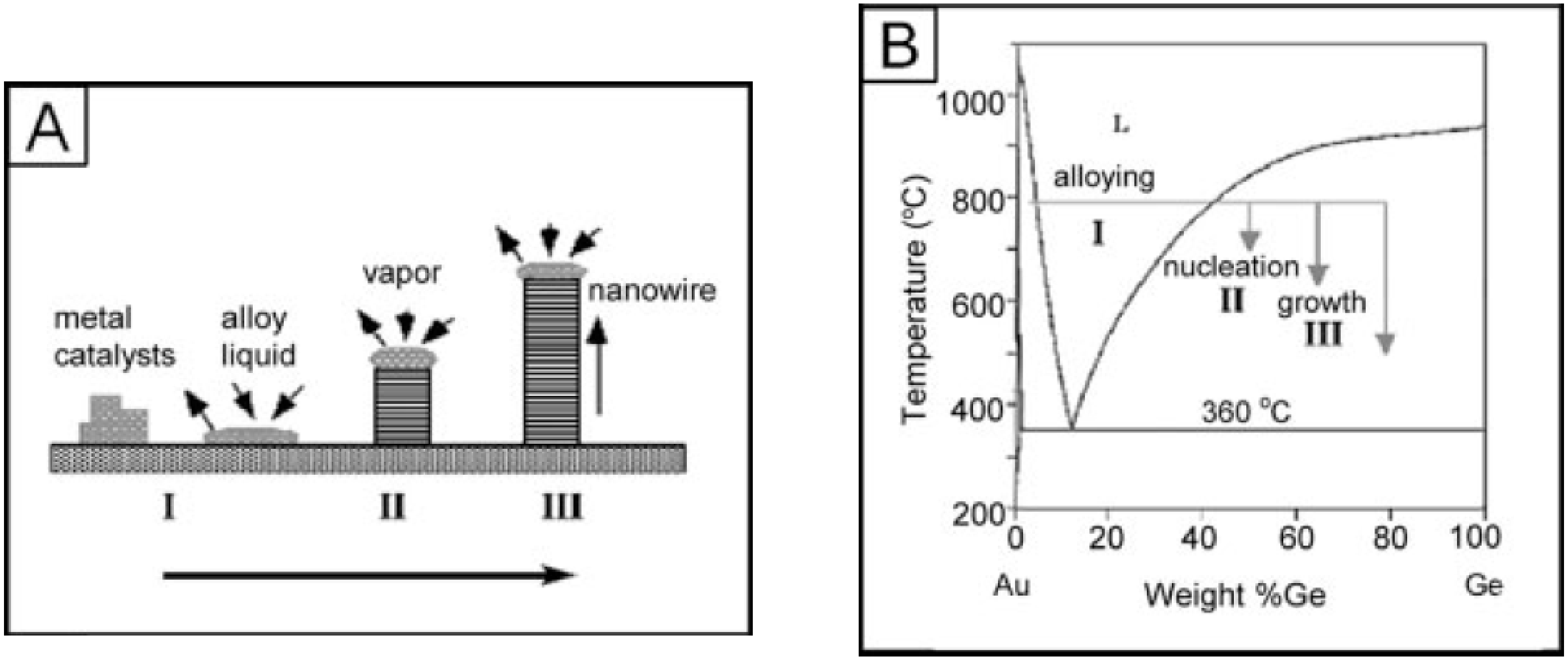
Section III:

Synthesis of Nanowires

Most commonly used methods

- CVD (Chemical Vapor Deposition)
- Solution phase synthesis
- Electrodeposition

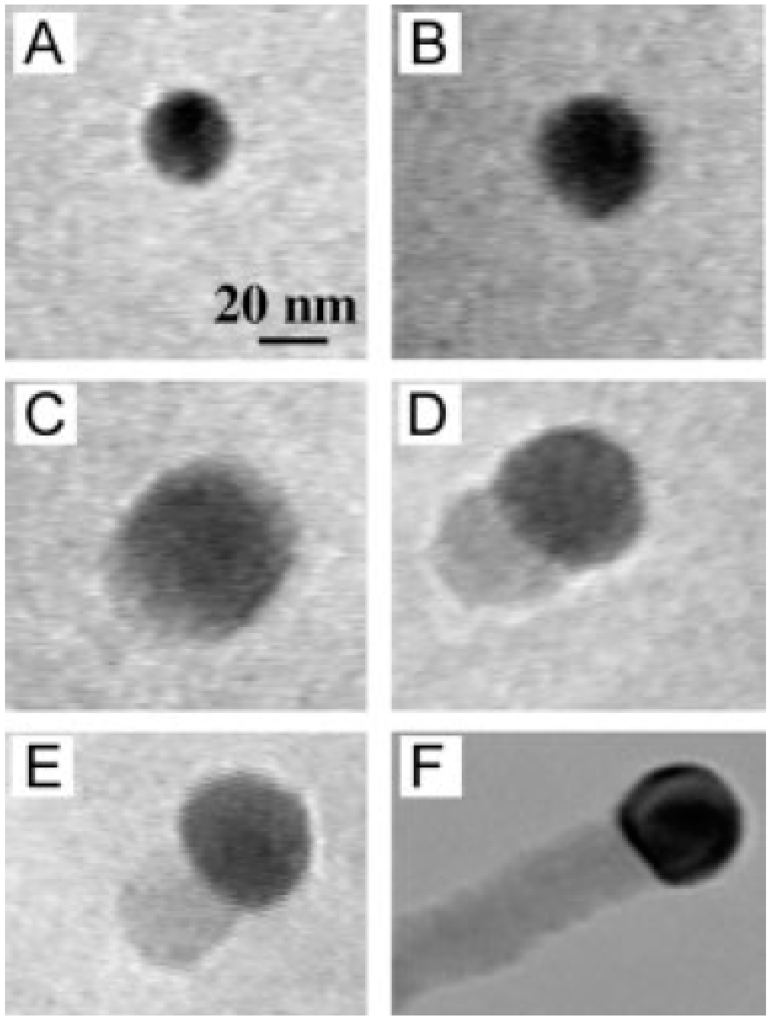
Vapor Liquid Solid (VLS) growth (in CVD)



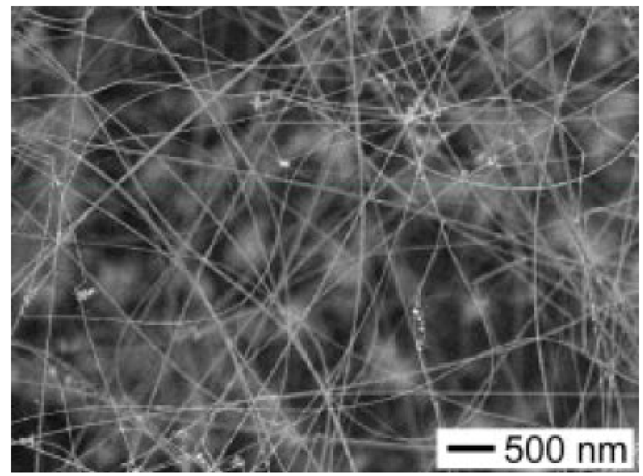
I : Metal catalyst reacts with vapor of Ge (from the decomposition of GeI_2)
II: Au and Ge form a liquid eutectic when temp above (361 C)
III: Droplet becomes supersaturated in Ge, Ge starts to precipitate on liquid Au, at the solid liquid interface.

R. S. Wagner, W. C. Ellis, Applied Physics Letters, 1964, 4, 89;
Y. Xia et al, Advanced Matierals, 2003, 15, 353-387.

Example: Birth of a Ge Nanowire from an Au Catalyst Particle



Au catalyst + GeI_2 vapour



SEM images of Ge nanowires

Y. Wu, P. Yang, JACS 2001, 123, 3165

Case Study II:

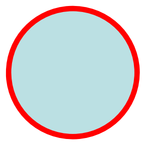
Electrodeposition of Nanowires/Nanorods

in Nanoporous Templates

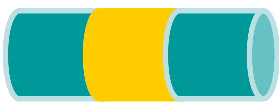
↓

Lab Session II (after spring break)

Promising Nano-Building Blocks – Nanowires (Nanorods)

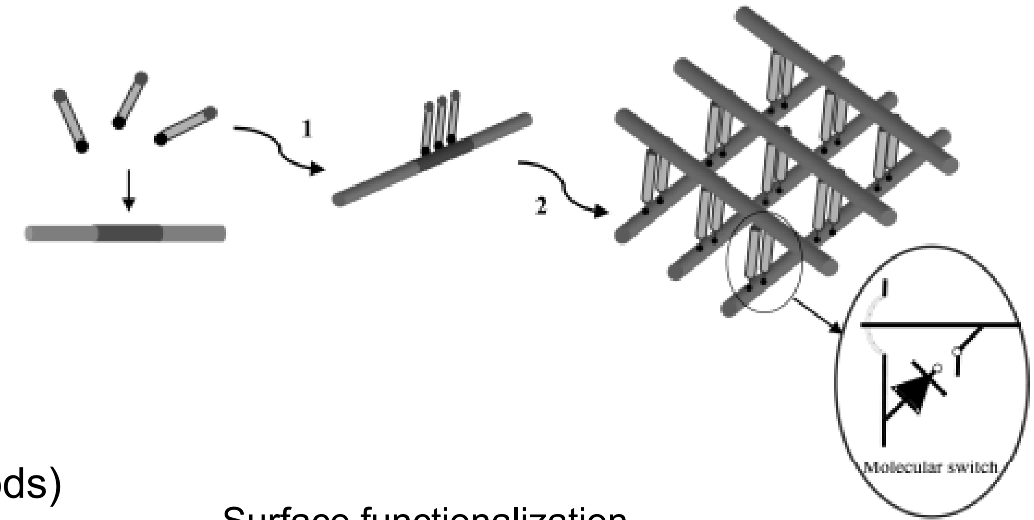


Nanoparticles
(1-100nm)



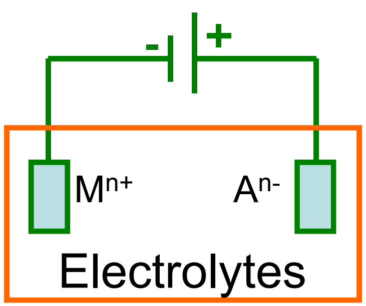
Nanowires (nanorods)

Anisotropic nanoparticles



Kovtyukhova & Mallouk, *Chem. European J.*, **2002**, *8*, 4354-4363

Surface functionalization → Integrated structures or devices
Assembly/integration

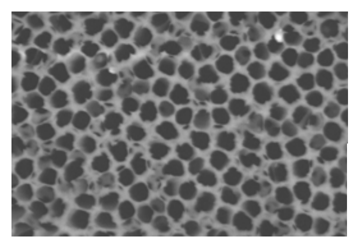


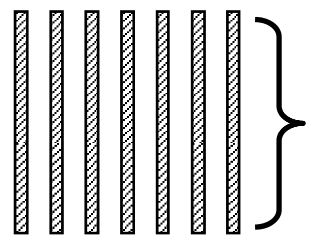
$M^{n+} + n\,e \rightarrow M$

Reduction

Electrodeposition

Nanoporous membranes (alumina or polycarbonate)



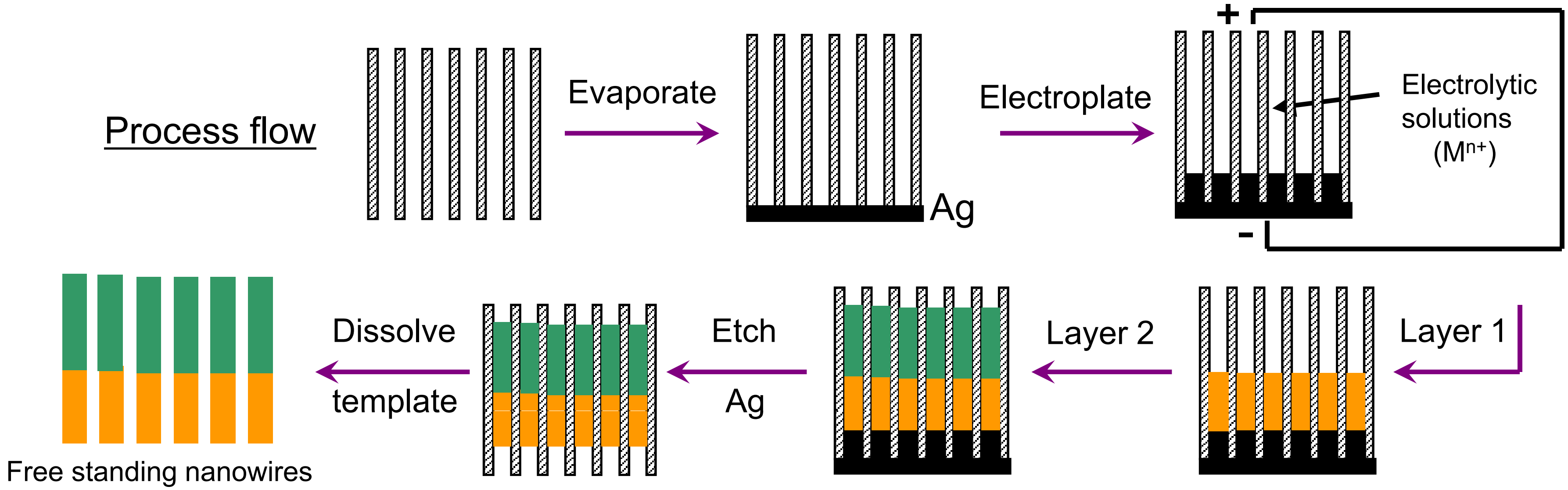


length ≤50 μm

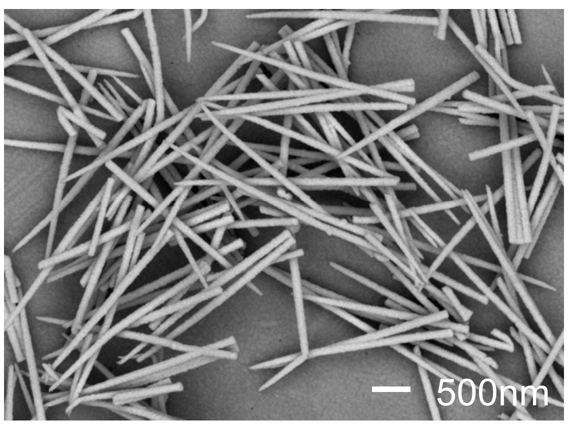
diameter (d)= 15-200nm

- Templates commercially available, and easy to make
- Very large scale production (10^9-10^{10} wires/cm^2)
- Relatively easy to fabricate and very good to pattern

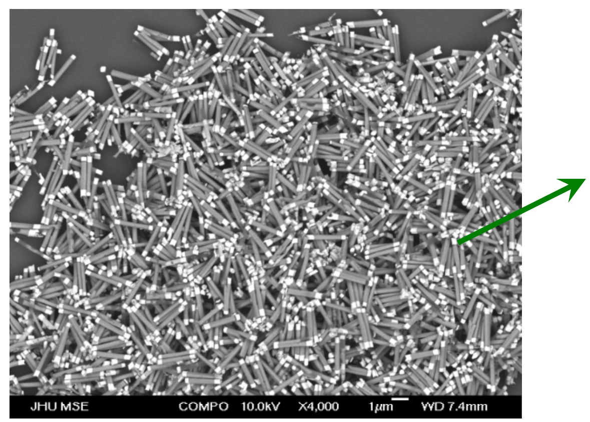
Fabrication of Large-scale One- and Multi-component Nanowires



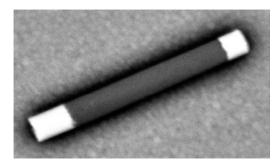
- Nanowires with one- and multi-component segments



One-component nanowires
(gold nanowires, d=50nm)



Multi-component nanowires

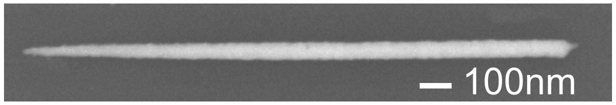


Gold-Nickel-gold
(d=200nm)

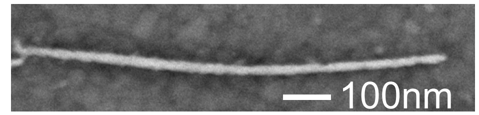
Gu, Ye, Gracias. *Journal of Materials (JOM)* **2005**, *57*, 60-64

Hybrid Nanowires with Controlled Size and Functionality

- Nanowires with different diameters

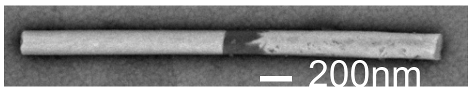


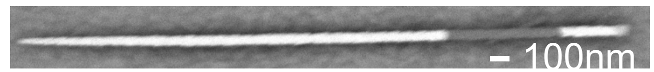
Au nanowire, d=50nm



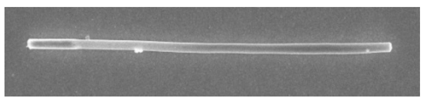
Au nanowire, d=15nm

- Symmetrical and asymmetrical nanowires

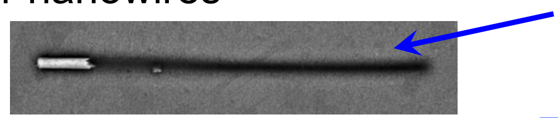




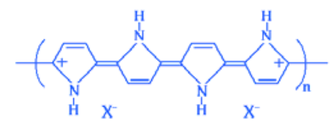
- Inorganic-organic nanowire: metal-polymer nanowires



Au-Polypyrrole nanowire, d=200nm

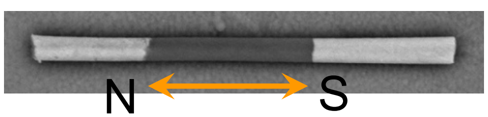


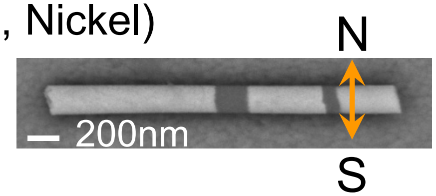
Polypyrrole

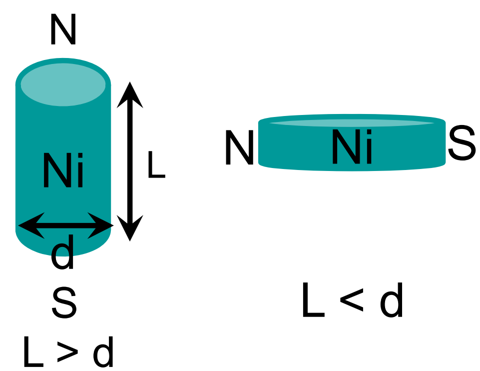


- Nanowires with functional segments

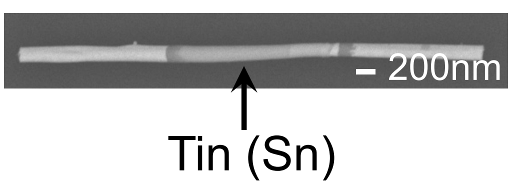
With ferromagnetic segments (e.g., Nickel)







With sensor segments



Anneal →

$Sn \rightarrow SnO_2$: excellent sensor materials

Summary and perspective

- Section I: Nanoparticles synthesis
- Section II: Carbon Nanotube synthesis
- Section III: Nanowires/nanorods
- Molecular based nanomaterials
  (organic molecules, polymers,…)
- Bio-related nanomaterials and nanostructures
  (DNA, peptide, virus, etc)
- New nano-building blocks ●●●