Fabrication of nanostructures and nanoscale devices.
Parts 1-2.

Galina A. Tsirlina

galina.tsirlina@nanocenter.si
galina.tsirlina@protonmail.com

See the lectures at https://www.nanocenter.si/qt-future/education-2/

Parts 1-2, Outline

Definition of nanotechnology

Size effects

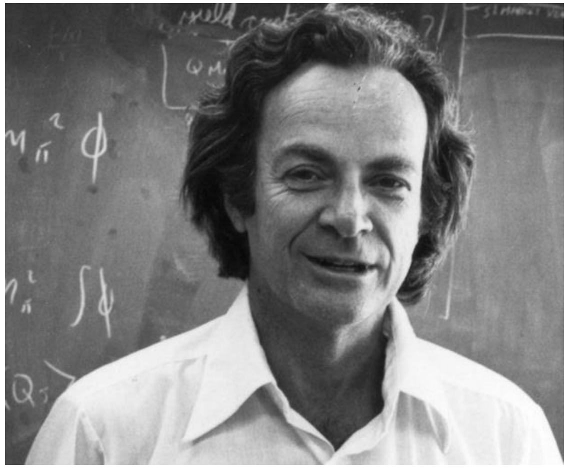
Nanometrology
- ✓ Characterization of single objects (TEM, SEM, probe techniques; image distortions)
- ✓ Compositional analysis (EDX, vibration spectroscopy, X-ray scattering)

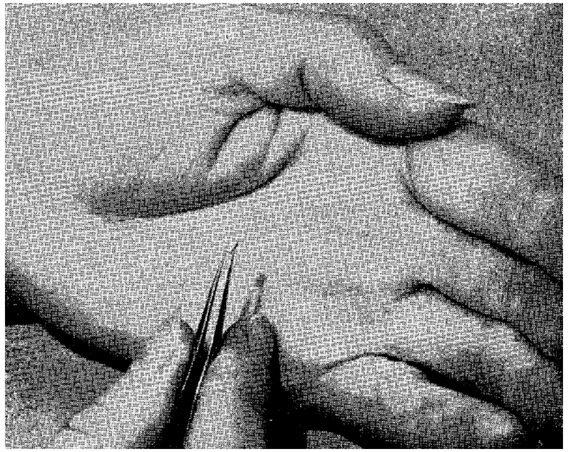
Fabrication of 0D objects
- ✓ Semiconductor quantum dots
- ✓ Colloidal metals
- ✓ Characterization of sols (UV-vis spectra, dynamic light scattering)

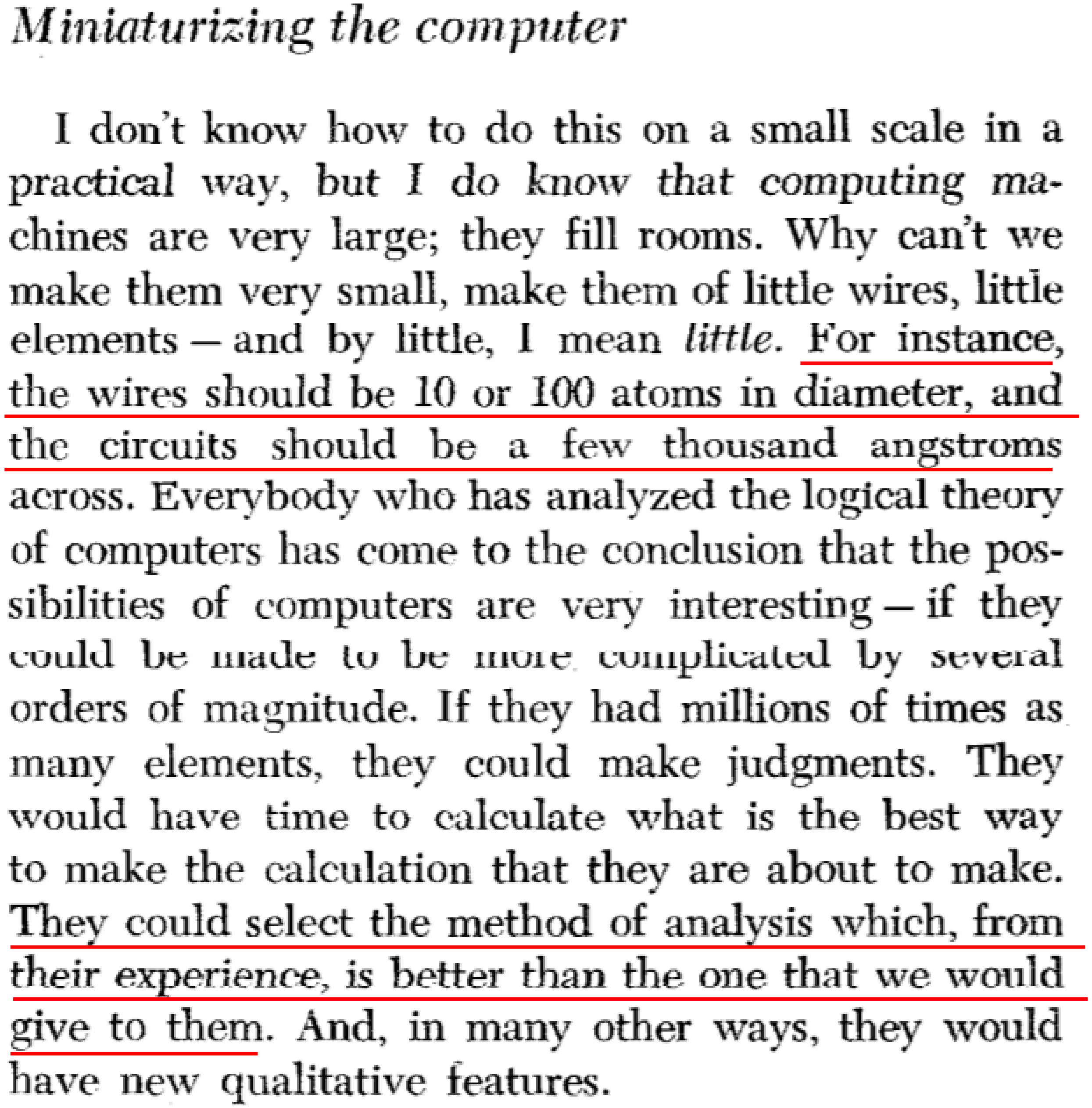
Fabrication of 1D objects
- ✓ Carbon nanotubes (free-standing, SW, MW)
- ✓ Ordered templates for fabrication of nanowires (track membranes, AAO)
- ✓ Templated fabrication of nanowires (filling under pressure, electrodeposition)
- ✓ Isolation of single nanowires and nanotubes

Richard P. Feynman,

"There's Plenty of Room at the Bottom" (Dec 1959)



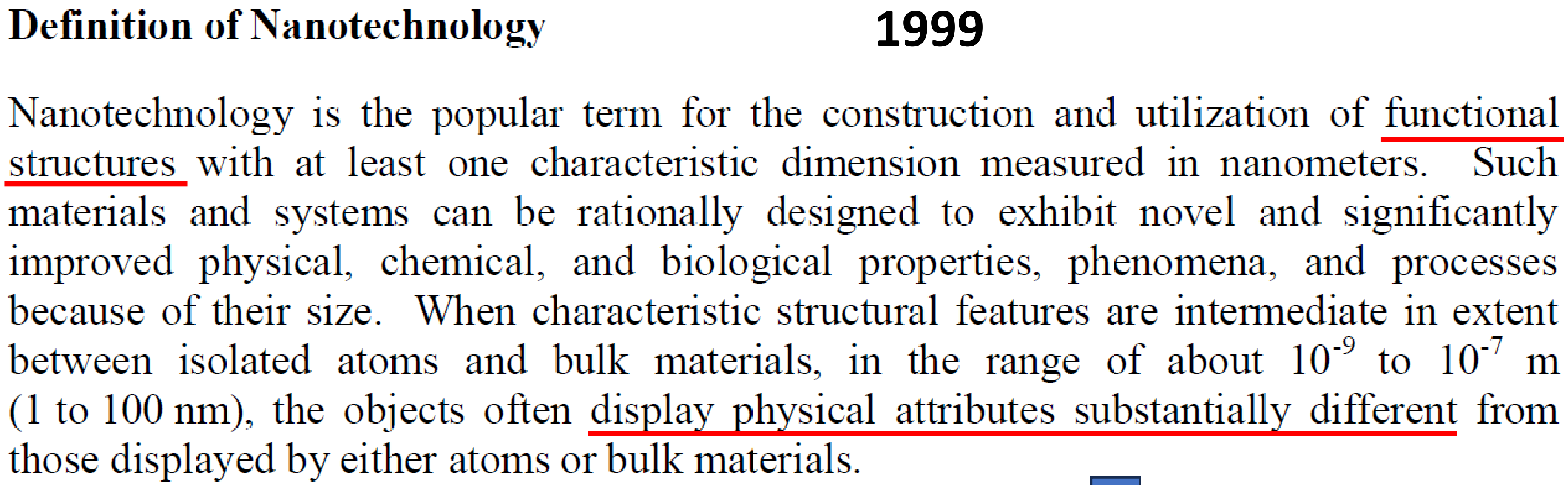




Miniaturizing the computer

I don't know how to do this on a small scale in a practical way, but I do know that *computing machines* are very large; they fill rooms. Why can't we make them very small, make them of little wires, little elements — and by little, I mean *little*. For instance, the wires should be 10 or 100 atoms in diameter, and the circuits should be a few thousand angstroms across. Everybody who has analyzed the logical theory of computers has come to the conclusion that the possibilities of computers are very interesting — if they could be made to be more complicated by several orders of magnitude. If they had millions of times as many elements, they could make judgments. They would have time to calculate what is the best way to make the calculation that they are about to make. They could select the method of analysis which, from their experience, is better than the one that we would give to them. And, in many other ways, they would have new qualitative features.

Engineering and Science 23 (1960) 22-36. ***Reprinted:*** 10.1109/84.128057

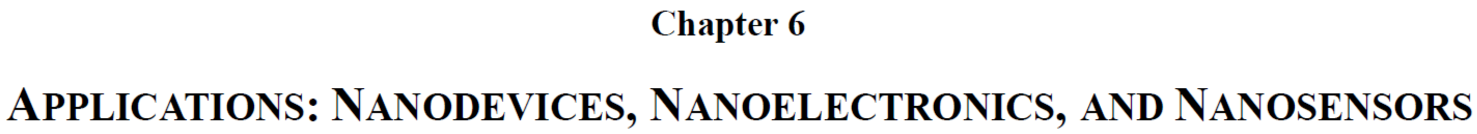


Definition of Nanotechnology

1999

Nanotechnology is the popular term for the construction and utilization of functional structures with at least one characteristic dimension measured in nanometers. Such materials and systems can be rationally designed to exhibit novel and significantly improved physical, chemical, and biological properties, phenomena, and processes because of their size. When characteristic structural features are intermediate in extent between isolated atoms and bulk materials, in the range of about 10^{-9} to 10^{-7} m (1 to 100 nm), the objects often display physical attributes substantially different from those displayed by either atoms or bulk materials.

Not simply miniaturization, but a search for valuable size-dependent properties and effects.



Chapter 6

APPLICATIONS: NANODEVICES, NANOELECTRONICS, AND NANOSENSORS

Giant Magnetoresistance Read Head (IBM, already commercialized)

Molecular electronics
Field-Effect Transistor based on Carbon Nanotube
Single Electron Logic Elements and Memory
Spin Devices
Metal-Oxide Semiconductor (MOS) Integrated Circuits
Resonant Tunneling Devices
Quantum Computing
Optical and Chemical Sensors

Operating principles were already justified for all these groups of devices at the turn of the XX century, and can be found in scientific publications.

Implementation was mostly successful for thin films (2D nanoobjects), and technological issues seemed to be the most important.

Timescale

Mie theory
1908

1930s

1980s

1990s

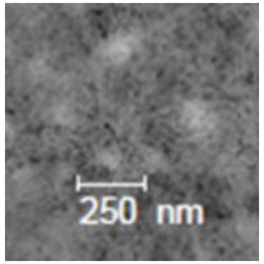
Characterization techniques

Optical spectra exclusively

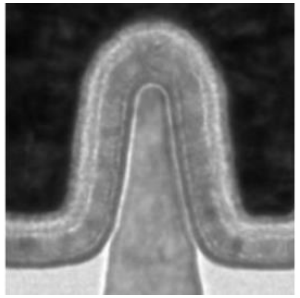
Electron microscopy

Probe microscopy

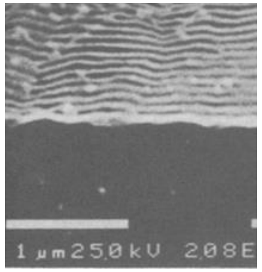
"Nanometrology" involves advanced techniques, incl. X-ray scattering and X-ray spectroscopy



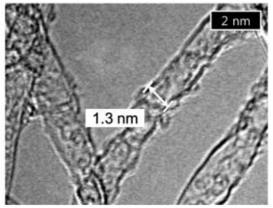
Langmuir-Blodgett monomolecular films



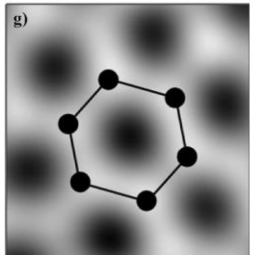
Atomic layer deposition



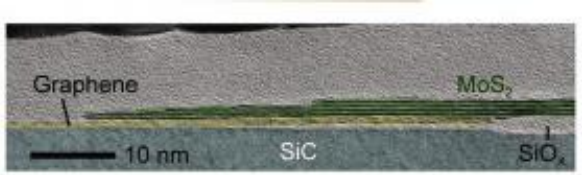
Magnetic superlattices



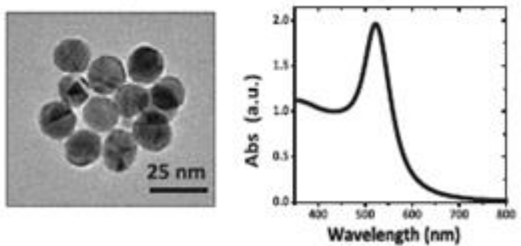
Carbon nanotubes (CNT)



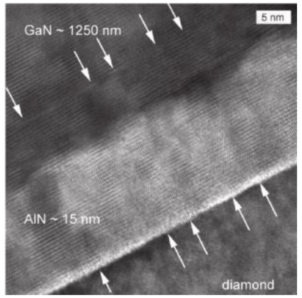
Graphene and other 2D materials (vdW)



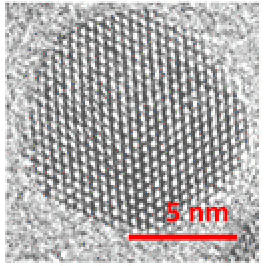
Heterostructures of 2D materials



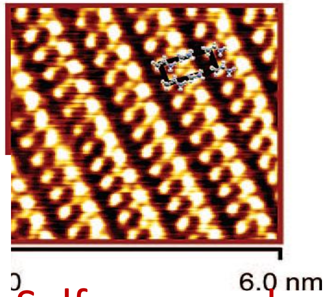
Colloidal metals (sols)



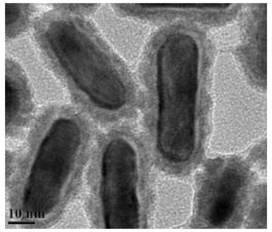
Semiconductor heterostructures



Quantum dots (SC)



Self-arranged monolayers (SAM)



Core-shell particles

Many other particular findings appeared starting from 1990s.

Devices related to nano- and optoelectronics were developed as based on combinations of nm-size fragments.

1857

1960s

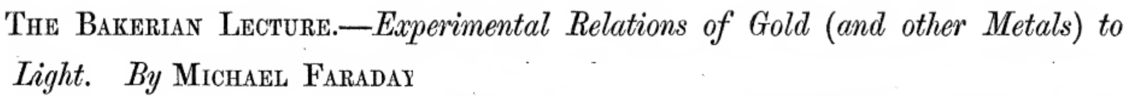
1974

1980s

1990s
First companies

2000s ....
National initiatives

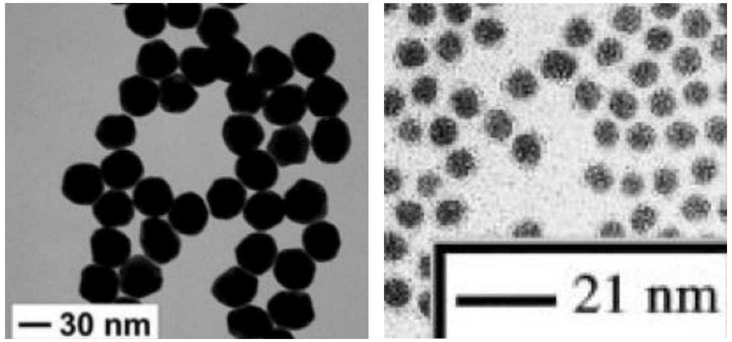
Objects, materials



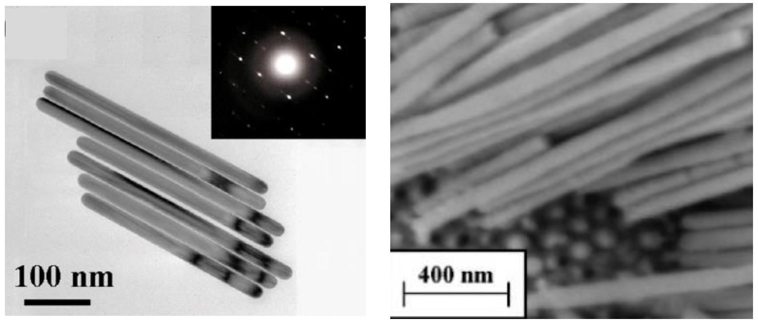
THE BAKERIAN LECTURE.—*Experimental Relations of Gold (and other Metals) to Light.* By MICHAEL FARADAY

Brief Classification, fragments and structures

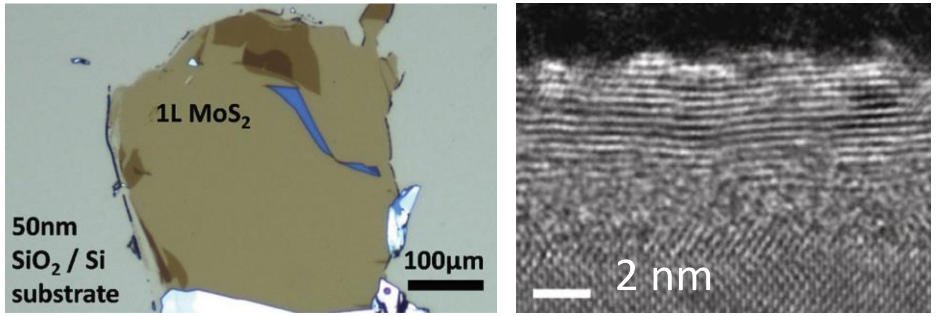
0D: nanocrystals and nanoparticles



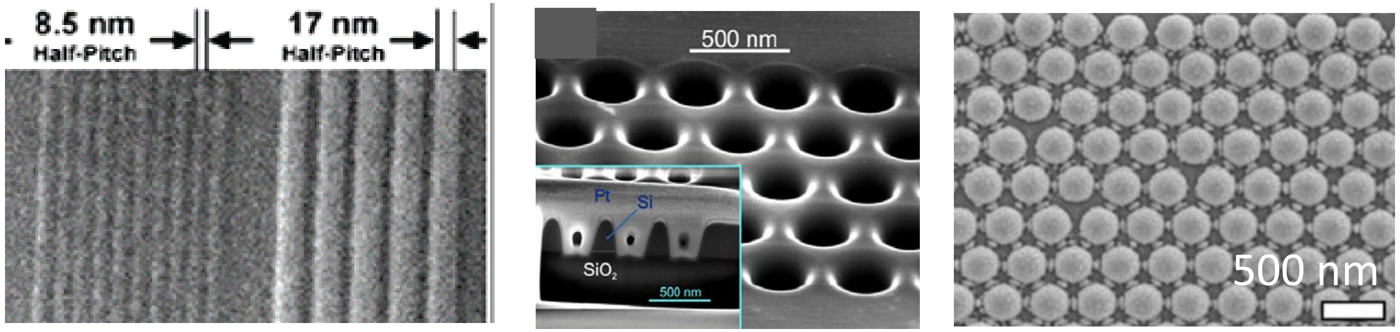
1D: nanowires and nanotubes



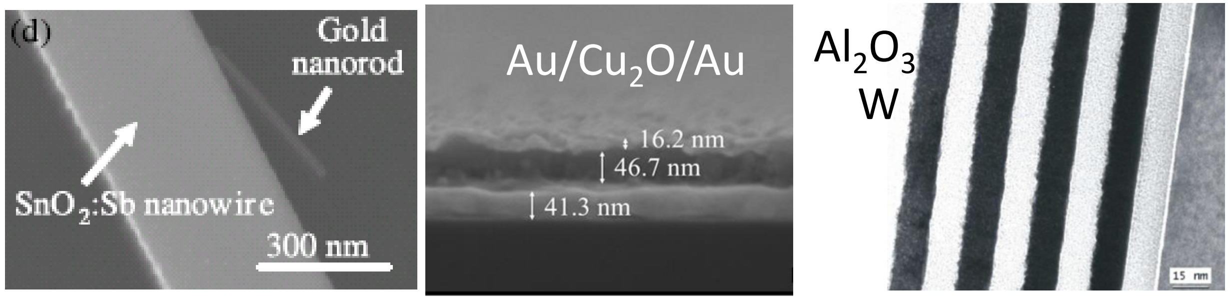
2D: thin films and 2D flakes



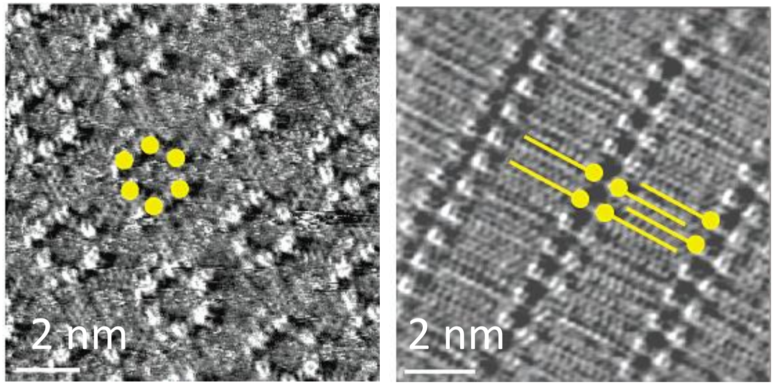
Ordered assemblies of identical fragments on supports

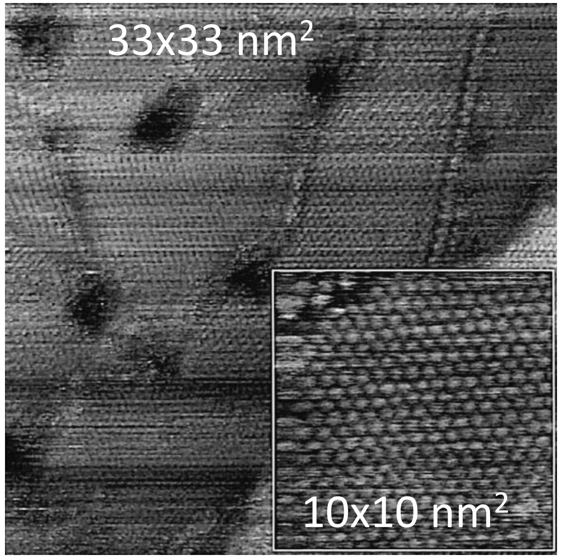


Heterostructures: combinations of different fragments



Molecular modified structures:





Materials typically applied for technology

Functional materials: metals, alloys, oxides, binary II-VI and III-V semiconductors, conducting polymers

Supports: silicon, insulating oxides <crystallographic orientation of the surface is important>, flexible polymers

Supplementary materials: insulating polymers (resists, track membrane templates); porous oxides

Principal technological schemes

For fragments:

Bottom-up (*deposition, sputtering, etc; assumes nucleation and growth of particles*)

or

Top-down (*milling, thinning of the fibers, cutting, etc*)

For structures:

Subsequent fabrication of fragments (*sometimes requires protection of the fragments formed earlier*)

or

immobilization of separately prepared fragments

or

combined multi-step technologies

Nanoelectronics

- spintronics
- cryoelectronics (*superconductor junctions and digital logics*)
- single electron devices (SETs)
- elements of organic electronics

Quantum computing

- superconductor qubits
- spin-based qubits
- electromagnetic traps for atoms and ions
- single electron qubits

Nanoelectronic emitters and detectors

- semiconductor light diodes
- single photon detectors (*semiconductor, superconductor*)
- emitters of electrons based on nm-size materials
- SQUID detectors
- SET-electrometers

Photonics and non-linear optics

- photonic crystals (*filters*)
- quantum micro resonators
- nanoplasmonics
- photonic integrated circuits
- single-photon sources

Tentative list of devices, which step-by-step technology we can discuss at the end of this course (Nov 24, 2023).

Please, send me your suggestions
galina.tsirlina@nanocenter.si
on or before Nov 9.

We shall vote for device the most interesting for the audience on Nov 10.

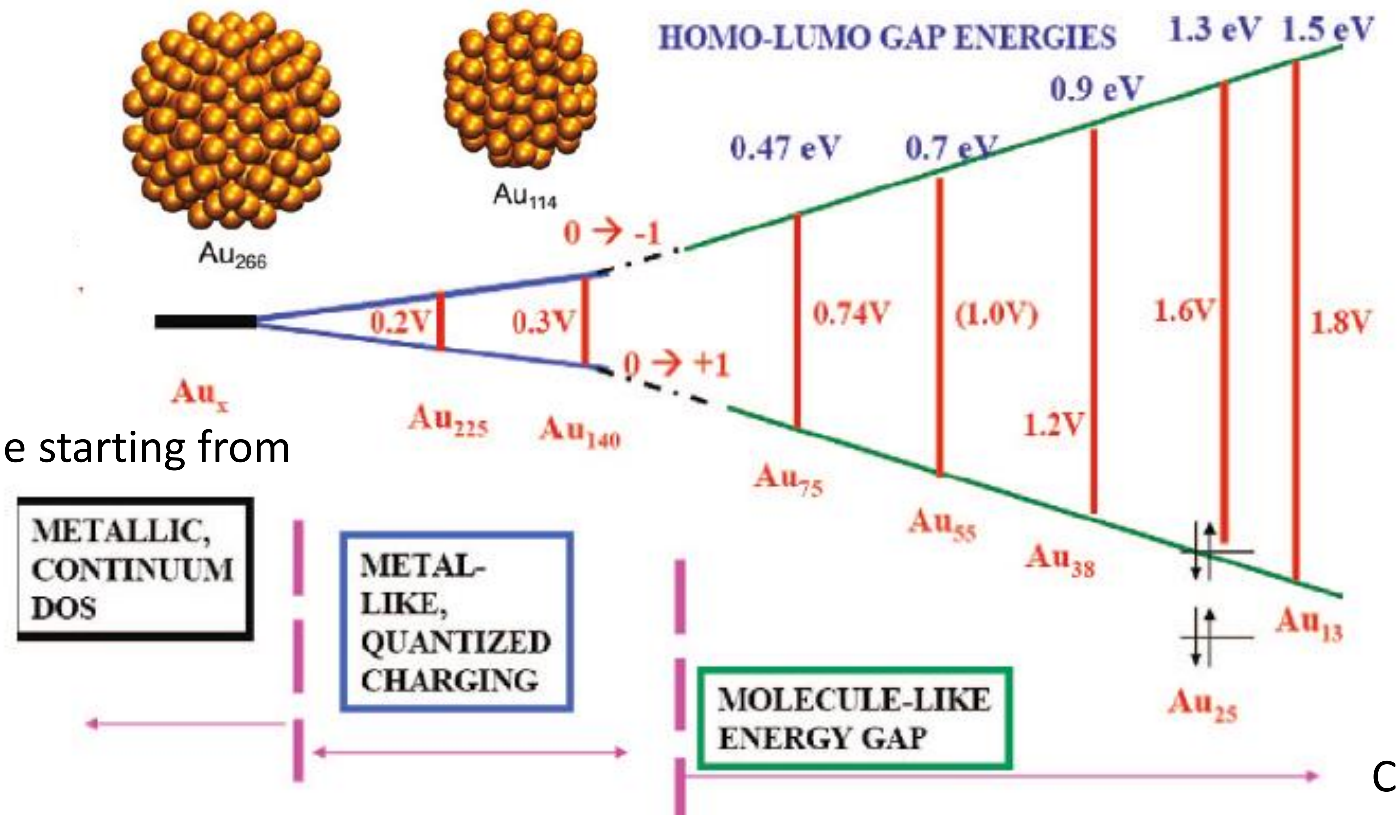
You can suggest something else as well,
in frames of nanotechnology definition.

Size effects

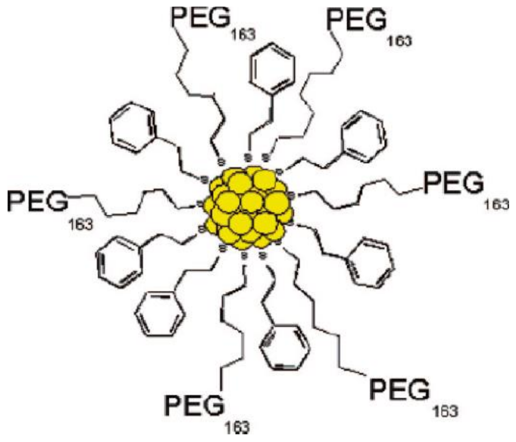
1. **Crystal shape**
2. **Interatomic distance/lattice parameter**
3. **'Additional' free energy (interfacial contribution)**
4. **Conductivity**
5. **Optical properties**

………………

> "Not simply miniaturization, but a search for valuable size-dependent properties and effects."



Au_{25}, stabilized by organic molecules

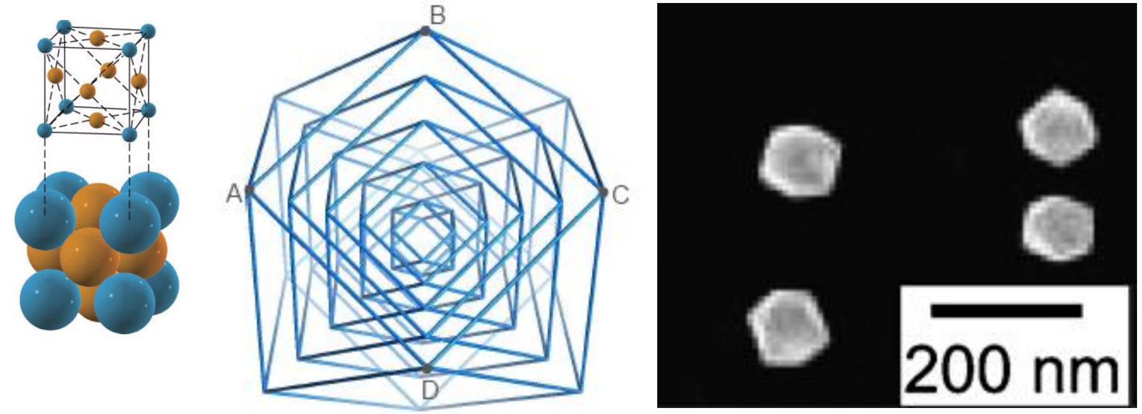


Quantization is noticeable starting from ~ 2 nm size (metals)

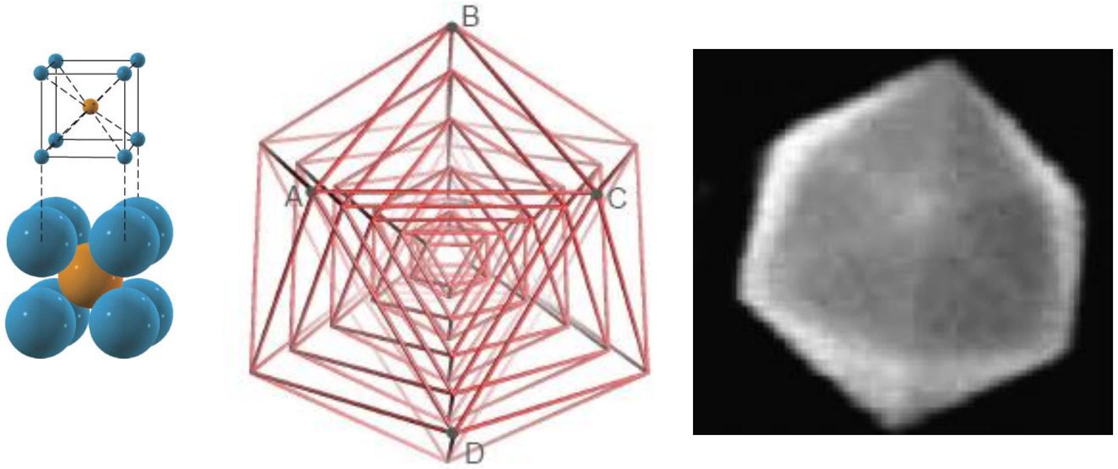
Atomic mass 197 g/mol
Density 19.3 g/cm^3

Chem. Rev. 108 (2008) 2688

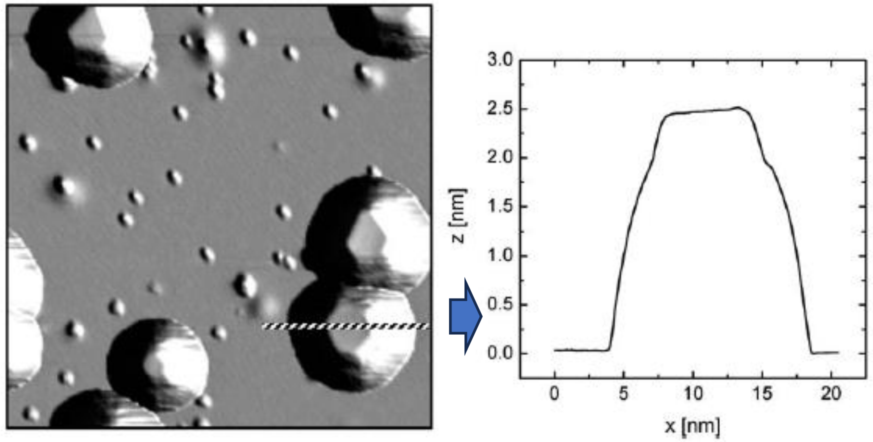
Size dependent properties of materials. 1. Crystal shape



Cubic octahedron (for face-centered cubic lattice, **fcc**)

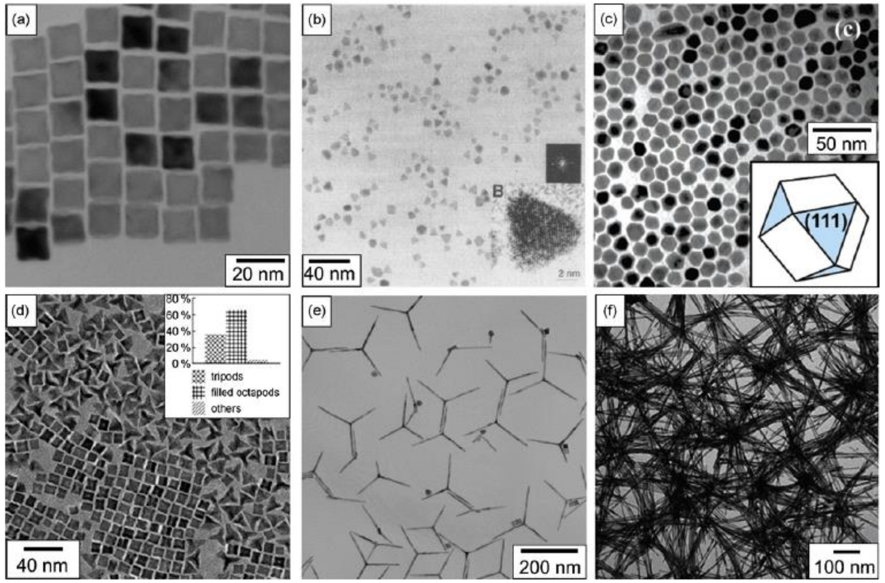


Icosahedron (for body-centered cubic lattice, **bcc**)



Gold on highly oriented pyrolytic graphite (HOPG): facetting

Progress Surface Sci. 81 (2006) 53

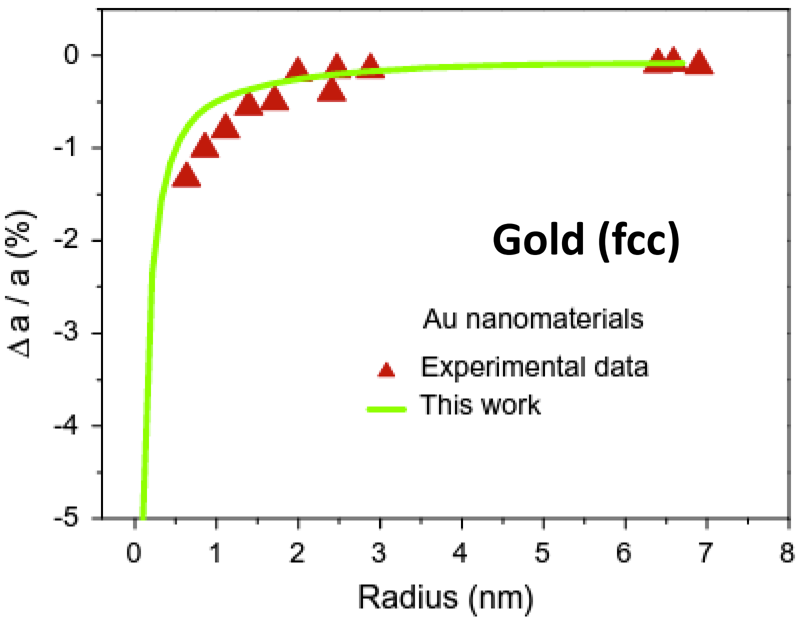


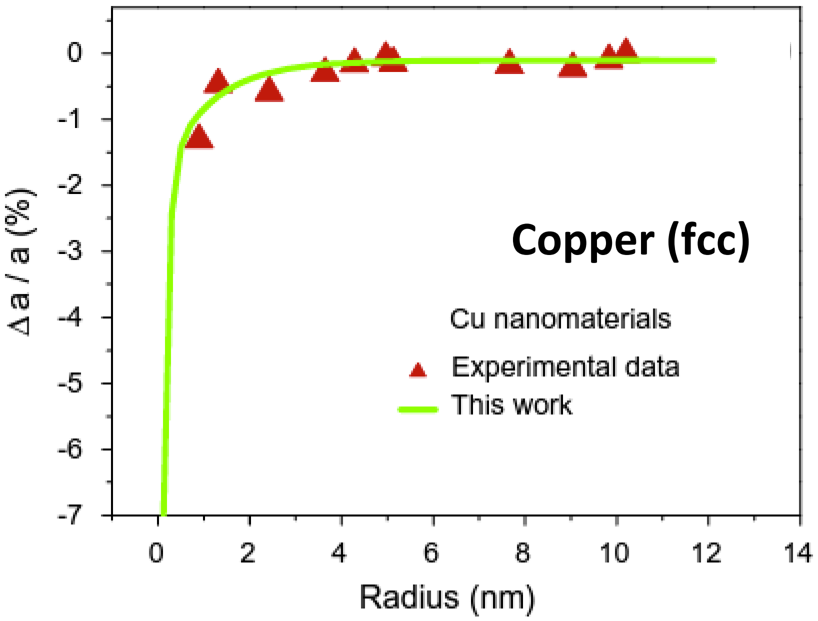
Other shapes remain **metastable**, despite can be long-living: example for platinum

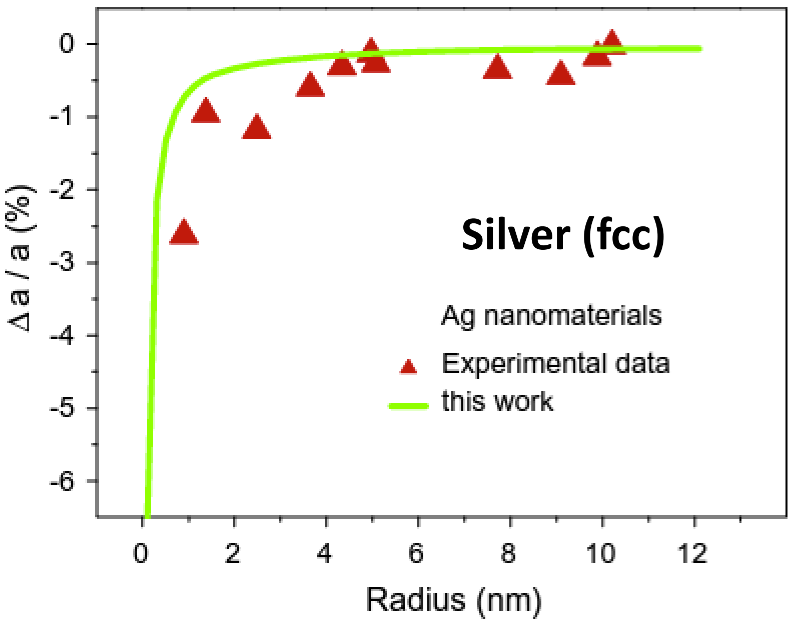
Nano Today 4 (2009) 143

Size dependent properties of materials. 2. Interatomic distance/lattice parameter

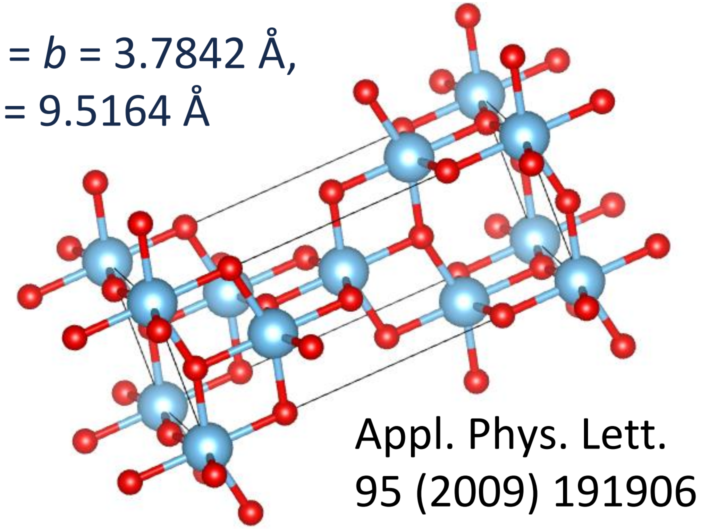
Materials&Design 83 (2015) 159



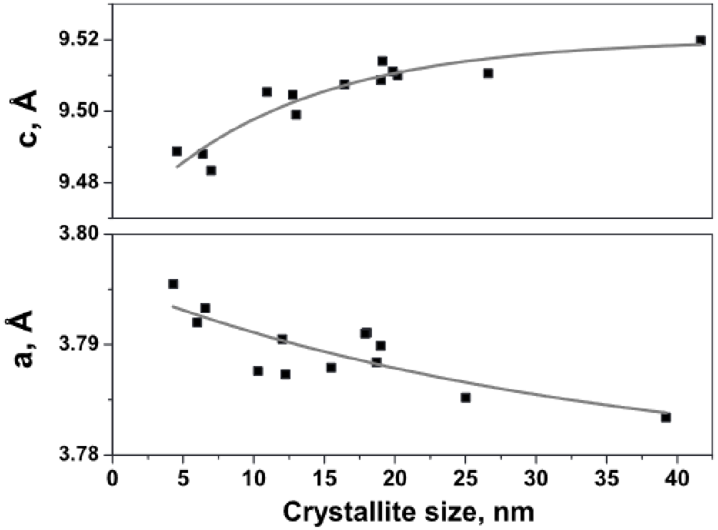


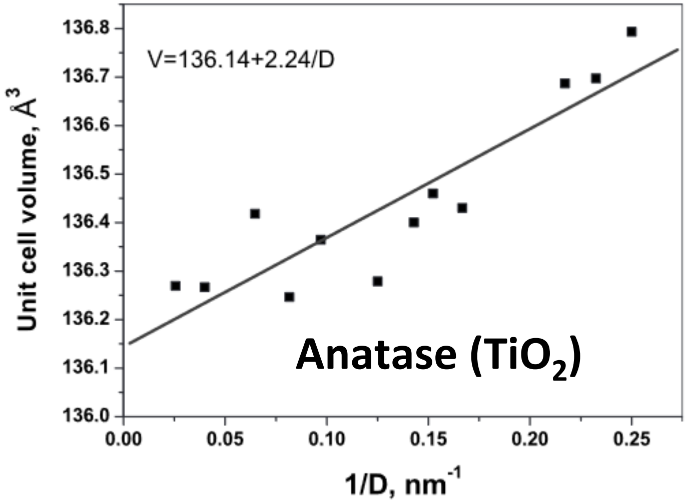


a = *b* = 3.7842 Å,
c = 9.5164 Å



Appl. Phys. Lett.
95 (2009) 191906





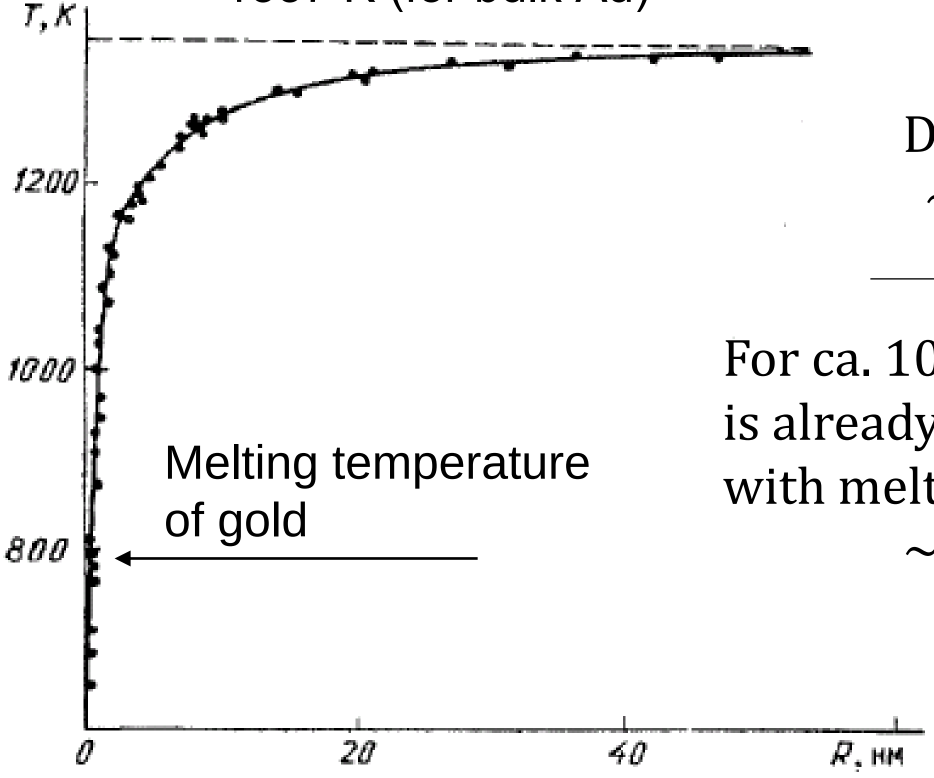
Size dependent properties of materials. 3. ‘Additional’ free energy (interfacial contribution)

Energy spent for formation of
a single spherical particle of radius *r*

$$A = 4\pi r^2\sigma$$

Surface tension

1337 K (for bulk Au)



Melting temperature
of gold

Particle size, nm

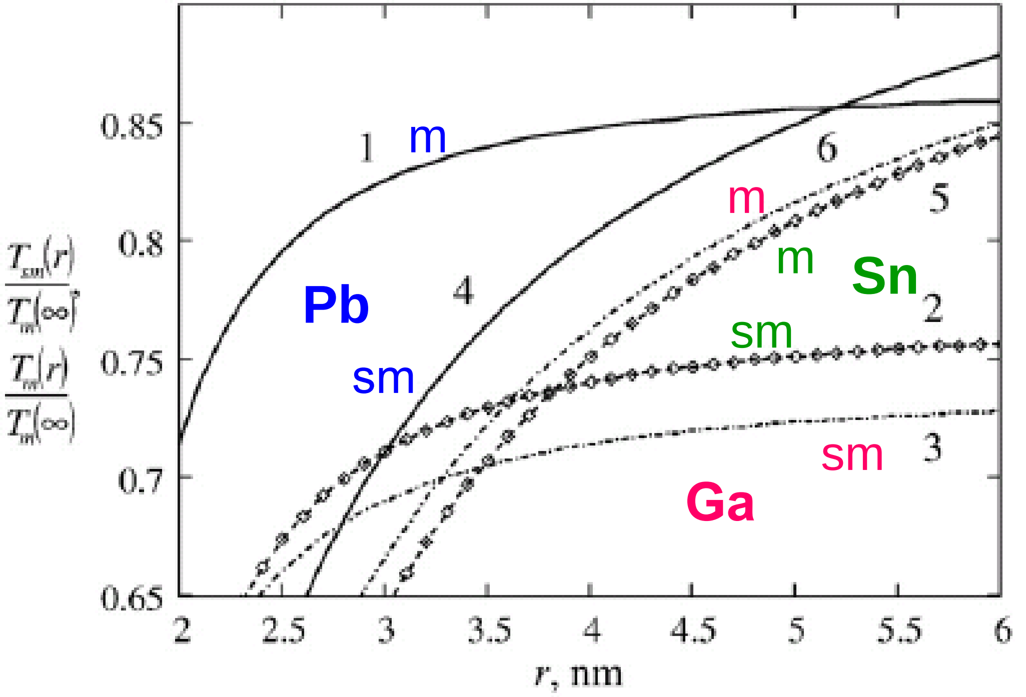
Phys. Rev A 13 (1976) 2287

$\sigma \sim 1.5\ \mathrm{J/m^2}$

Density
$\sim 20000\ \mathrm{kg/m^3}$

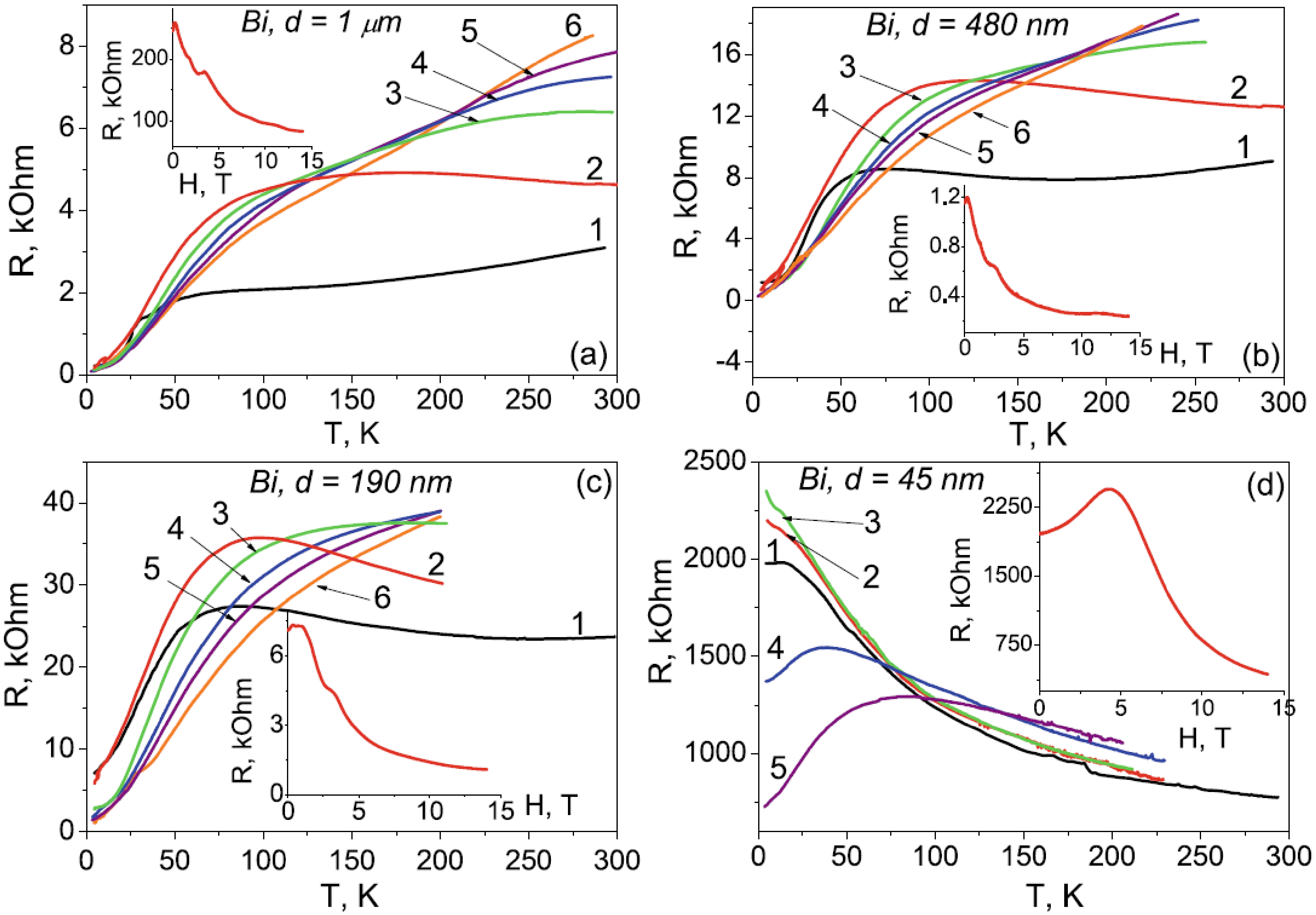
For ca. 10 nm particle, *A* is already comparable with melting enthalpy
$\sim 70\ \mathrm{kJ/kg}$

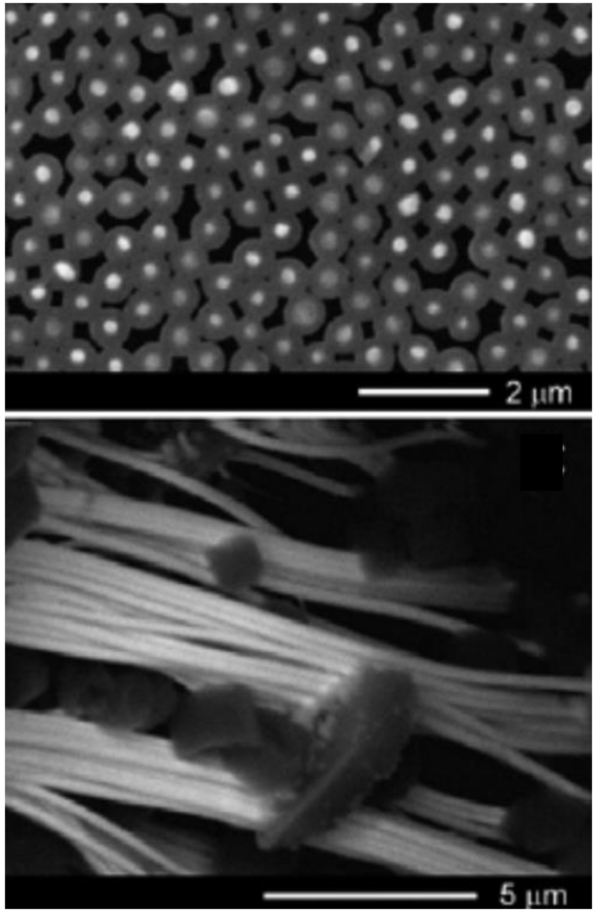
Melting (m) and
near-surface melting (sm)



Mater. Lett. 63(2009)1525

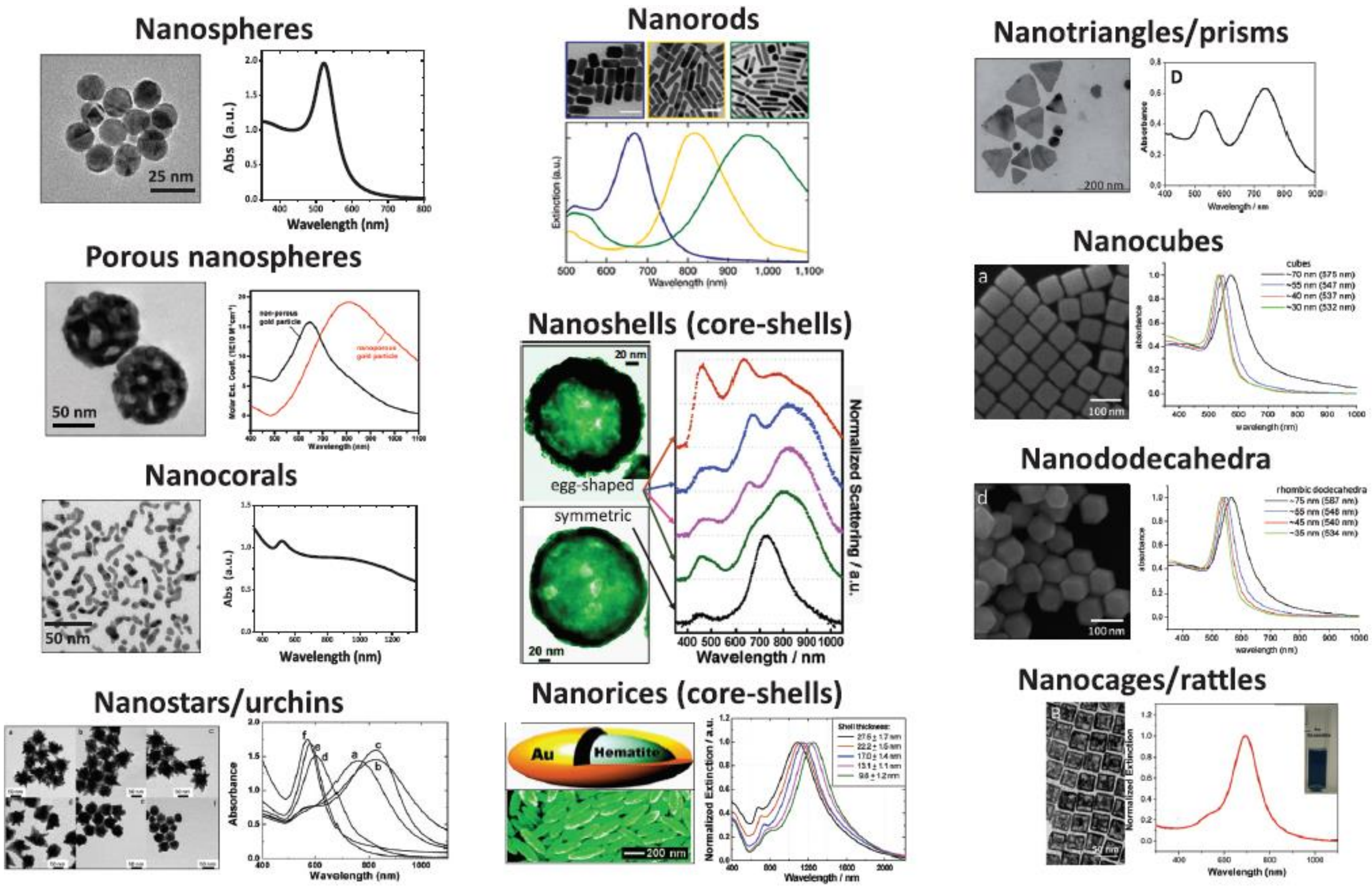
Size dependent properties of materials. 4. Conductivity, example for Bi wires (glass insulated)





J Low Temp Phys 158 (2010) 530

Size (and shape) dependent properties of materials. 5. Optic absorbance, example for Au particles



J. Phys.: Condens. Matter 29 (2017) 203002

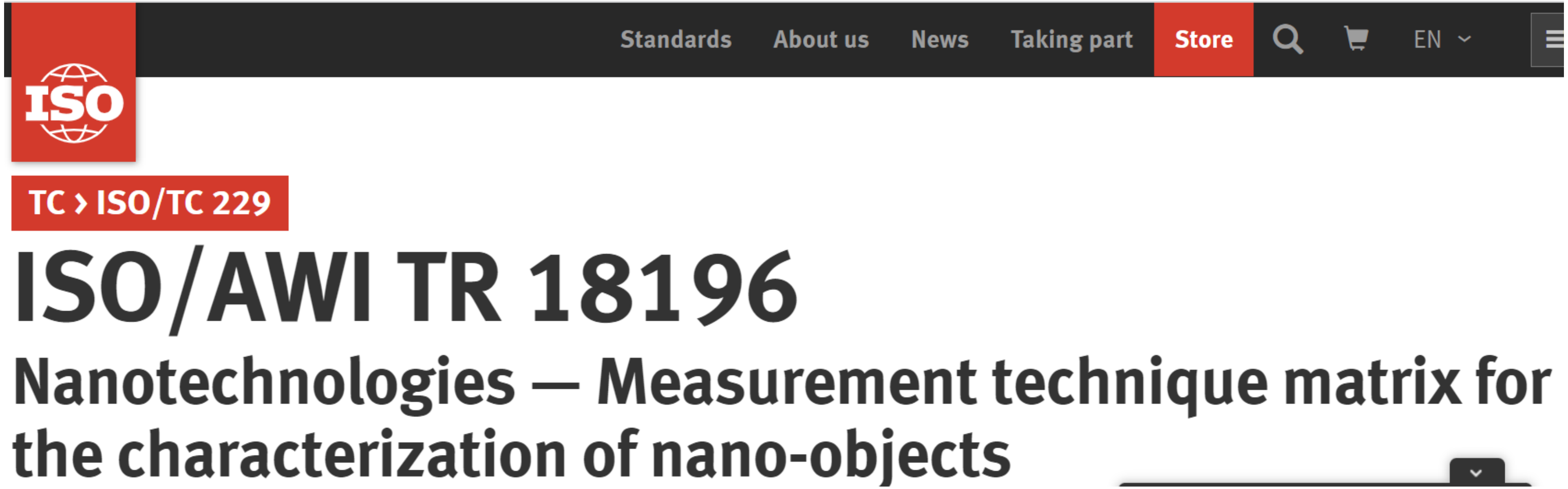
Nanometrology

Electron microscopy: Scanning (SEM) and Transmission (TEM) <*vacuum exclusively*>

Low-energy electron diffraction (LEED) <*vacuum exclusively*>

Probe microscopy: Scanning Tunneling (STM), Atomic Force (AFM), … <*any medium*>

X-ray energy-dispersive spectral analysis



TC › ISO/TC 229

ISO/AWI TR 18196

Nanotechnologies — Measurement technique matrix for the characterization of nano-objects

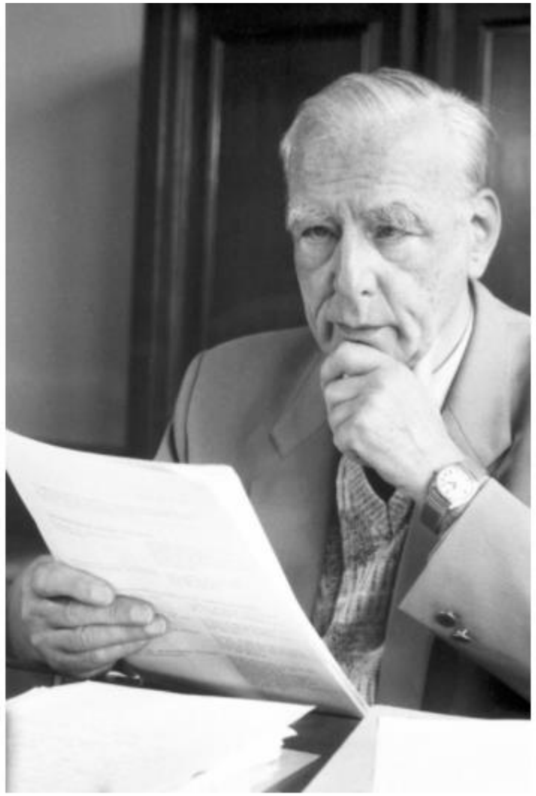


Photo from the Nobel Foundation archive.

Ernst Ruska

Prize share: 1/2

Photo from the Nobel Foundation archive.

Gerd Binnig

Prize share: 1/4

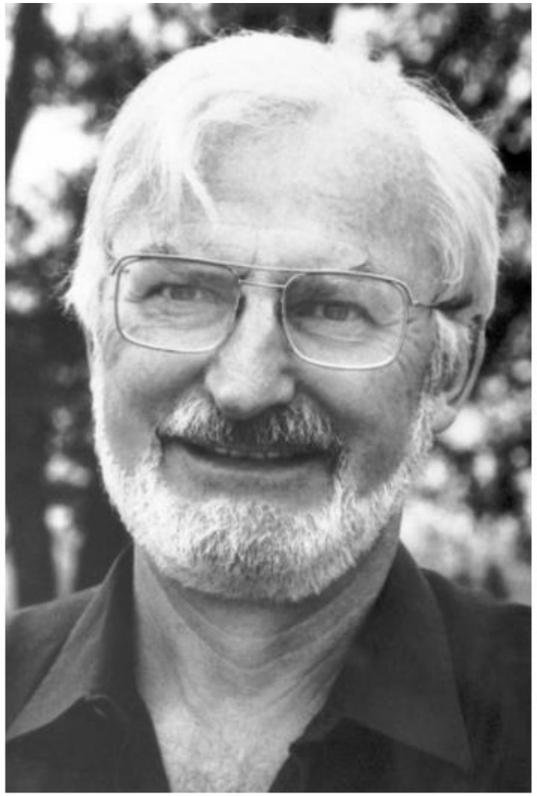


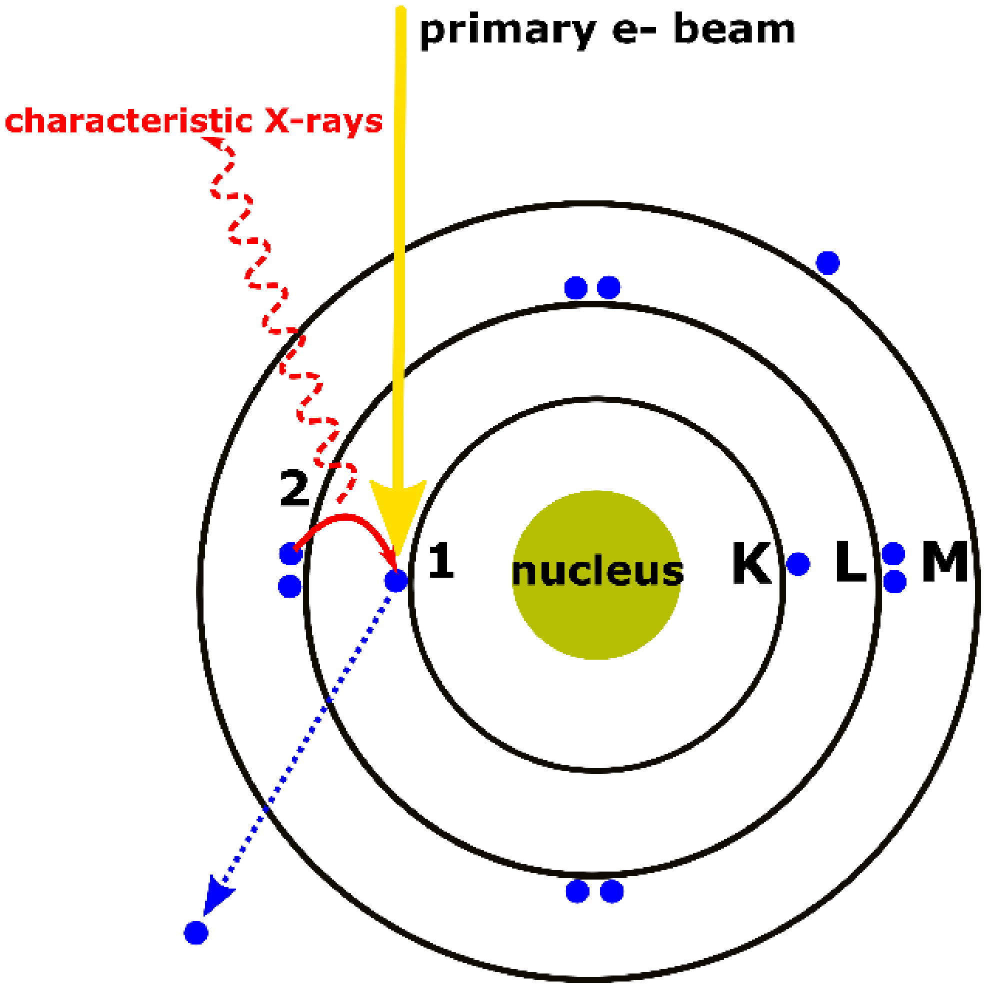
Photo from the Nobel Foundation archive.

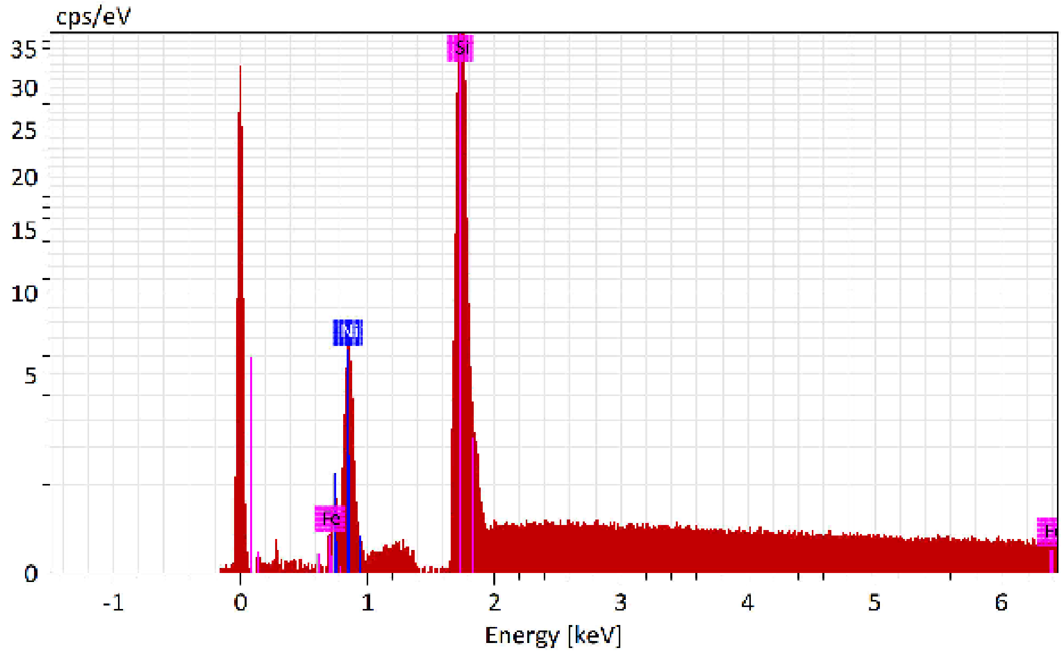
Heinrich Rohrer

Prize share: 1/4

The Nobel Prize in Physics 1986 was divided, one half awarded to Ernst Ruska "for his fundamental work in electron optics, and for the design of the first **electron microscope**", the other half jointly to Gerd Binnig and Heinrich Rohrer "for their design of the **scanning tunneling microscope**."

Energy-dispersive X-ray spectroscopy (EDX, or EDS): elemental analysis in configuration of electron microscopes





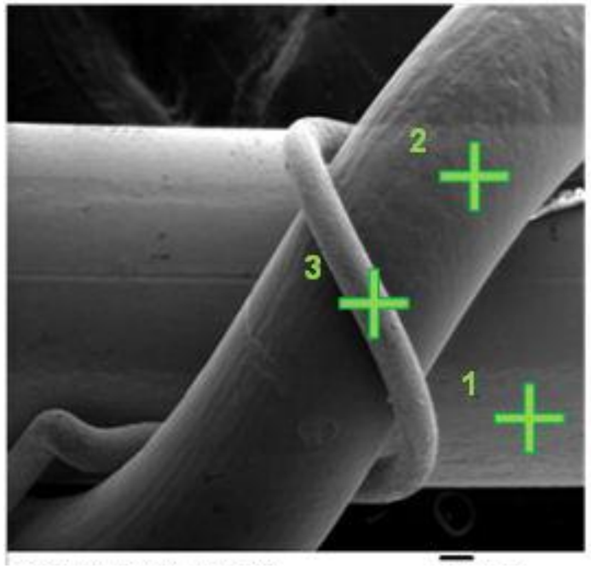
Acquisition

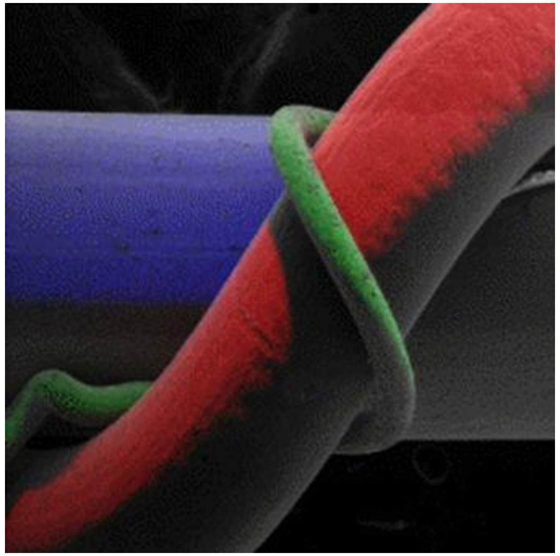
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Carbon	6	301	0.00	0.00	0.00	0.00	0.00
Silicon	14	434054	83.54	83.54	91.38	1.72	2.06
Nickel	28	56377	16.46	16.46	8.62	1.92	11.68
		Sum	100.00	100.00	100.00		

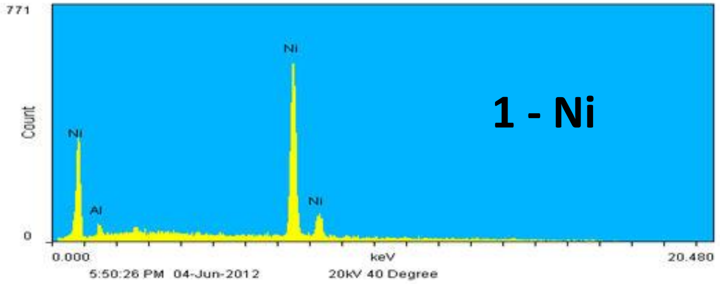
https://www.thermofisher.com/

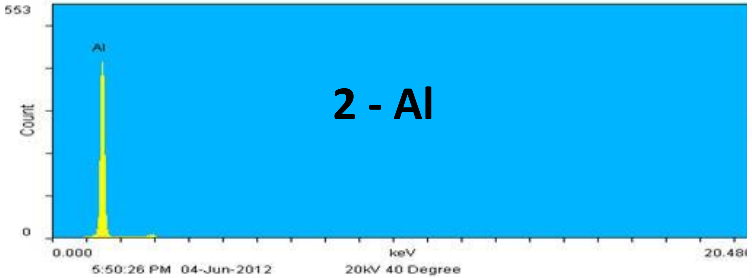
Light elements cannot be detected with a reasonable accuracy

Electron microscopy, SEM: mapping of the elements with μm resolution

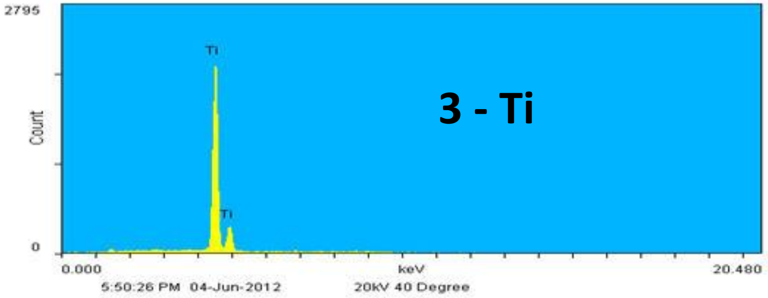




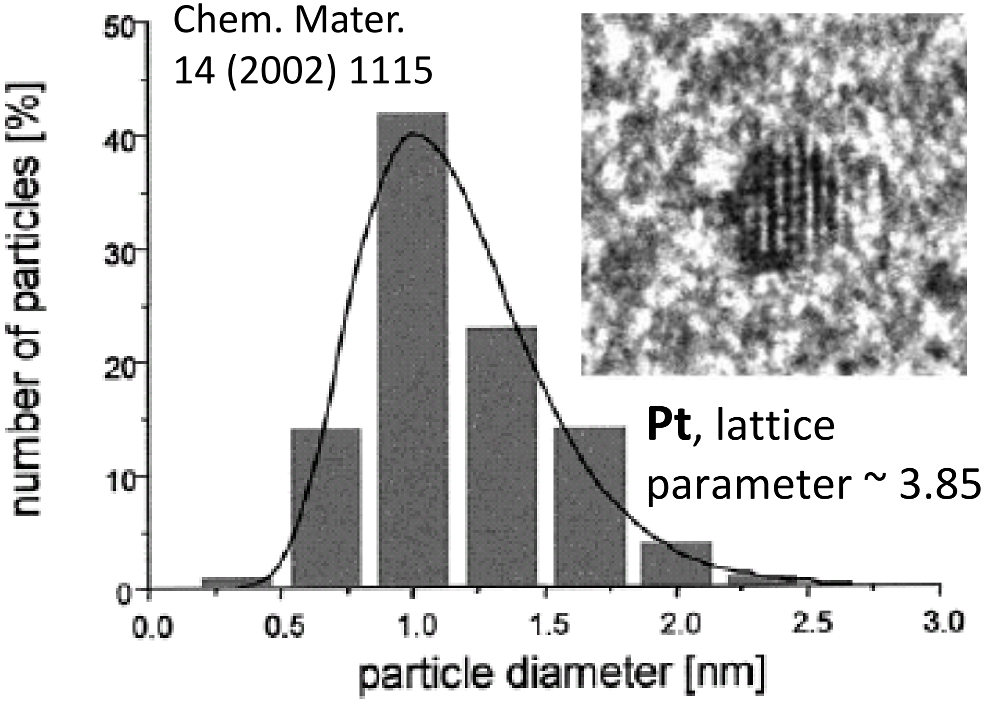




EDX spectra

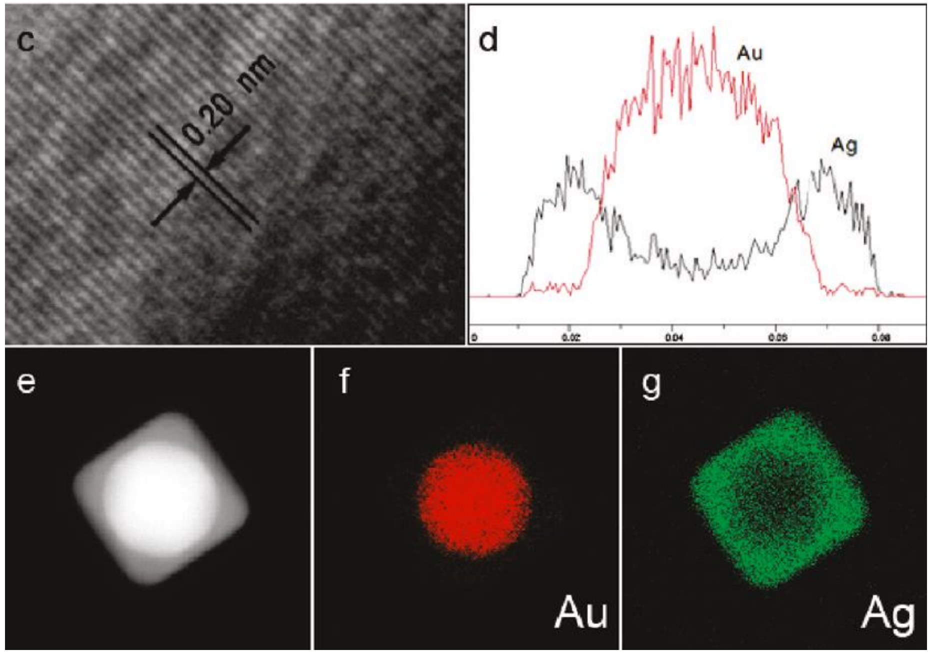


Electron microscopy, TEM: atomic resolution and mapping of the elements



Chem. Mater.
14 (2002) 1115

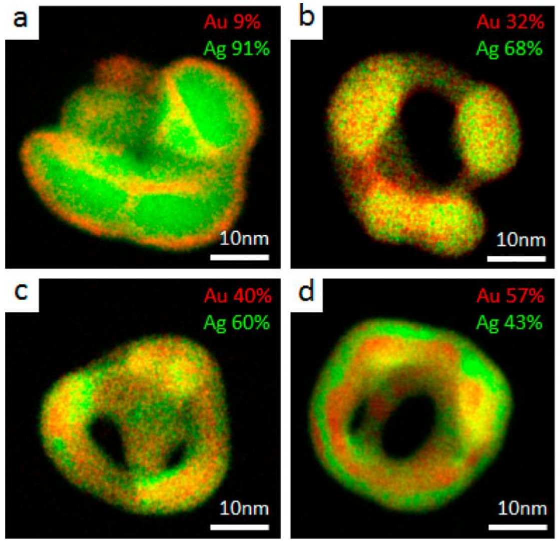
Pt, lattice parameter ~ 3.85 A

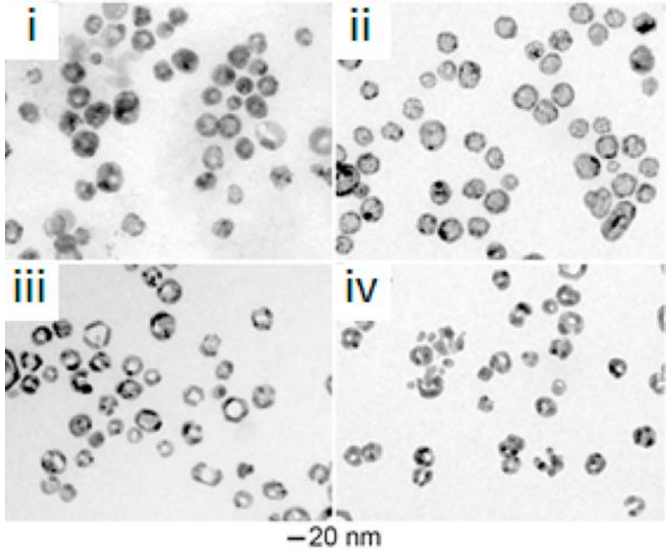


Au/Ag combined in one particle

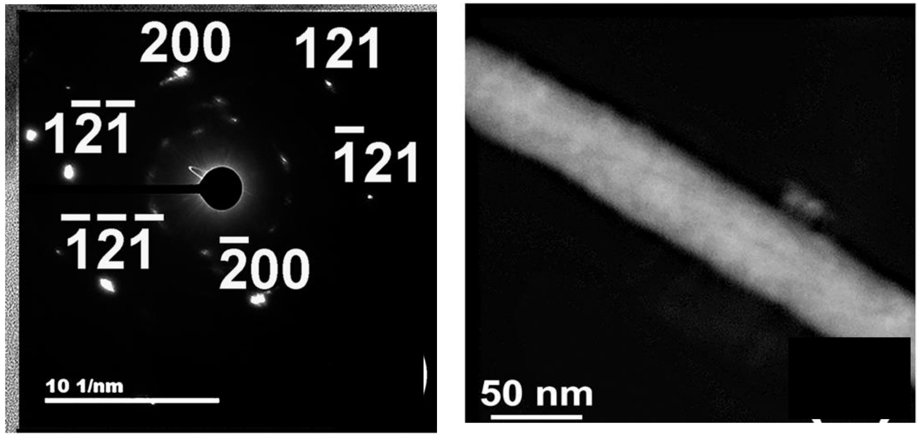
J. Phys. Chem. C
115 (2011) 9417

Nano Lett.
14 (2014) 1921



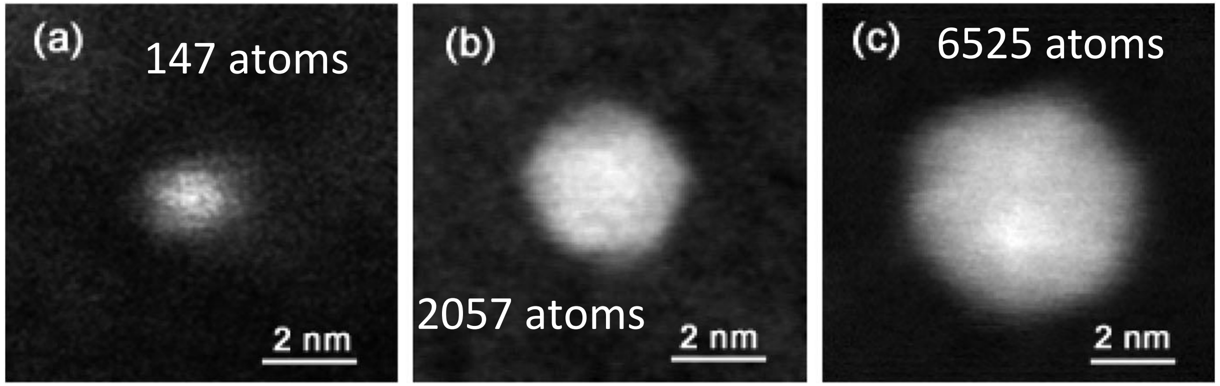


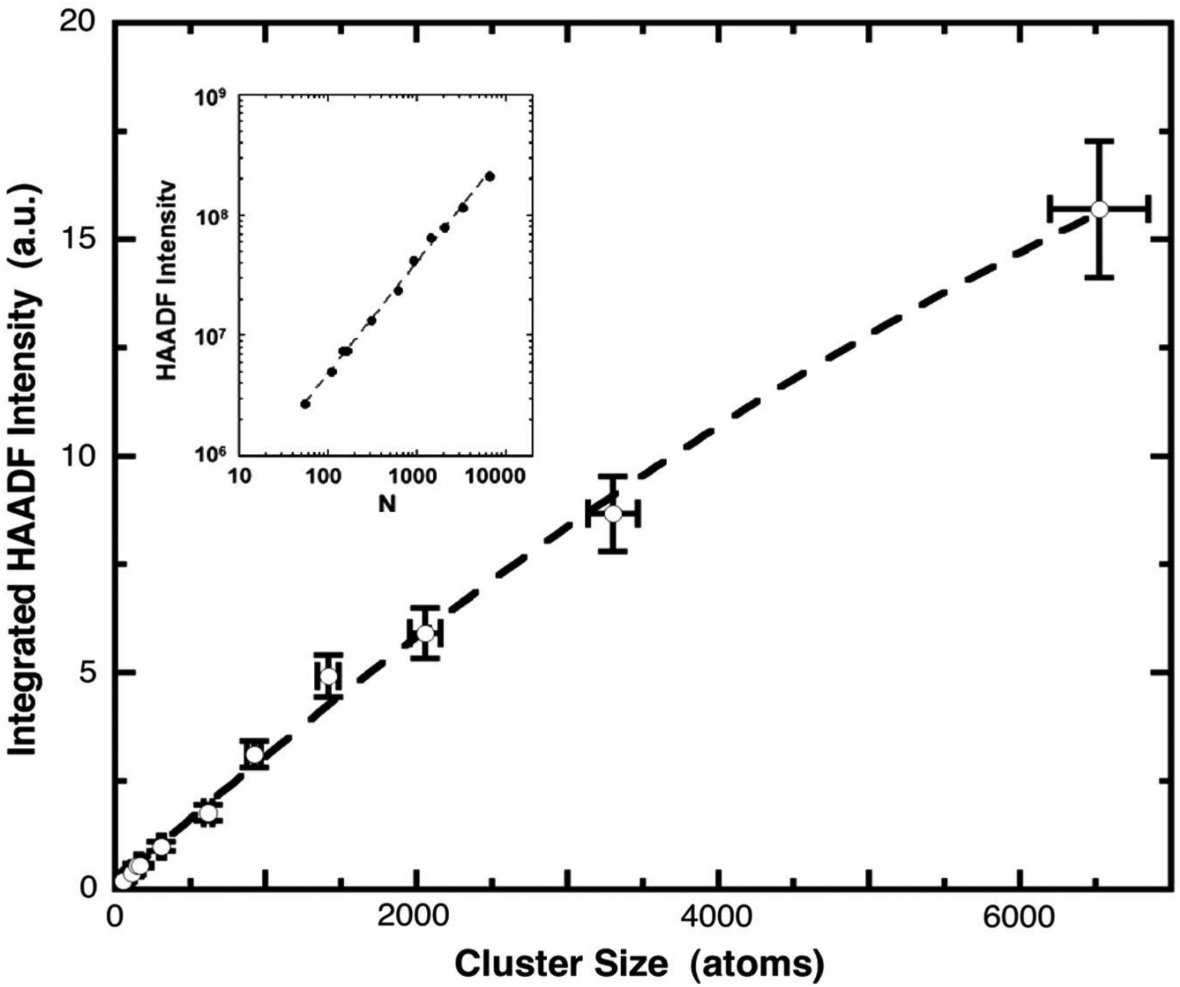
Fe wire, LEED pattern confirms single crystal



J. Sol-Gel Technol. 81 (2017) 327

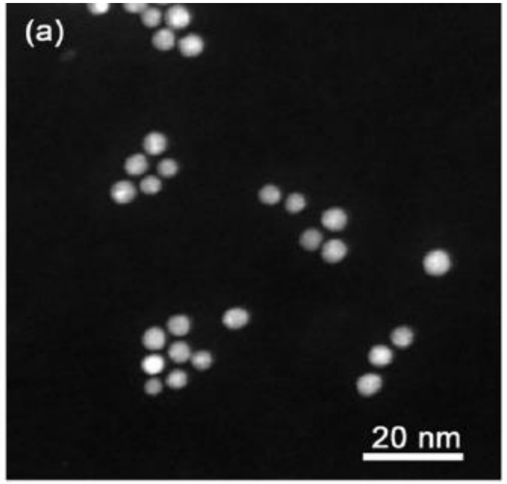
High-angle annular dark-field scanning transmission electron microscopy, HAADF-STEM

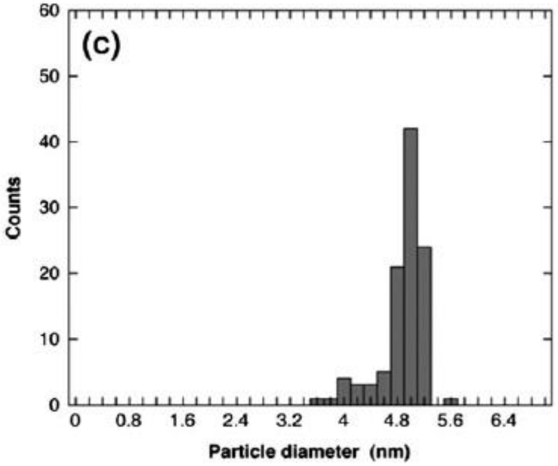




Intensity for each element can be calibrated using the particles of known size.

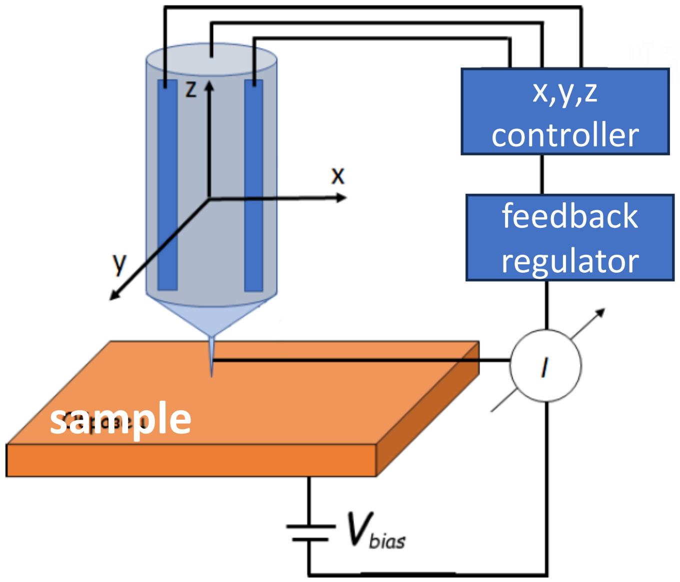
Example for gold.



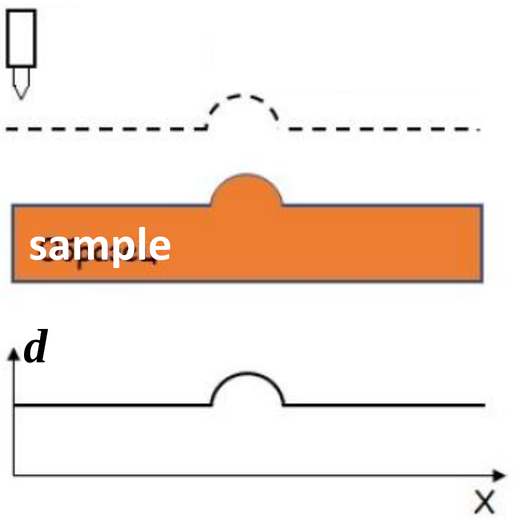


Phys. Rev. Lett. 101 (2008) 246103

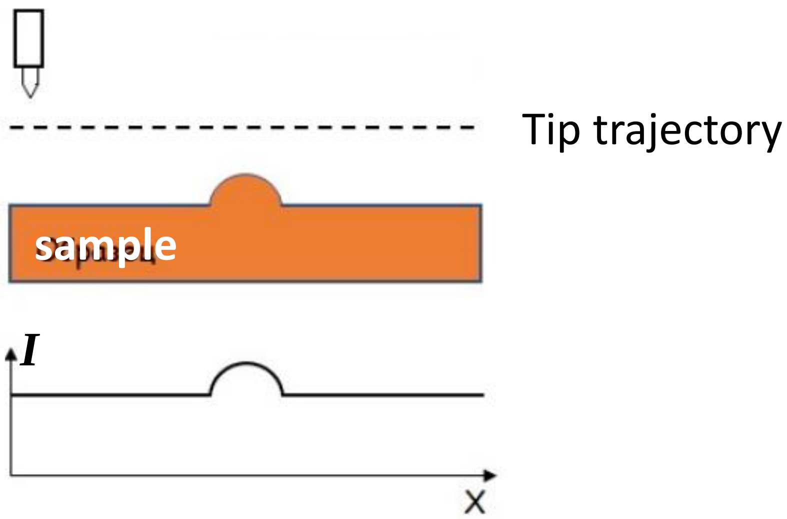
Scanning tunneling microscopy (STM)



Constant current I



Constant distance d



Current vs distance dependence (at low V_{bias} and temperature)

Mean electron work function

Probability of electron tunneling

$$D(\epsilon) \propto e^{\frac{-2\sqrt{2m(U-\epsilon)}d}{\hbar}}$$

distance

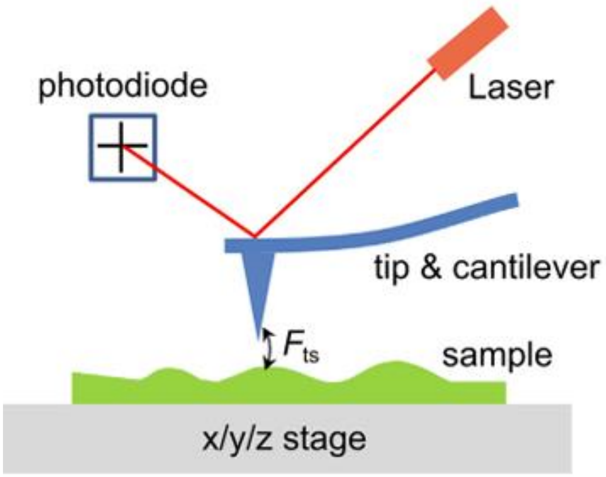
m , ε – electron mass and energy

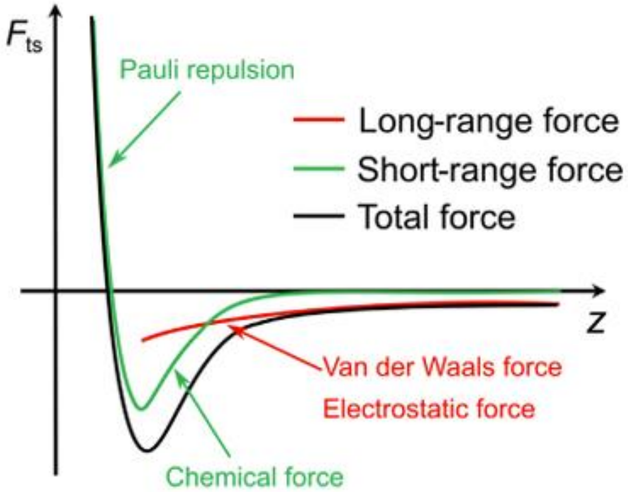
Only for conductive samples!

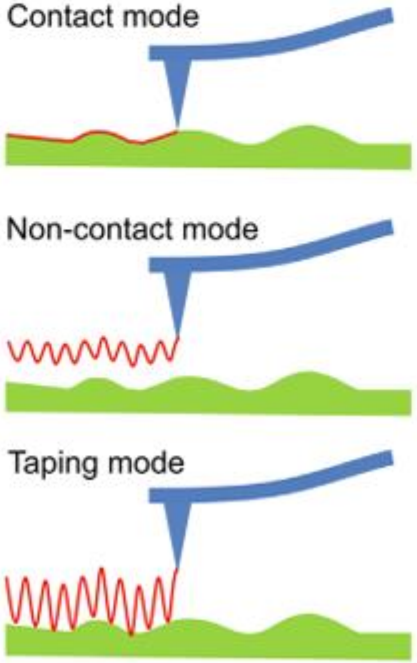
$$I(V_{bias}) = \frac{2e}{\hbar}\int_{-\infty}^{+\infty} D(\epsilon)(f_L(\epsilon) - f_R(\epsilon))d\epsilon$$

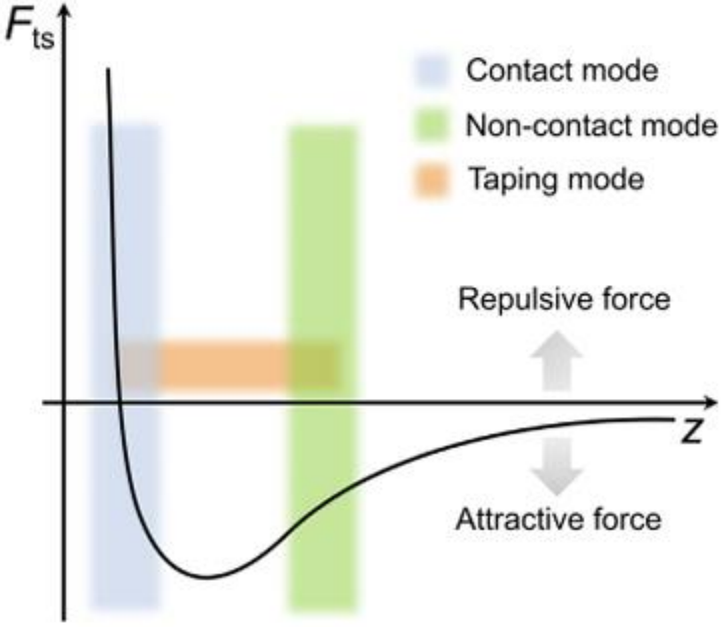
Fermi-Dirac functions for tip and sample materials

Atomic Force Microscopy (AFM): works for non-conductive samples as well



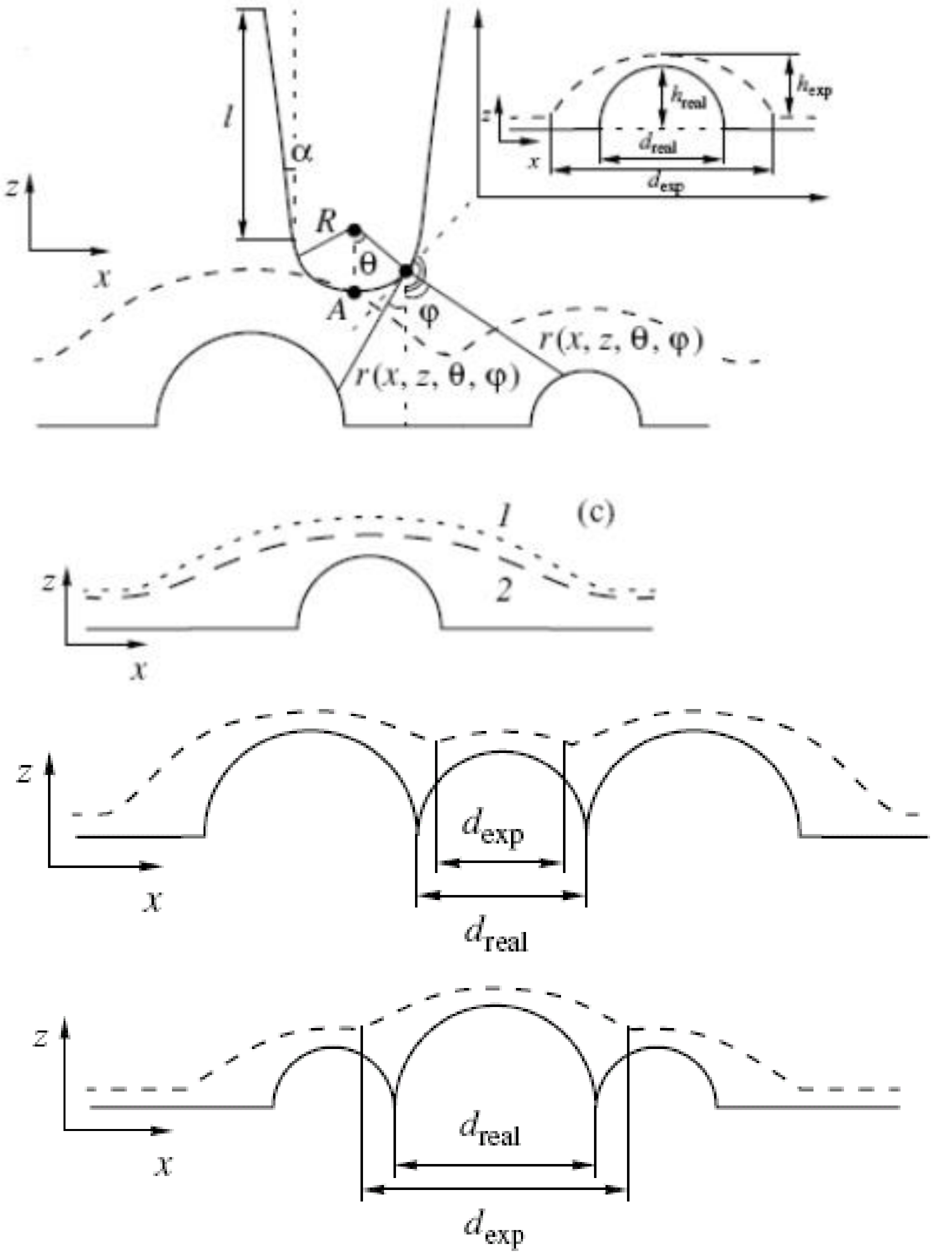






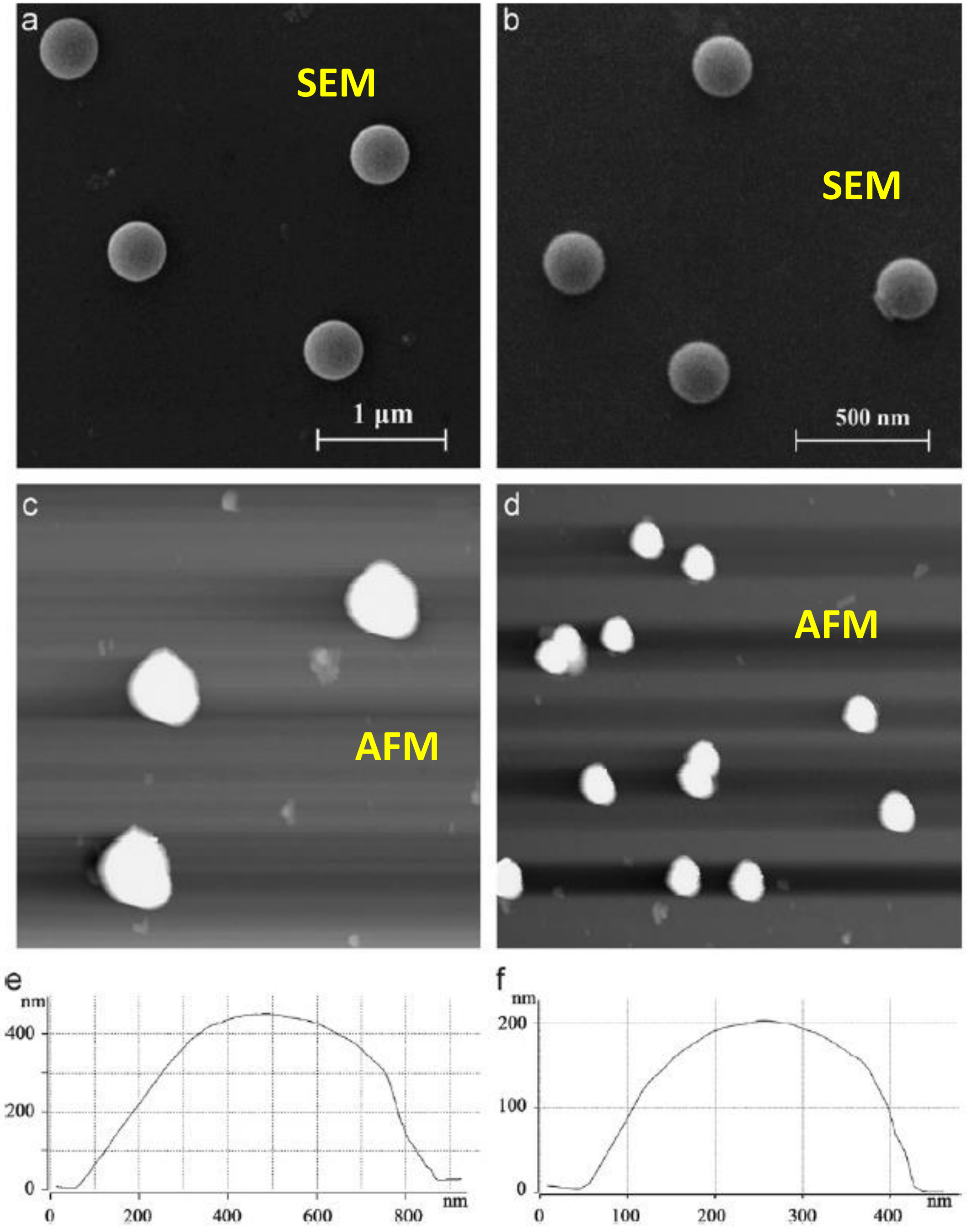
Surface Sci. Rep. 77 (2022) 100549

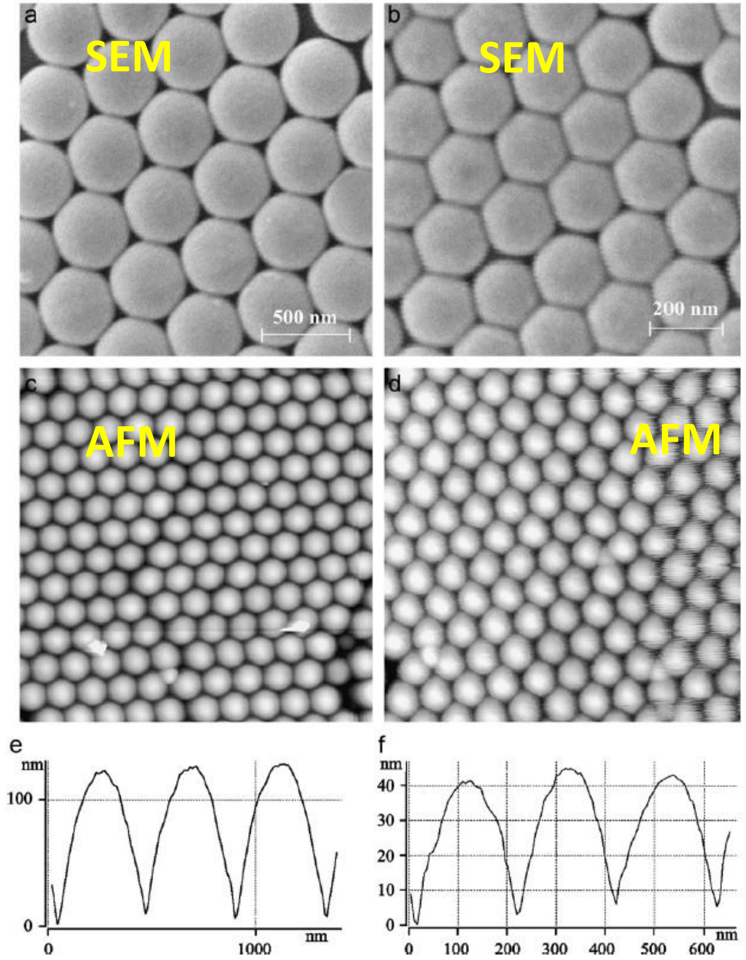
Image distortion: the effect of the tip curvature



Tip shape can be estimated

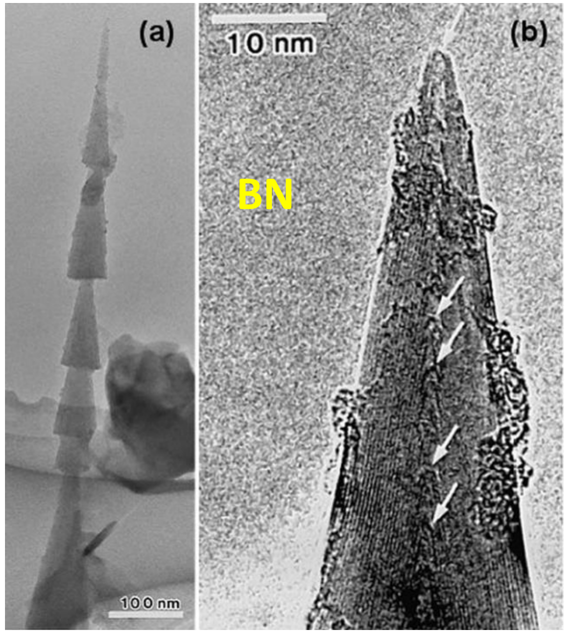
from the images of standard samples (e.g., polystyrene spheres)

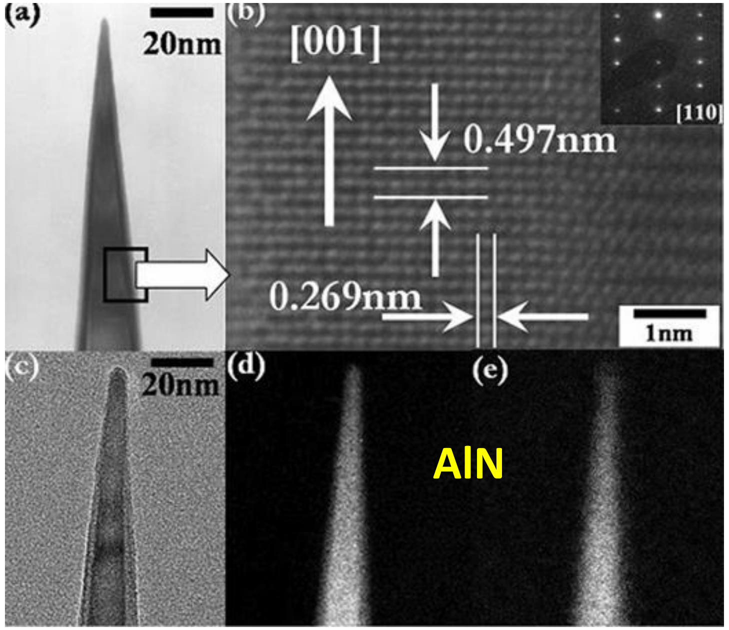


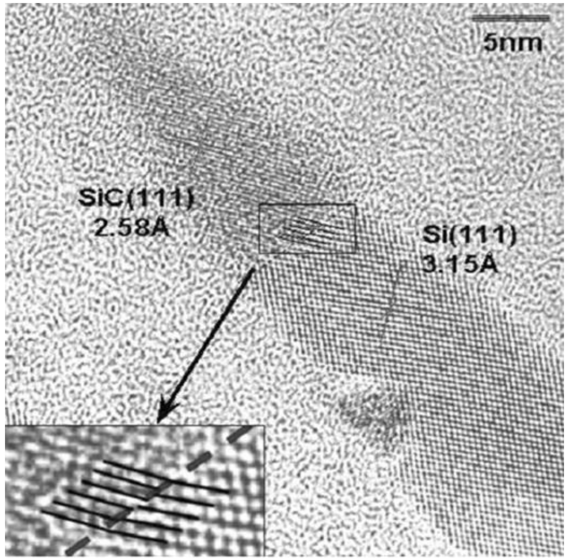


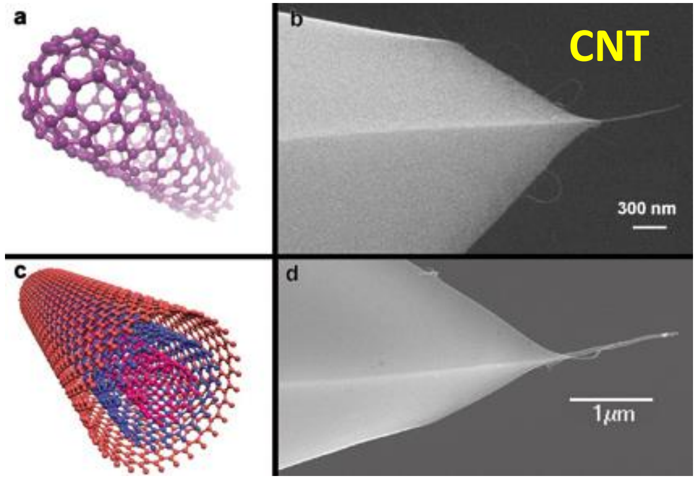
Ultramicroscopy 108 (2008) 975

Tip shape can be defined by 'natural' crystallography of certain materials









Critical Reviews Solid State Mater. Sci. 31 (2006) 15

General problem of microscopy:

Local, less representative for the sample as a whole

Problem of electron microscopy:

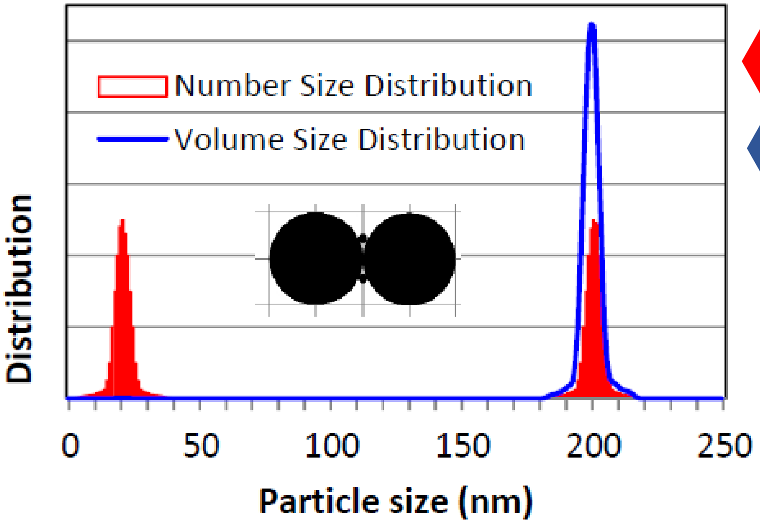
Vacuum is required, samples fabricated in gas or liquid medium can undergo some changes

Problem of probe microscopy:

Images can be affected by the shape of tip

Possible solution of all these problems:

To combine both techniques, and **to involve more macroscopic structural techniques** in parallel



🟥 From microscopy

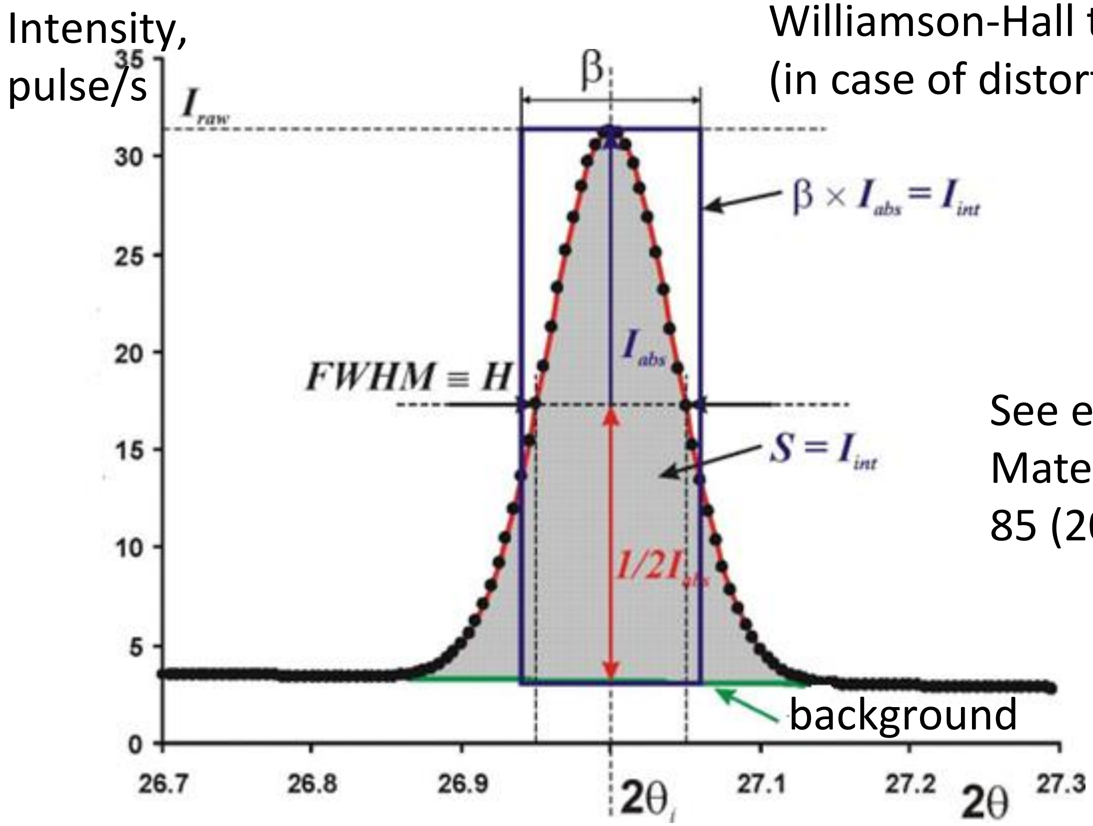
🟦 From XRD

$$\beta = \frac{K_\beta \lambda}{r\cos\theta}$$

Scherrer formula (works in the absence of lattice distortions)

$$\beta\cos\theta = \frac{\lambda}{r} + 4\varepsilon\sin\theta$$

Williamson-Hall technique (in case of distortions ε)



See examples in: Mater. Charact. 85 (2013) 111

Nanometrology: books and reviews

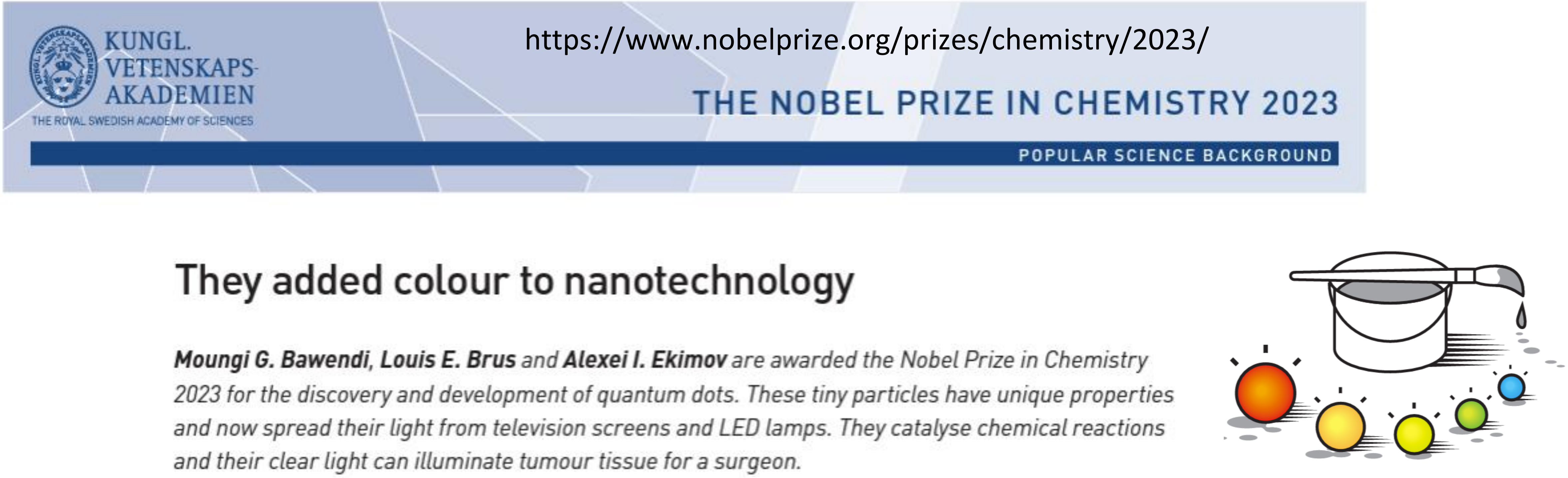
- R. Garcia, R. Perez, Dynamic atomic force microscopy methods, Surface Sci. Rep. 47 (2002) 197-301.
- H.-J. Gao, L Gao, Scanning tunneling microscopy of functional nanostructures on solid surfaces: Manipulation, self-assembly, and applications, Progr. Surface Sci. 85 (2010) 28-91.
- Introductory guide to nanometrology (editors P.-E. Hansen and G. Roebben), 2010.
- R. K. Leach, R. Boyd, T. Burke et al., The European nanometrology landscape, Nanotechnology 22 (2011) 062001.
- R. Herrera-Basurto, B.M. Simonet, In ‘Encyclopedia of Analytical Chemistry’, Wiley, 2013.
- Acoustic Scanning Probe Microscopy (editors F. Marinello, D. Passeri, E. Savio), Springer, 2013.
- A.F. Thünemann, F. Emmerling, and V.-D. Hodoroaba, Review of existing calibration or reference materials <Technical Report on the EU FP7 NanoDefine Project>, 2014.
- D. Hussain, K. Ahmad, J. Song, H. Xie, Advances in the atomic force microscopy for critical dimension metrology, Meas. Sci. Technol. 28 (2017) 012001.
- Nanocharacterization techniques (editors A. L. Da Roz, M. Ferreira, F. de Lima Leite, O. N. Oliveira, Jr.), Elsevier, 2017.
- N.G. Orji, M. Badaroglu, B.M. Barnes et al., Metrology for the next generation of semiconductor devices, Nature Electronics 1 (2018) 532-547.
- P. Klapetek, Quantitative Data Processing in Scanning Probe Microscopy: SPM Applications for Nanometrology, 2018 (2nd Edition).
- B.R. Masters, Superresolution Optical Microscopy, Springer Series of Optical Science, No 227, 2020.
- R. Xu, J. Guo, S. Mi et al., Advanced atomic force microscopies and their applications in two-dimensional materials: a review, Mater. Futures 1 (2022) 032302.

0D materials, dedicated to recent (2023) Nobel Prize

Stabilization of small particles in solid matrix and in solutions

Narrow size distribution (ideally particles should be of identical size)

Core-shell particles: additional tool to modify electronic/optical properties



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THE ROYAL SWEDISH ACADEMY OF SCIENCES

https://www.nobelprize.org/prizes/chemistry/2023/

THE NOBEL PRIZE IN CHEMISTRY 2023

POPULAR SCIENCE BACKGROUND

They added colour to nanotechnology

Moungi G. Bawendi, Louis E. Brus *and* ***Alexei I. Ekimov*** *are awarded the Nobel Prize in Chemistry 2023 for the discovery and development of quantum dots. These tiny particles have unique properties and now spread their light from television screens and LED lamps. They catalyse chemical reactions and their clear light can illuminate tumour tissue for a surgeon.*

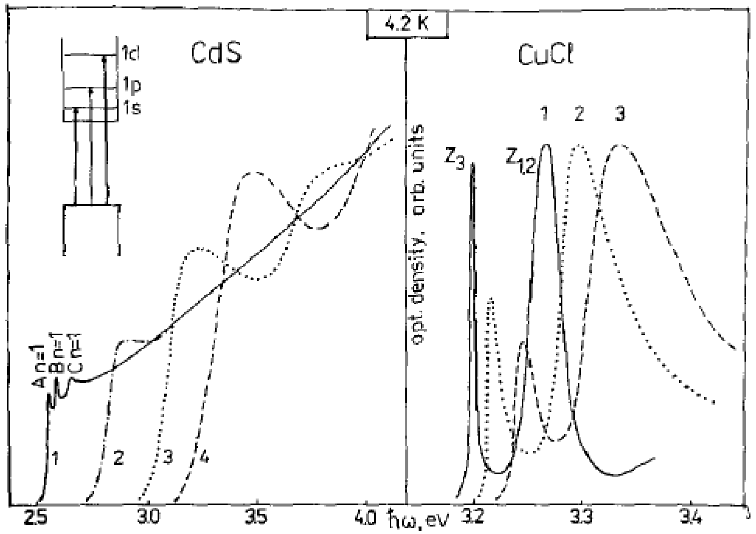
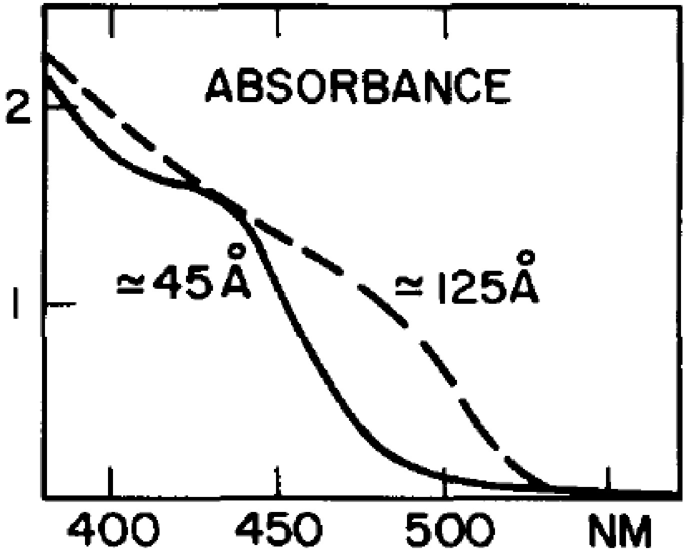


Fig.3. Size dependence of the absorption spectra of CdS and CuCl microcrystals.
CdS:(1) - $\bar{a}$ =320 Å;
(2) - $\bar{a}$ =23 Å;
(3) - $\bar{a}$ =15 Å;
(4) - $\bar{a}$ =12 Å;
CuCl:(1) - $\bar{a}$ =310 Å;
(2) - $\bar{a}$ =29 Å;
(3) - $\bar{a}$ =20 Å.

Solid State Commun. 56 (1985) 921

Semiconductor particles were **incapsulated in glass.**
They formed resulting from diffusive decomposition of the over-saturated solid solution of CuCl, or CdS, or….
in silicate glass.

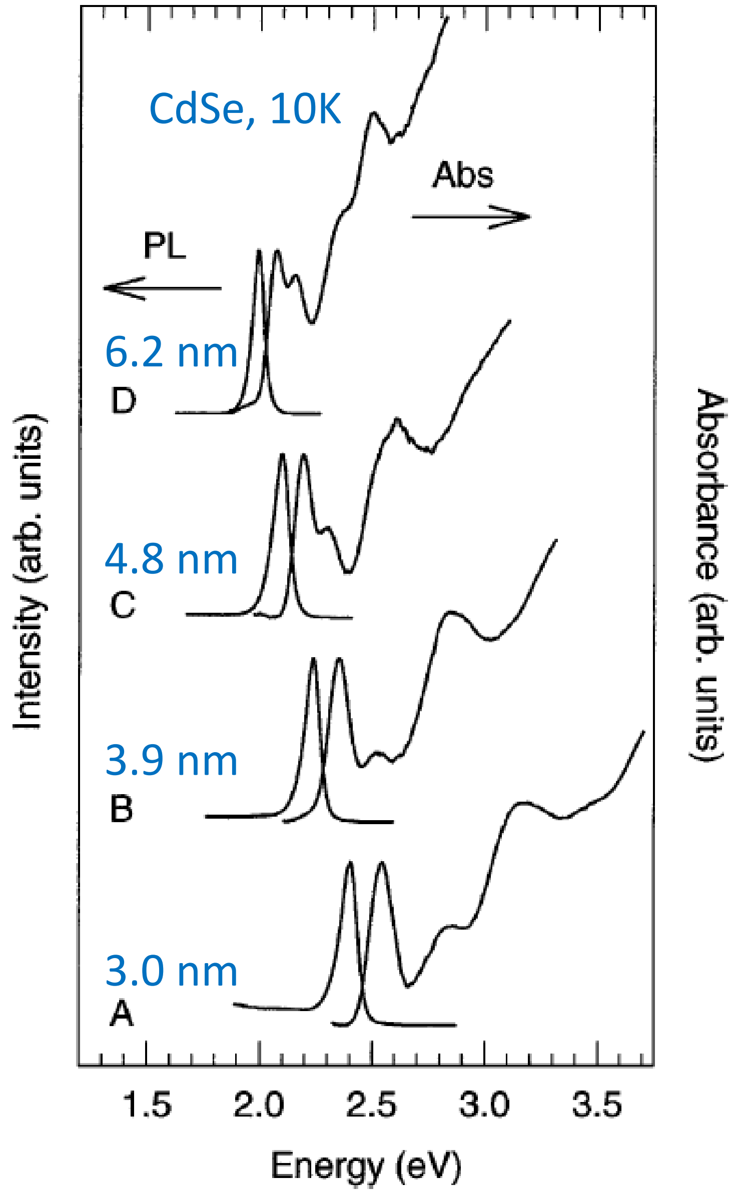


J. Chem. Phys. 79 (1983) 1086

CdS particles were **polymer-stabilized in aqueous solution.**

They demonstrated a noticeable size distribution, which shifted to larger size in the course of ageing.

Mean size was initially 4.5 nm, and shifted to 12.5 nm in a day.



Phys. Rev. B 54 (1996) 8633

Monodispersed, can be separated from liquid and assembled on the support

In solid……………………In liquid………….In liquid and on support

Chemical synthesis of sols (solid particles dispersed in liquid, colloid)

$$\text{Reagent in solution} \xrightarrow{\textit{Chemical redox reaction}} \text{Supersaturation} \longrightarrow \text{Nucleation} \xrightarrow{\textit{Growth}} \text{Sol} \overset{\textit{Coagulation}}{\dashrightarrow} \text{Suspension or bulk solid}$$

Adsorbing substances (stabilizers)

$$H[Au^{III}Cl_4] + 3e \longrightarrow \mathbf{Au^0}$$

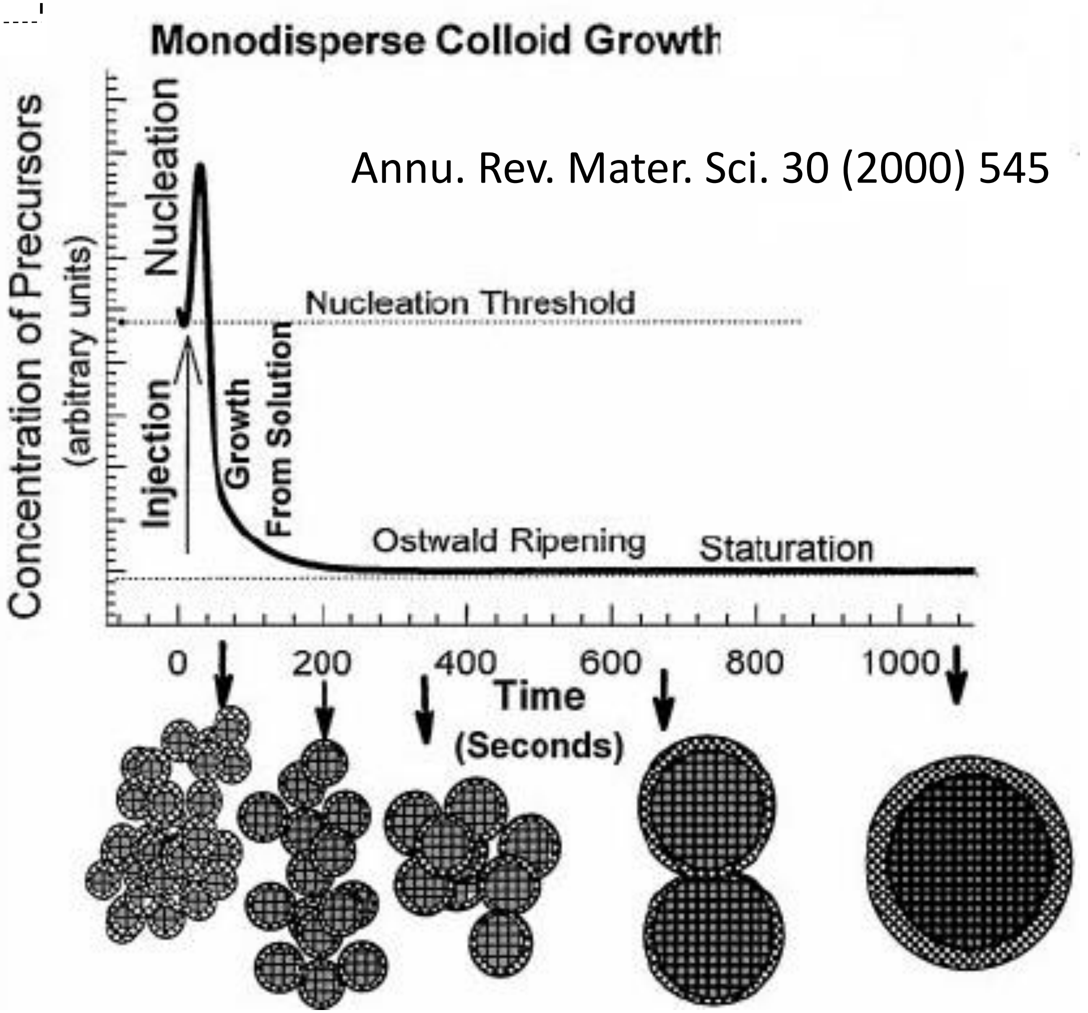
$$Na_2Te^{IV}O_3 + 6e \xrightarrow[Cd^{2+}]{} \mathbf{CdTe}$$

These electrons necessary for reduction of the target element are accepted from reagents able to oxidize <e.g., formaldehyde HCHO is oxidized to CO_2>

Factors affecting stabilization by surfactants:

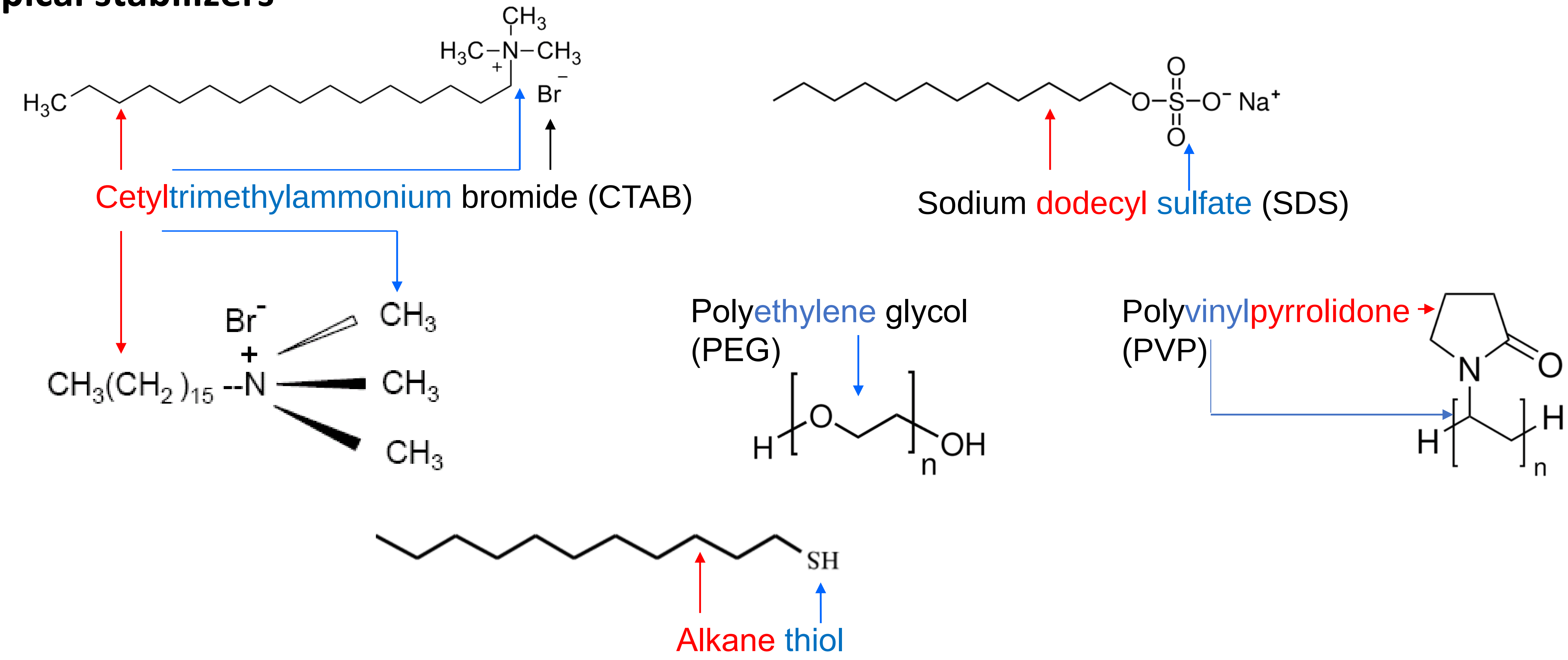
- **electrostatic repulsion** (all particles have the charge of the same sign, resulting from adsorption of certain **ions**);

- **prevention of growth** and coalescence by very large adsorbed ions/molecules forming close packed layers (steric stabilization by **nonionic** surfactants).



Annu. Rev. Mater. Sci. 30 (2000) 545

Typical stabilizers



Cetyltrimethylammonium bromide (CTAB)

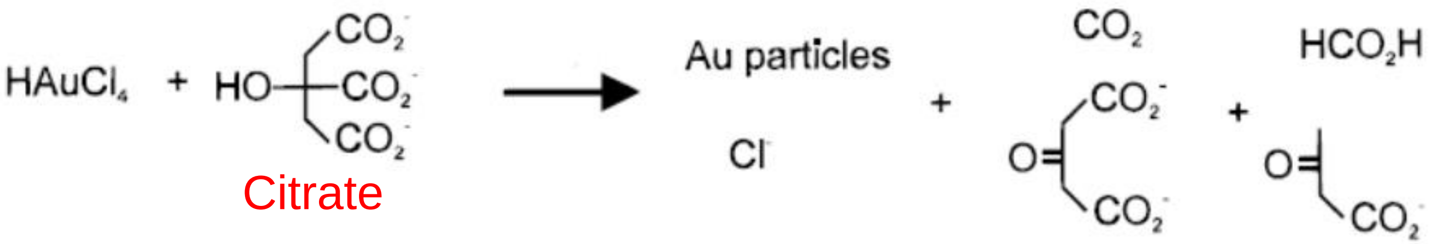
Sodium dodecyl sulfate (SDS)

Polyethylene glycol (PEG)

Polyvinylpyrrolidone (PVP)

Alkane thiol

Citrate sols: the anion of citric acid operates as reducing reagent + as stabilizer



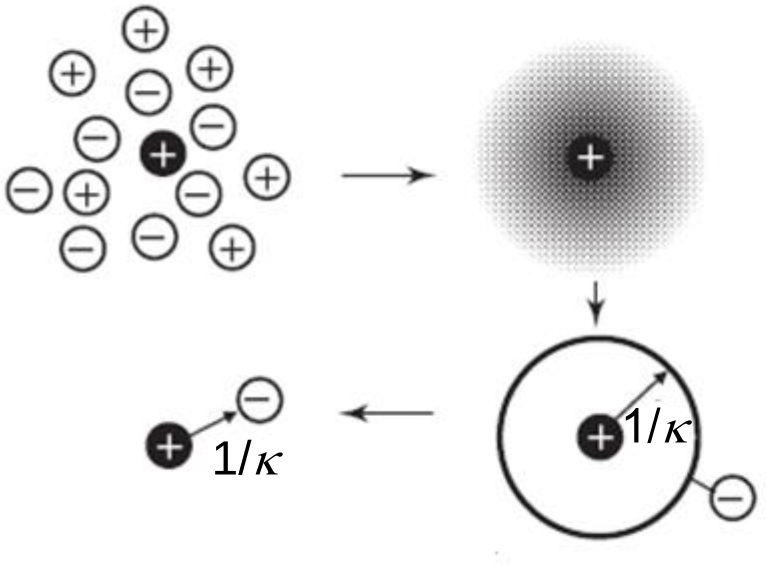
Citrate

Electrostatic stabilization, DLVO theory

B. **D**erjaguin, L. **L**andau,
Acta Physicochim. URSS 14 (1941) 633-662

E.J.W. **V**erwey, J.Th.G. **O**verbeek, *Theory of the Stability of Lyophobic Colloids: The Interaction of Sol Particles Having an Electric Double Layer*. Elsevier, 1948

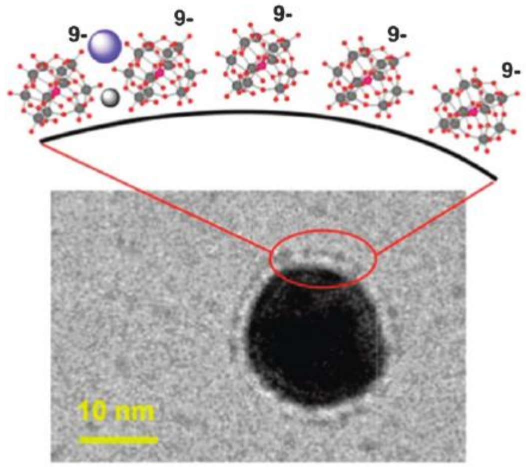
Ionic atmosphere → **Diffuse layer of ions**



$$1/\kappa = \sqrt{\frac{e^2}{\epsilon\epsilon_0 kT}\sum_{\substack{all\\ ions}}(nz^2)}$$

Radius of ionic atmosphere, depending on ions charges *z* and ions concentrations *n*

"Electric double layer" is conditional name, it is more complex than "double": a layer of chemisorbed species + diffuse layer of ions.



Cryo-TEM

Chem. Soc. Rev. 41 (2012) 7479

Repulsion between i и j particles

charges of particles

radii

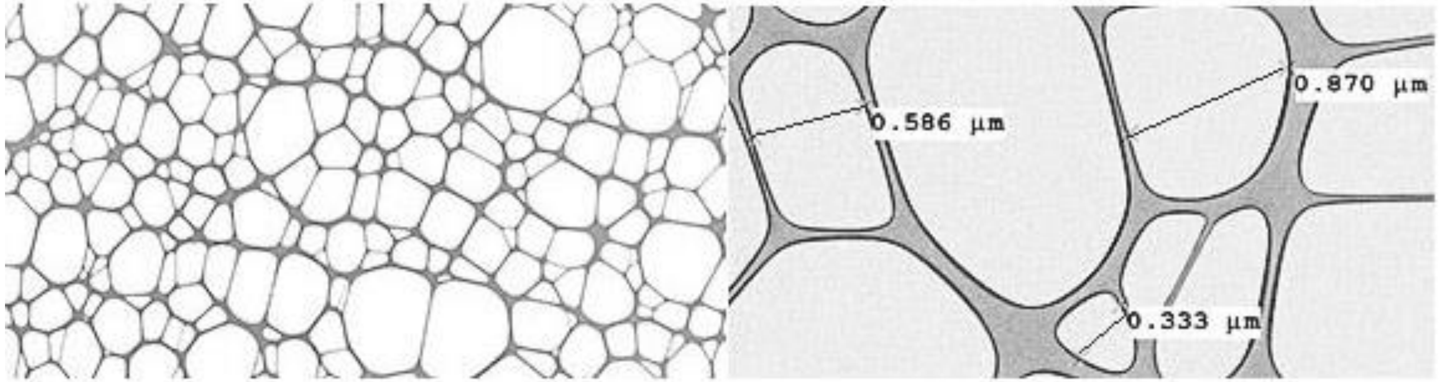
distance

$$u_{\mathrm{ij}}(r) = \frac{Z_{\mathrm{i}}Z_{\mathrm{j}}e^2}{4\pi\epsilon\epsilon_0}\left[\frac{\exp[k(a_{\mathrm{i}}+a_{\mathrm{j}})]}{(1+\kappa a_{\mathrm{i}})(1+\kappa a_{\mathrm{j}})}\right]\frac{\exp(-\kappa r)}{r}$$

How to deal with colloid particle (to say, with QD) in a vacuum? Q1

Pure Carbon Film: Carbon films with a thickness of 15-25nm with no Formvar used during manufacturing. Completely free of Formvar. Carbon films are thin and highly transparent to electrons. They exhibit very fine grain and minimal interference with specimen structure.

ULTRATHIN CARBON FILM SUPPORTED BY A LACEY CARBON FILM: The continuous ultrathin carbon film on lacey film allows for the thinnest carbon support film that still has adequate strength to withstand specimen preparation. The film (less than 3nm thick) lies across a carbon lacey film supported by a 400 mesh copper grid. The size of the holes in the lacey film differ widely from batch to batch but are generally in the range of ¼ µm to 5µm.



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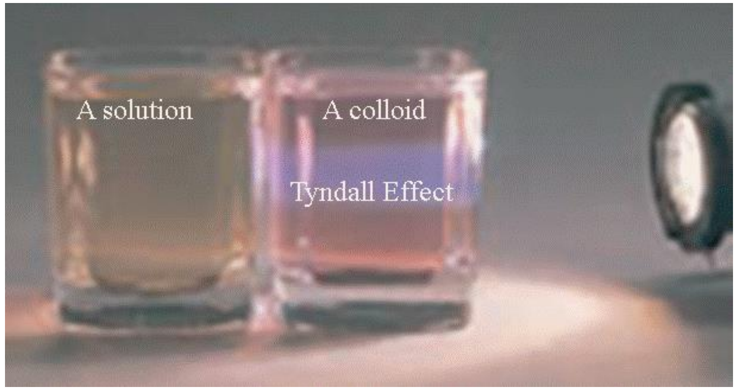
Substrates, Support Films
for Transmission Electron Microscopy Grids

Absorption spectra

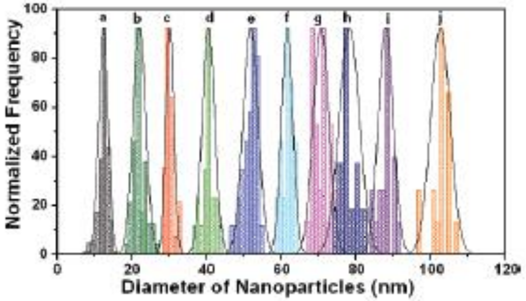
M. Faraday, Experimental relations of gold (and others metals) to light, Philos. Trans. Roy. Soc. London. 1857. V. 147. P. 145-181

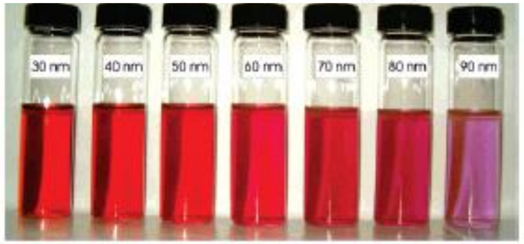
Tyndall effect, 1868: (size << λ)

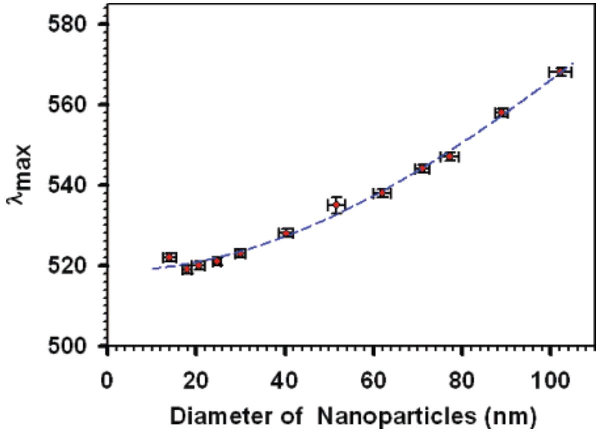


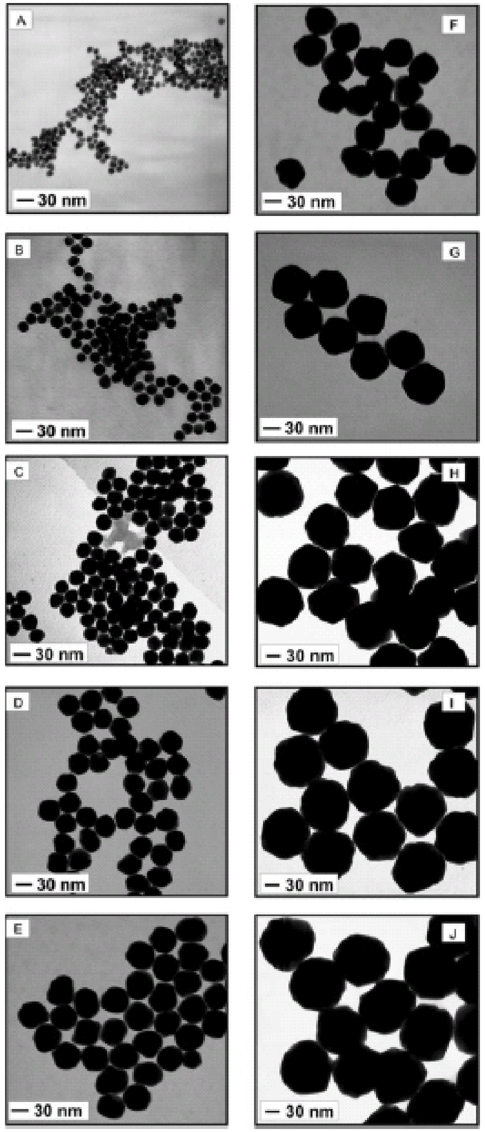
R. Zsigmondy: **ultramicroscope** (1902)

Theory of light scattering by particles of size comparable with λ:
G. Mie, Ann. Phys. 25 (1908) 377

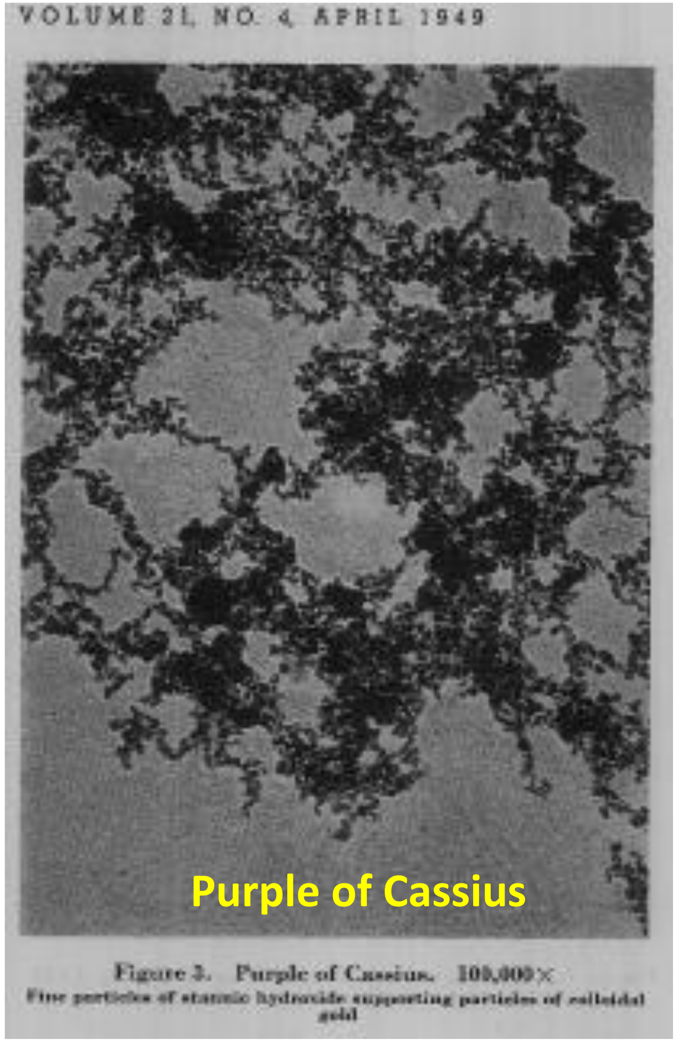








J. Phys. Chem. C 111 (2007) 14664



VOLUME 21, NO. 4, APRIL 1949

Purple of Cassius

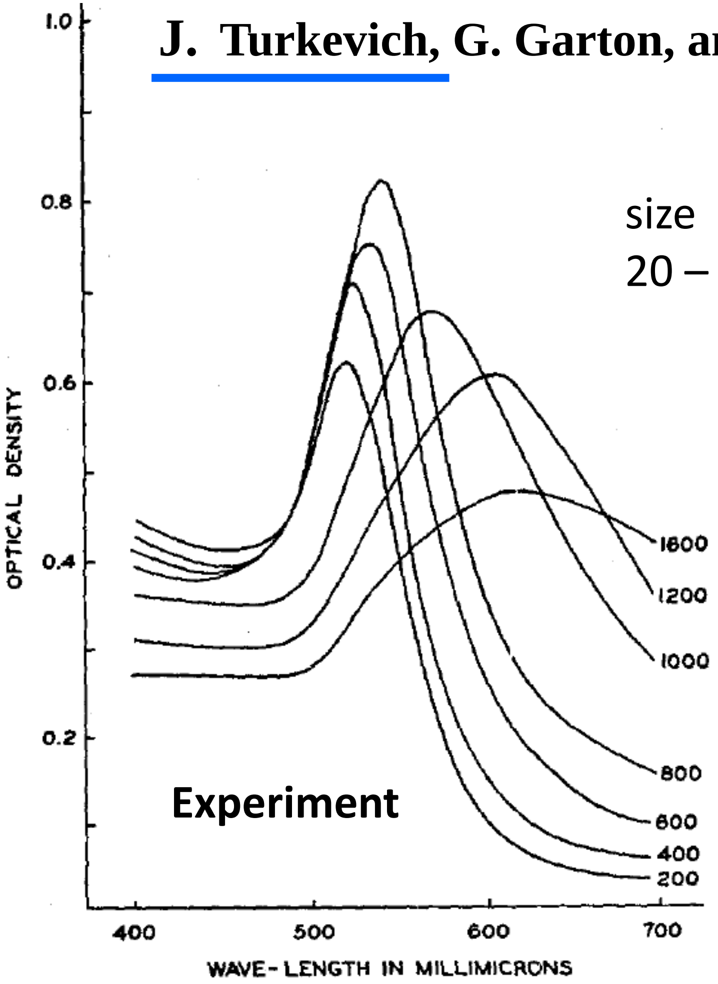
Figure 3. Purple of Cassius. 100,000×
Fine particles of stannic hydroxide supporting particles of colloidal gold

Anal. Chem. 21 (1949) 475

THE COLOR OF COLLOIDAL GOLD

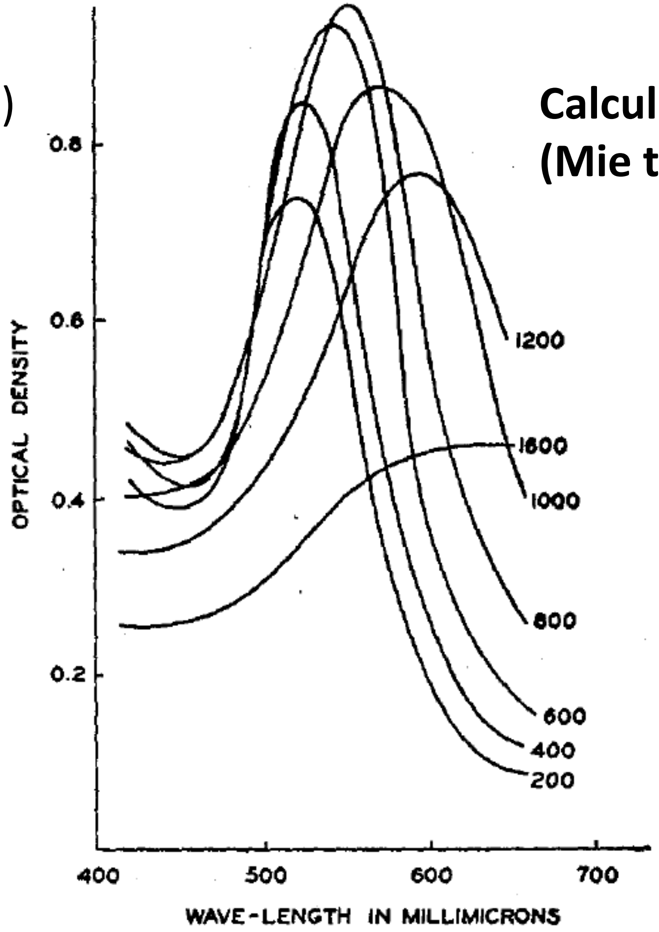
J. Colloid Sci. 9, Suppl.1 (1954) 26

J. Turkevich, G. Garton, and P. C. Stevenson



Experiment

size (shown in A)
20 – 160 nm

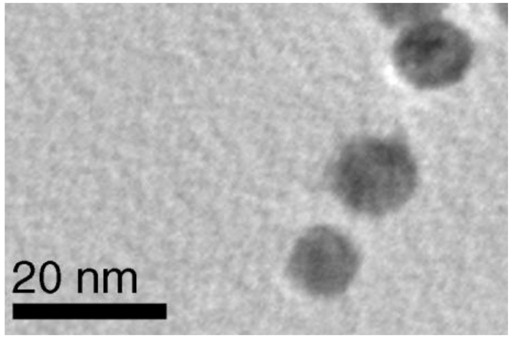


Calculated (Mie theory)

Electron Microscopy of Colloidal Systems

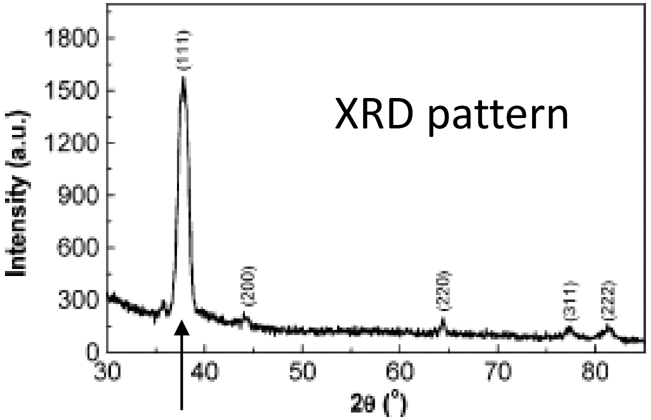
JOHN TURKEVICH, *Princeton University,* AND JAMES HILLIER, *RCA Laboratories, Princeton, N. J.*

Effect of shape: silver particles; triangle silver and its evolution

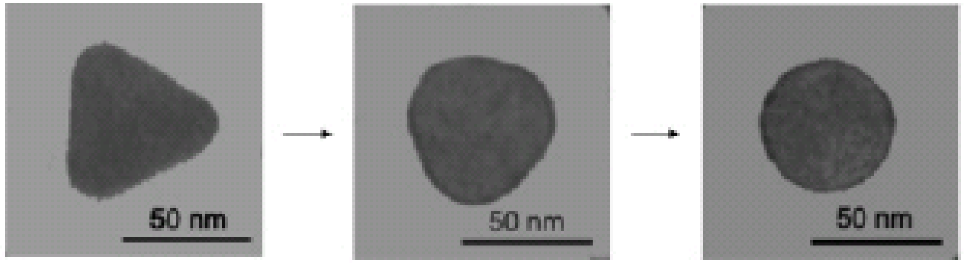


Particle Size/nm	λ_{max}/nm
10–14	395–405
35–50	420
60–80	438

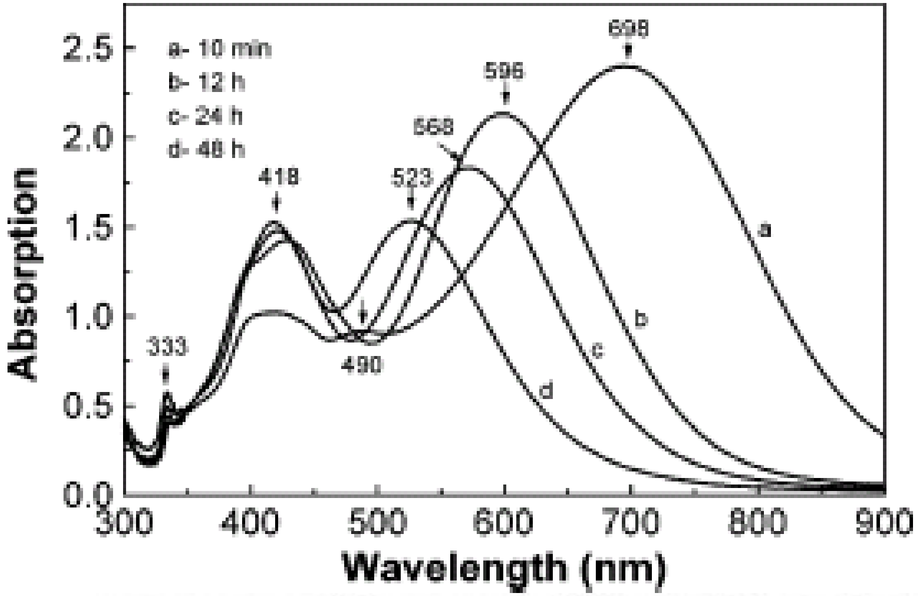
J. Chem. Educat.
84 (2007) 322

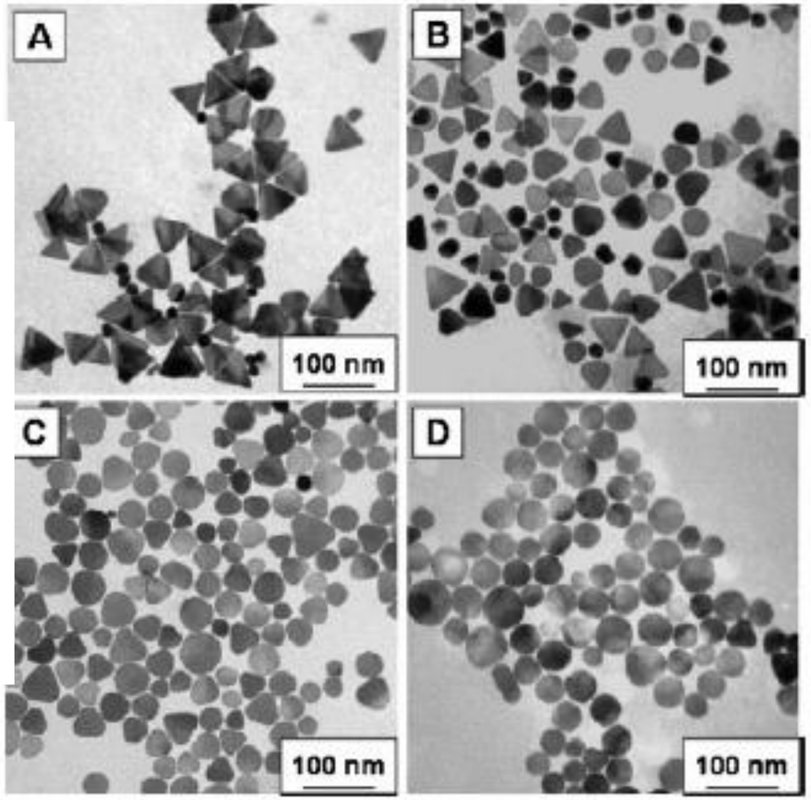


(111) texture

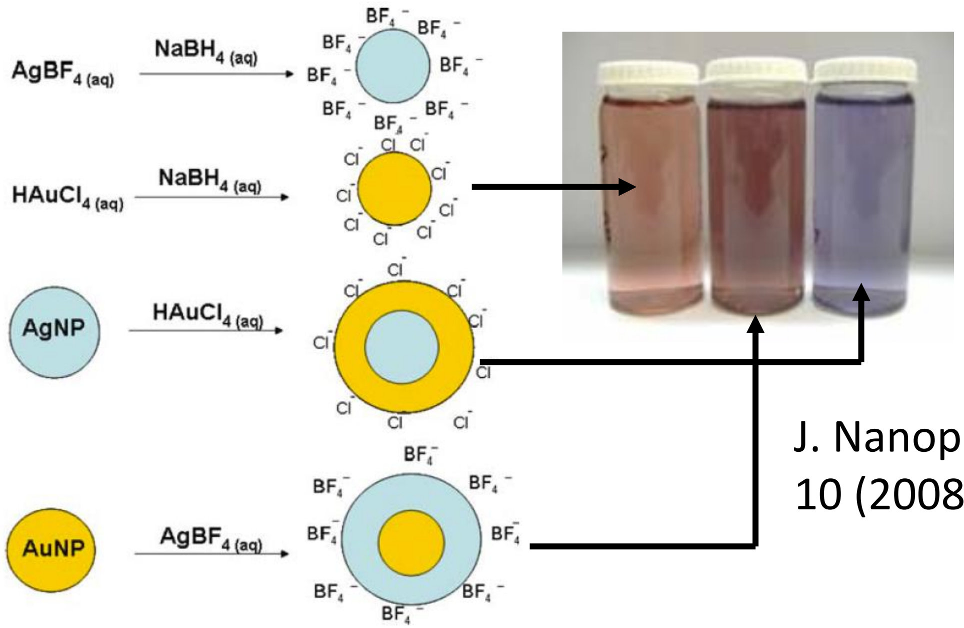


Langmuir 23 (2007) 2218



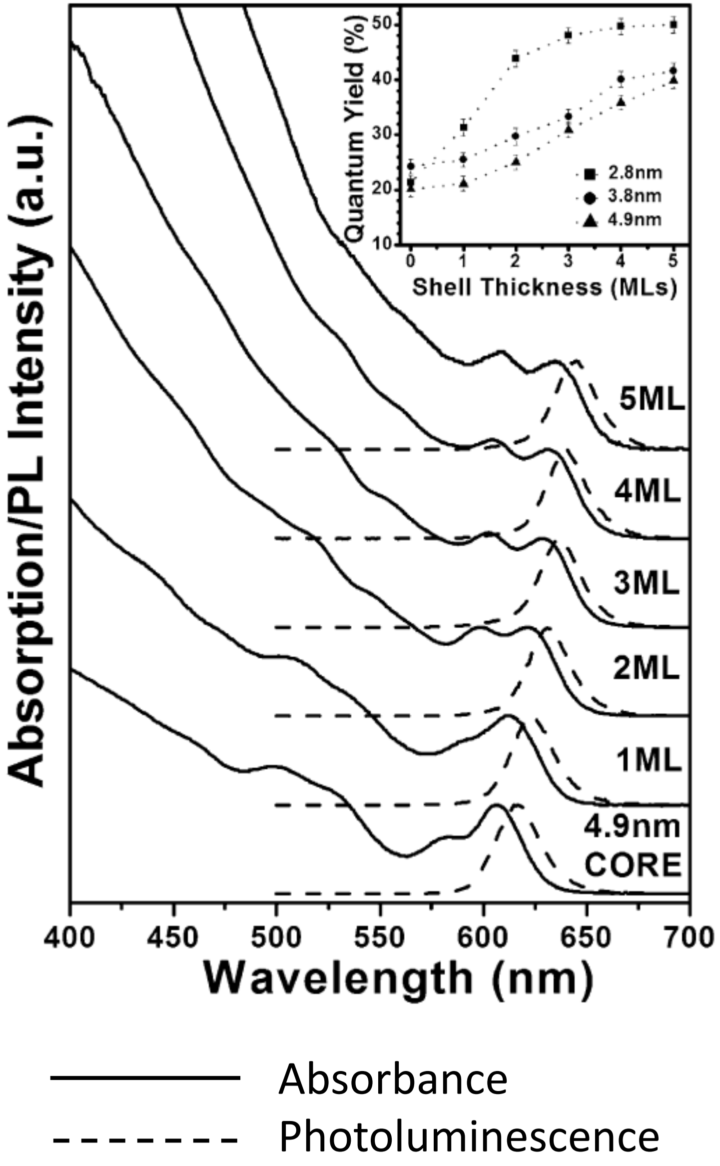


Core-shell: possibility to tune the properties



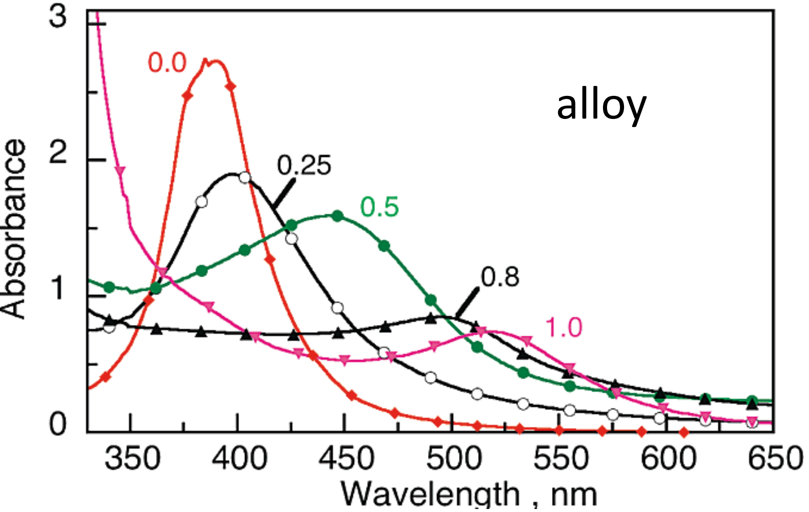
J. Nanopart. Res.
10 (2008) 97

CdSe core
CdS shell

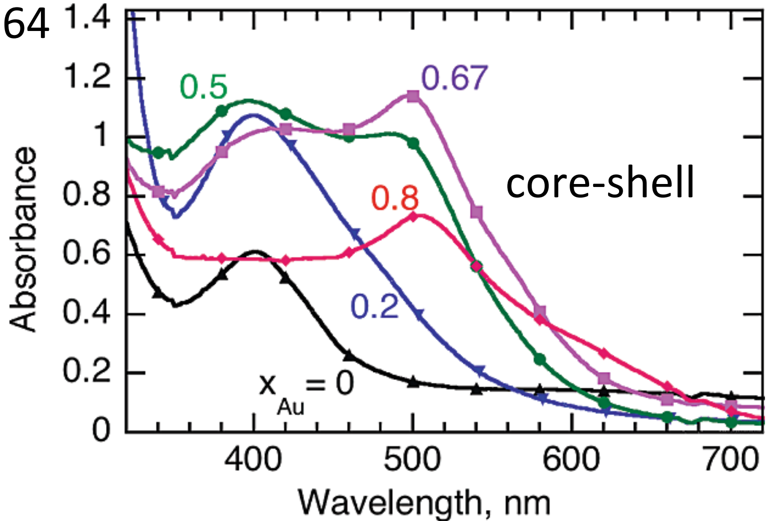


J. Phys. Chem. C 116 (2012)
15660

0…..1 are molar fractions of Au



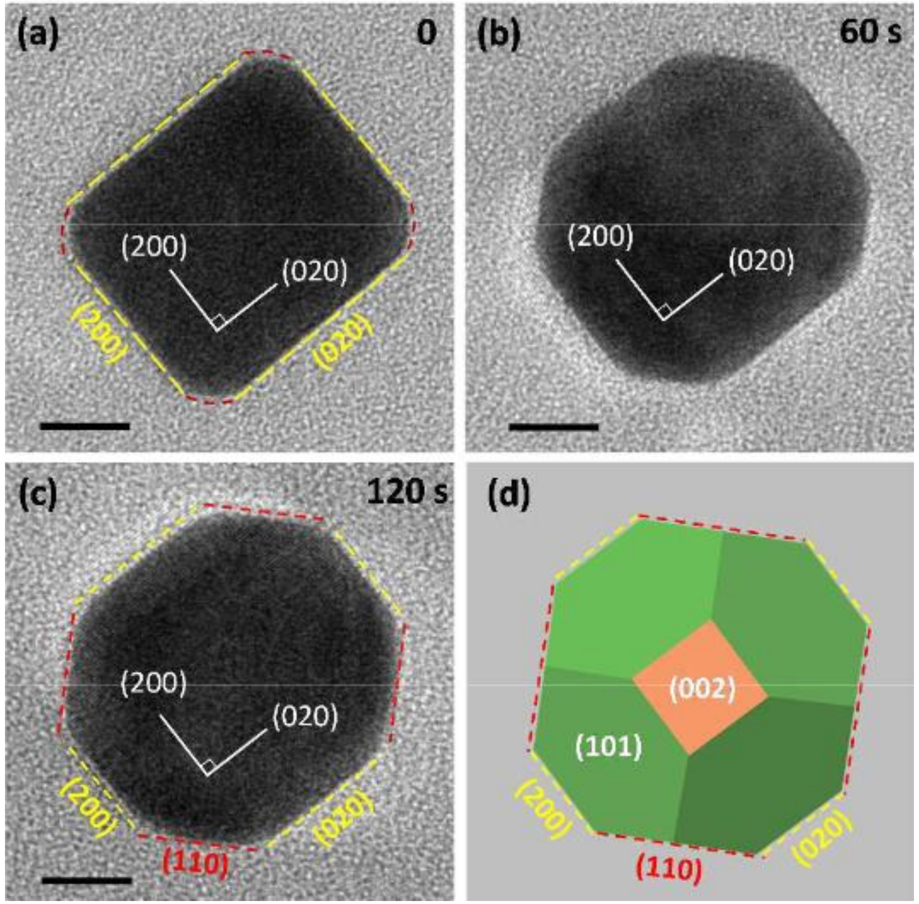
J. Phys. Chem. C 113 (2009)
11864



For fun

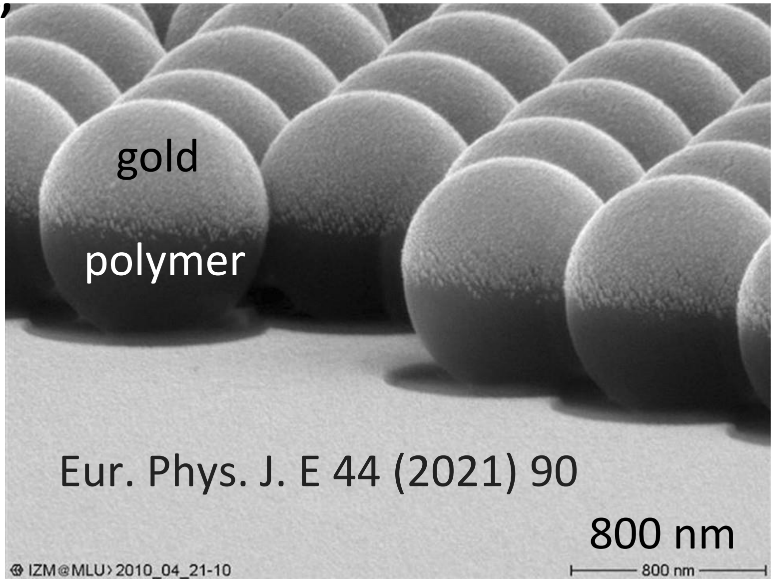
Dynamics of shape evolution, TEM, palladium

See movie (Supplementary File avi)
DOI 10.1039/C7CC07649E

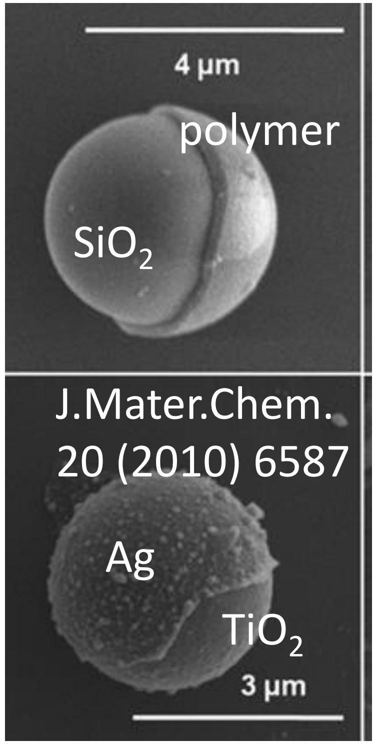


Chem. Commun. 53 (2017) 13213

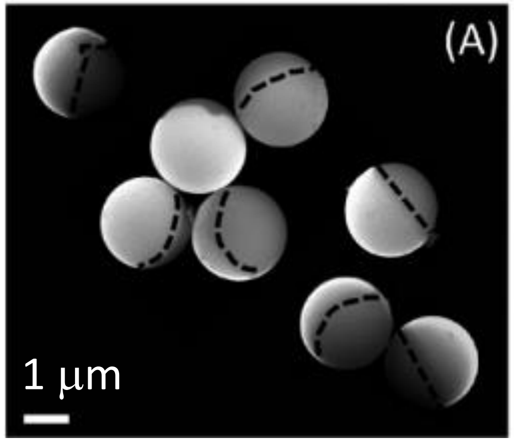
Janus particles (typically sub-μm), SEM, "swimmers"

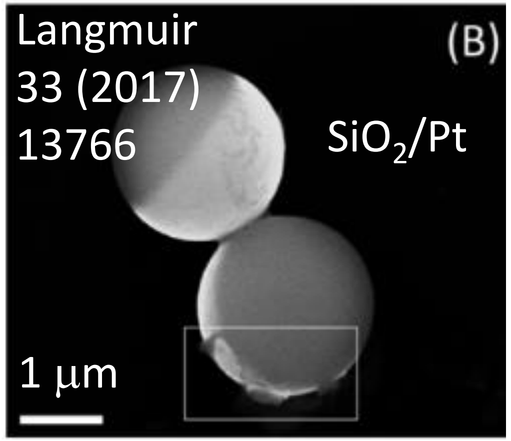


Eur. Phys. J. E 44 (2021) 90



J.Mater.Chem. 20 (2010) 6587



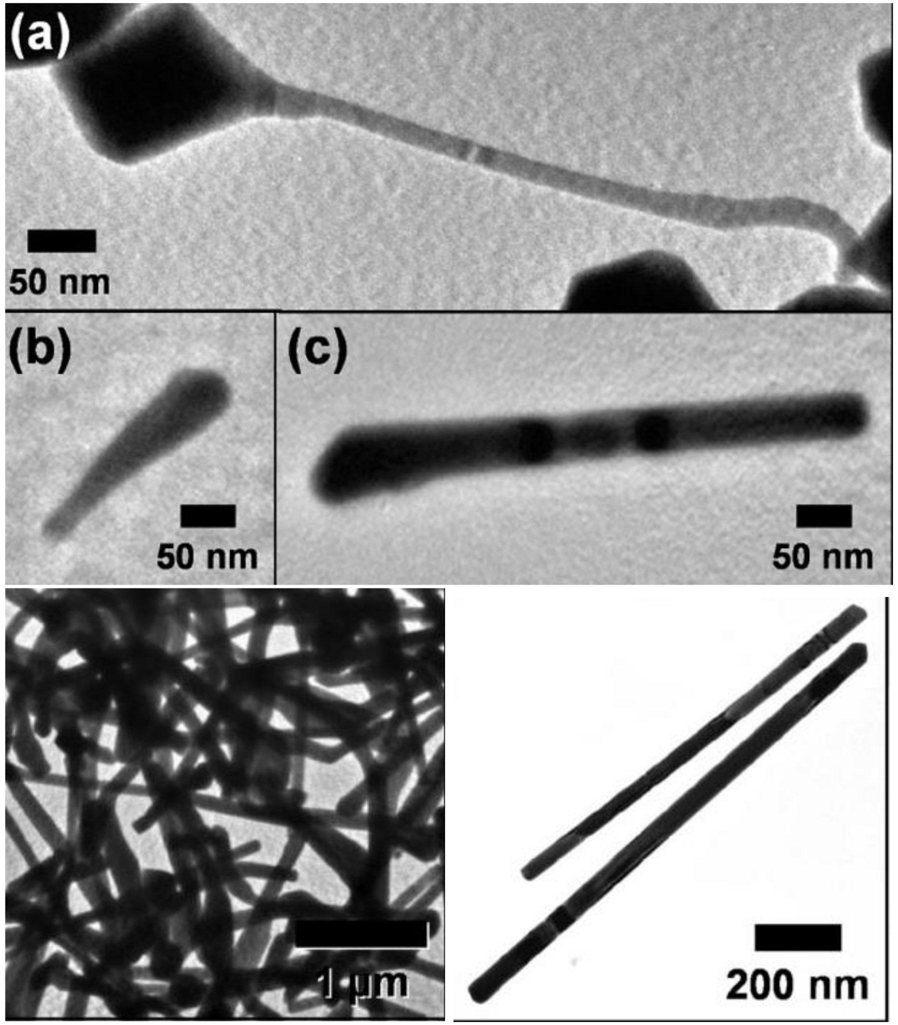


Langmuir 33 (2017) 13766

Lecture about Janus particles:
https://www.youtube.com/watch?v=vxW7_-ei8Bw

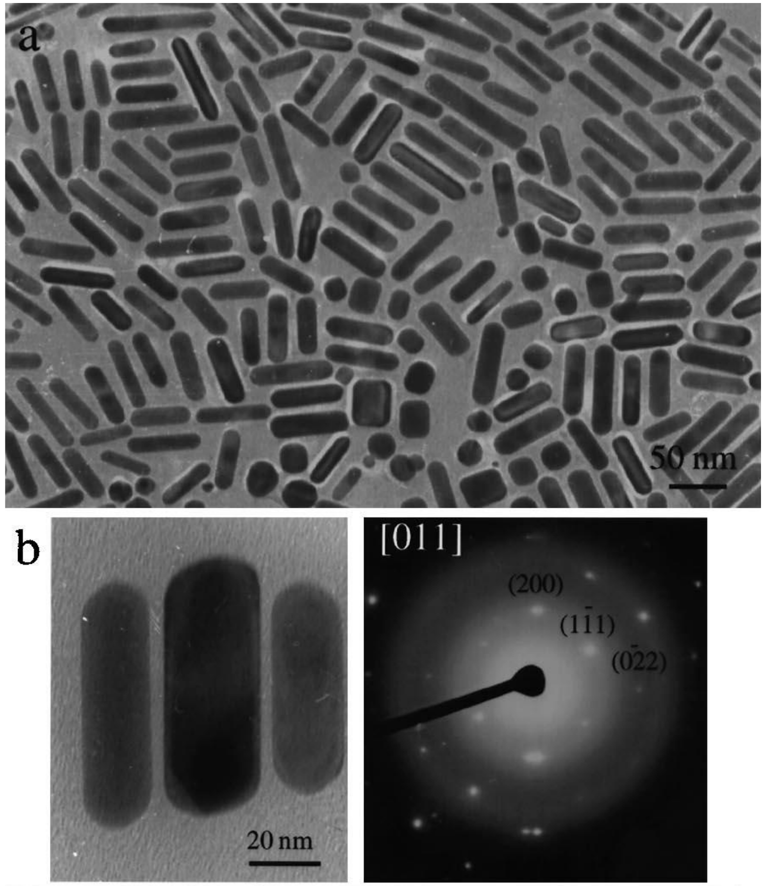
‘Nanorods’ and ‘nanowires’

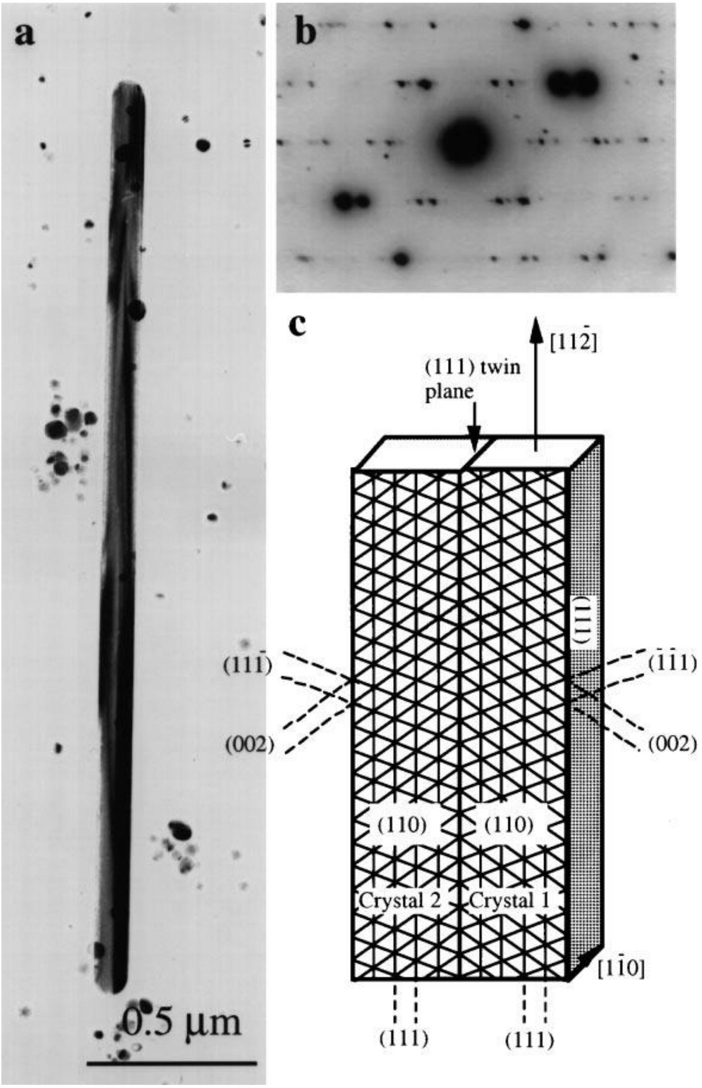
Indium, aspect ratios can exceed 50



J. Amer. Chem. Soc. 130 (2008) 8140

Gold, aspect ratios 3-7 (short) and >20 (long)





Surface Science 440 (1999) L809

0D material: books and reviews

Colloid systems are discussed in the course of Prof. P. Ziherl 'Fizika mehke snovi'.

- C.B. Murray, C.R. Kagan, M.G. Bawendi, Synthesis and Characterization of Monodisperse Nanocrystals and Close-Packed Nanocrystal Assemblies, Annu. Rev. Mater. Sci. 30 (2000) 545–610.
- C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, Chemistry and Properties of Nanocrystals of Different Shapes, Chem. Rev. 105 (2005) 1025-1102.
- K. Watanabe, D. Menzel, N. Nilius, H.-J. Freund, Photochemistry on Metal Nanoparticles, Chem. Rev. 106 (2006) 4301-4320.
- P.C. Ray, Size and Shape Dependent Second Order Nonlinear Optical Properties of Nanomaterials and Their Application in Biological and Chemical Sensing, Chem. Rev. 110 (2010) 5332-5365.
- R. Sardar, A. M. Funston, P. Mulvaney, R. W. Murray, Gold Nanoparticles: Past, Present, and Future, Langmuir 25 (2009) 13840-13851.
- Electrical Phenomena at Interfaces and Biointerfaces: Fundamentals and Applications in Nano-, Bio-, and Environmental Sciences (editor H. Ohshima), Wiley, 2012.
- N.E. Montl, A.F. Smith, C.J. Desantis, S.E. Skrabalak, Engineering plasmonic metal colloids through composition and structural design, Chem. Soc. Rev. 43 (2014) 3823-3834.
- Soft, Hard, and Hybrid Janus Structures: Synthesis, Self-Assembly, and Applications (editors Z.Lin, B. Li), World Scientific, 2017.

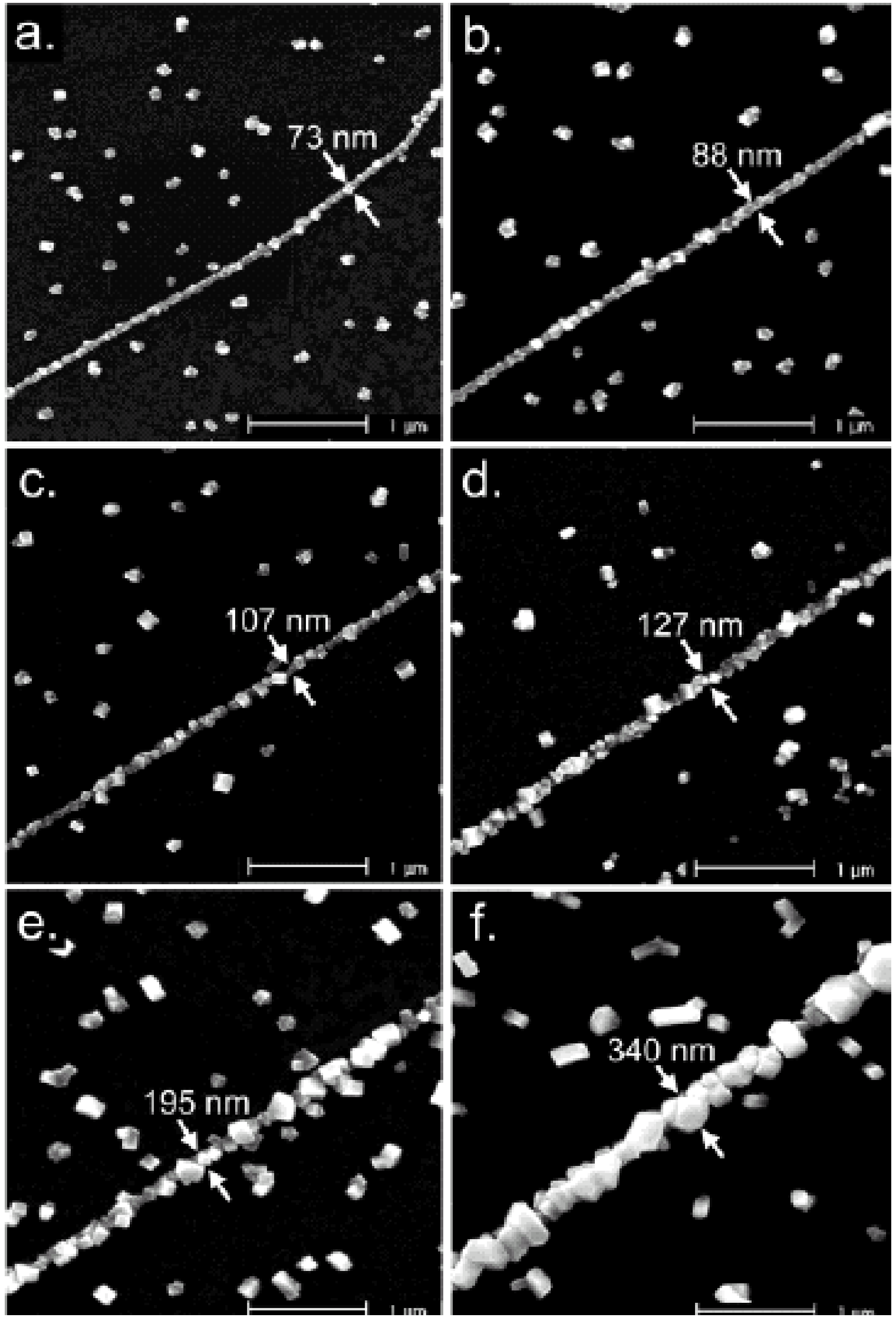
- K. M. Koczkur, S. E. Skrabalak, Metal Nanocrystals, ACS, 2020.
- A. Holmes, E. Deniau, C. Lartigau-Dagron, A. Bousquet, S. Chambon, N.P. Holmes, Review of Waterborne Organic Semiconductor Colloids for Photovoltaics, ACS Nano 15 (2021) 3927-3959.
- A. Rao, S. Roy, V. Jain, P.P. Pillai, Nanoparticle Self-Assembly: From Design Principles to Complex Matter to Functional Materials, ACS Appl. Mater. Interfaces 15 (2023) 25248-25274.

1D materials

Templates for fabrication of nanowires

Filling of templates

Chemical vapor deposition (CVD) of carbon nanotubes (CNT)

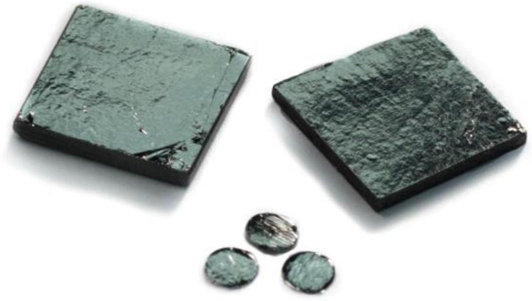


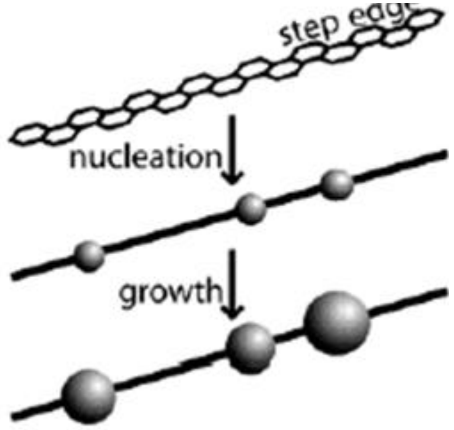
Early attempts of electrochemical formation of nanowires: «Step decoration»

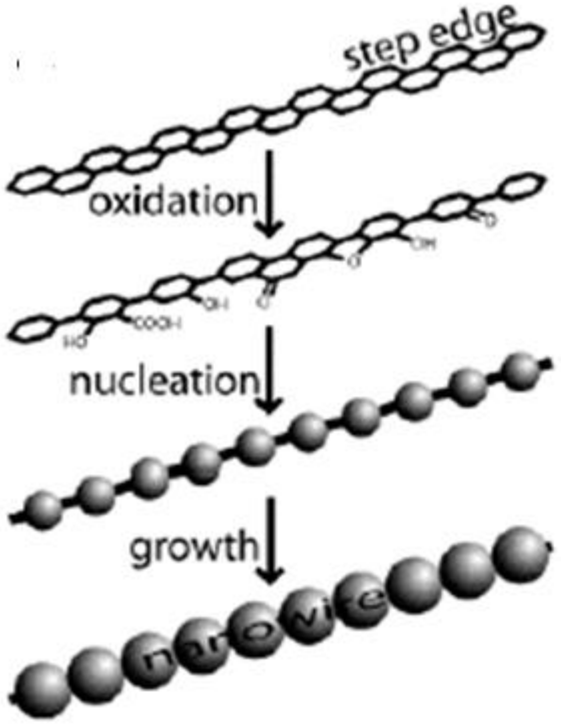
Deposition of metal or oxide results from ions reduction or oxidation in electrochemical cell.

The quantity of deposited material can be monitored by measuring deposition charge (Faraday law of electrolysis).

Highly oriented pyrolytic graphite (HOPG) provides steps as templates



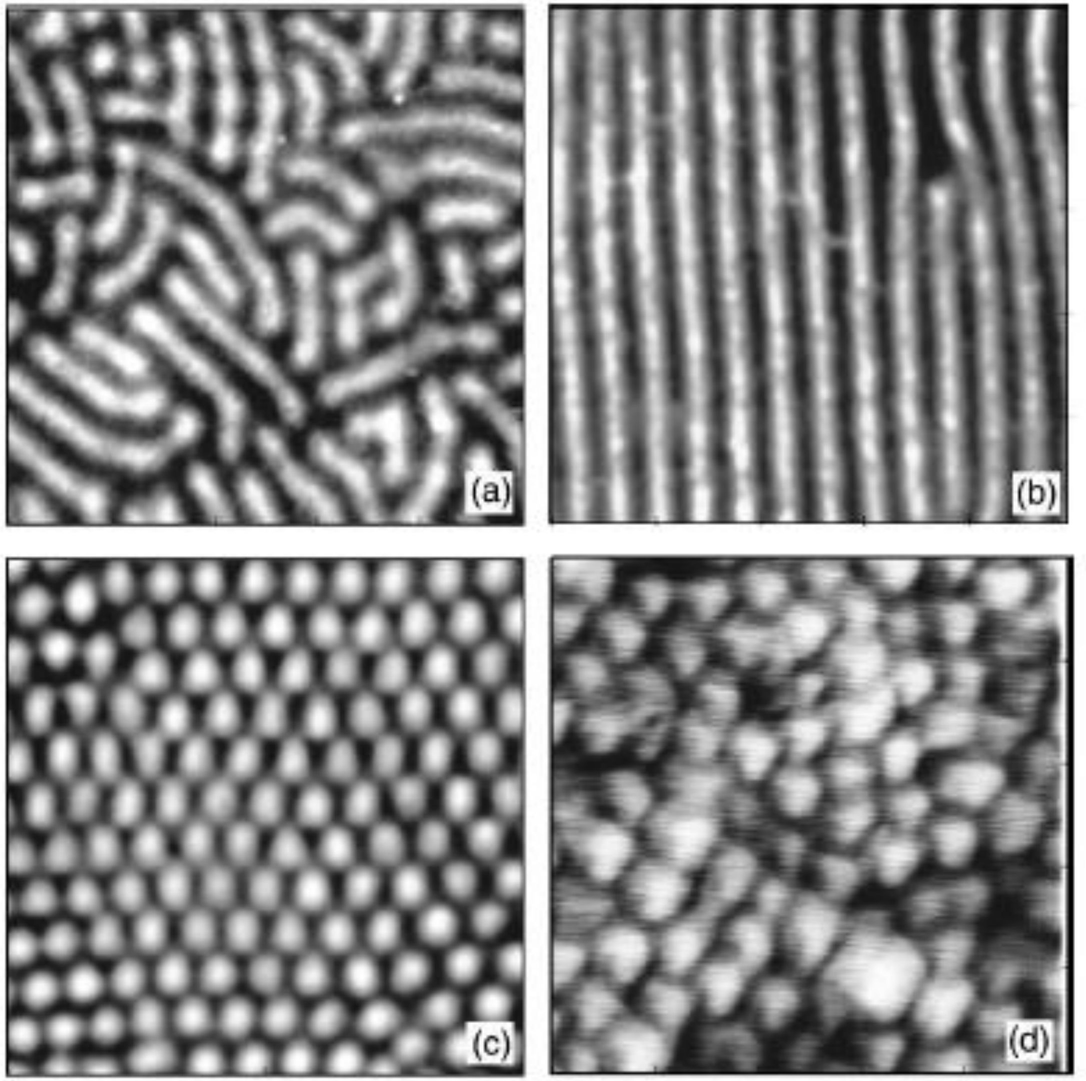




Another type of template: ‘Self-ordering’ in the course of aluminum anodization

40 V

50 V

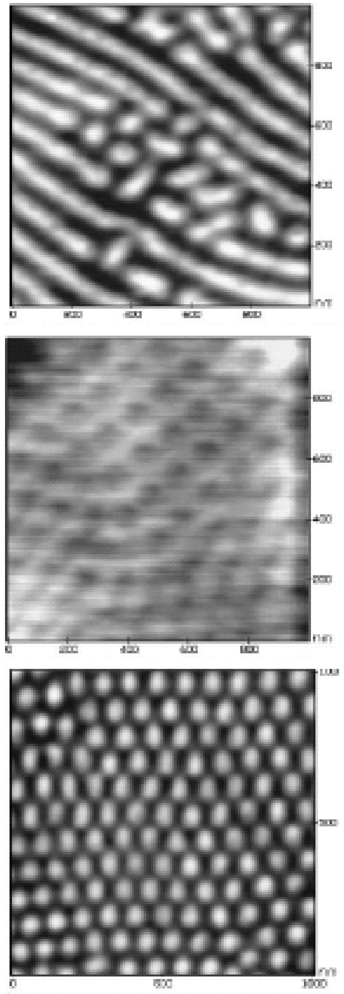


60 V

70 V

Aqueous ethanol + $HClO_4$

60 V



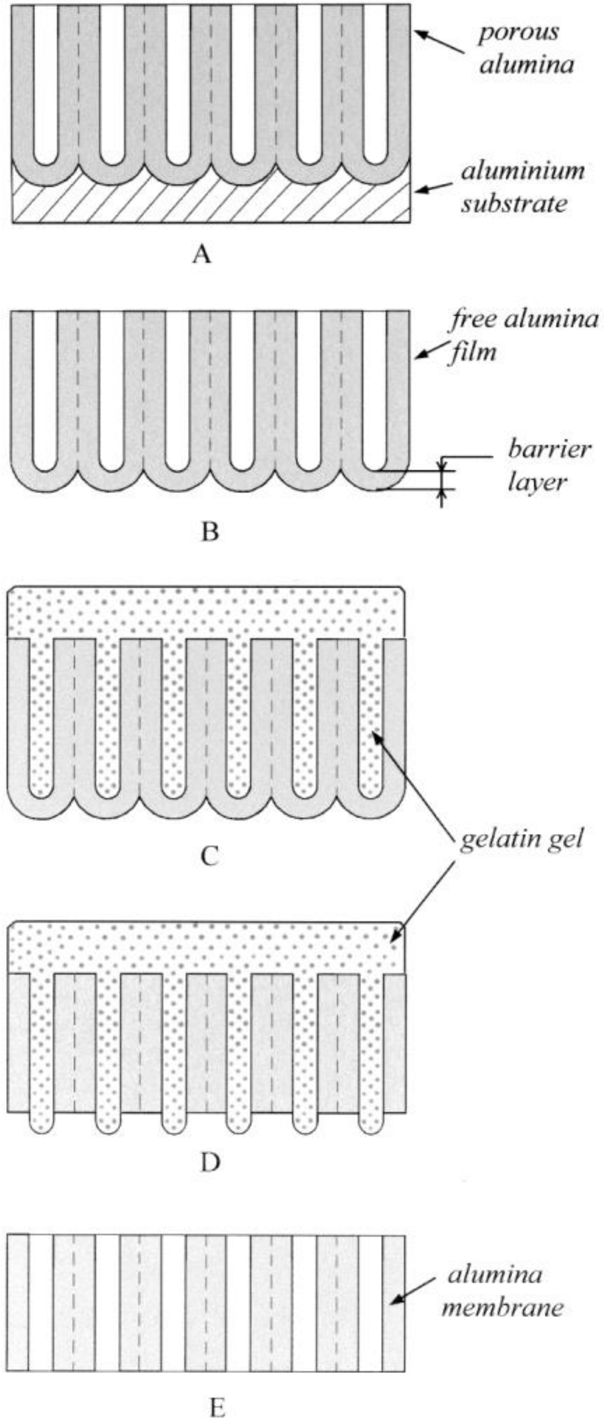
10 s

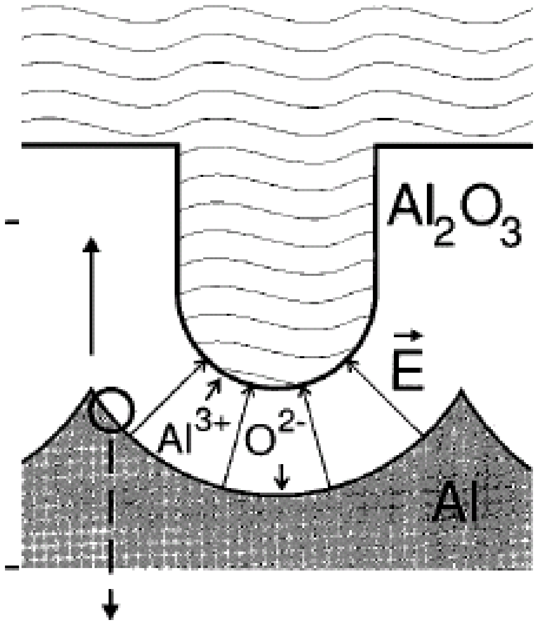
20 s

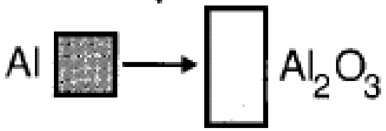
30 s

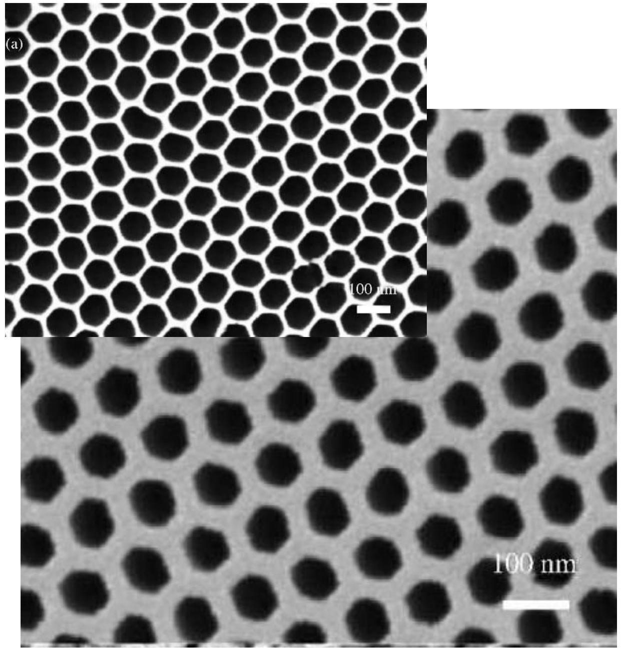
Phys. Rev. B 56 (1997) 12608

Hexagonal ordering results in formation of the parallel pores





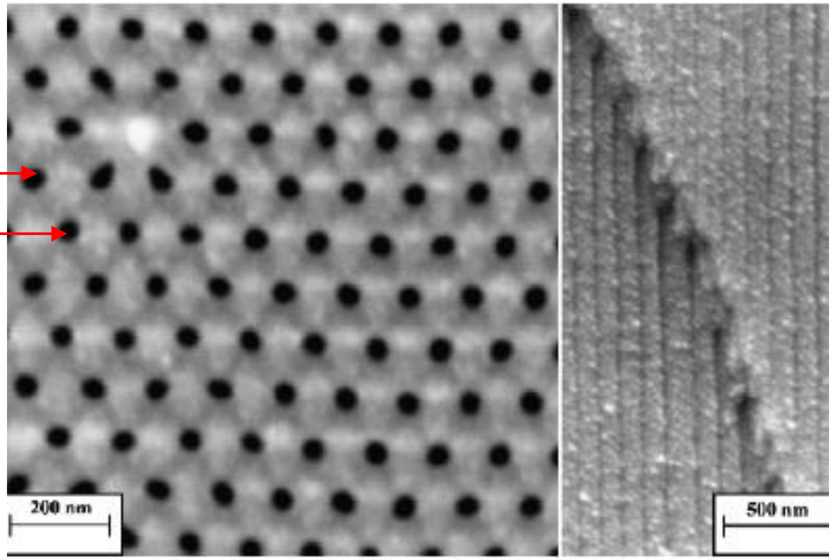




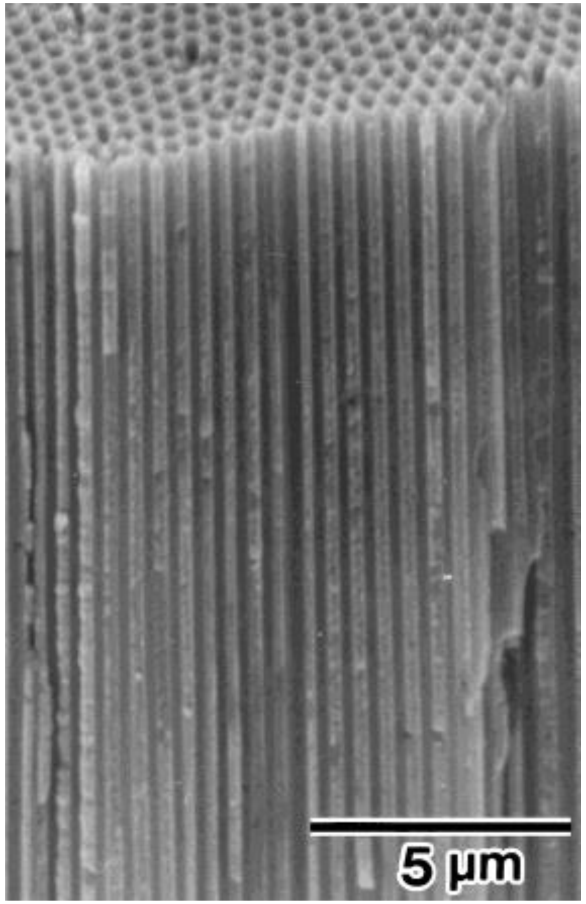
Diameters starting from 15-20 nm

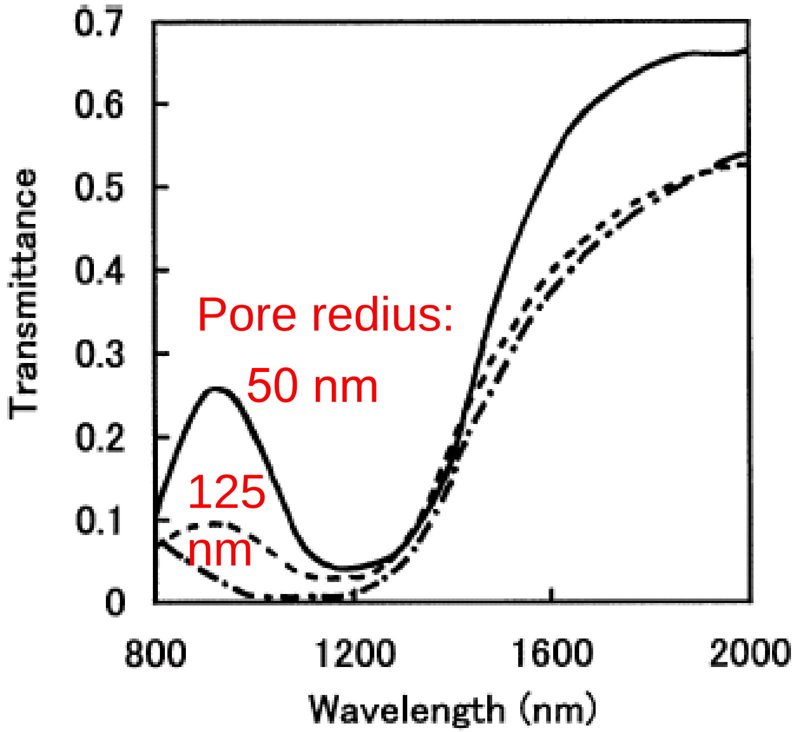
60-150 nm

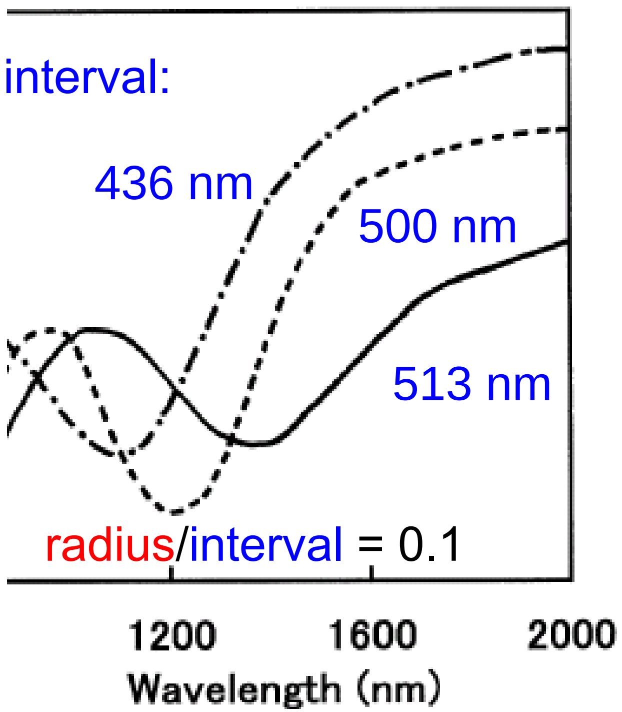
Up to 100-150 μm

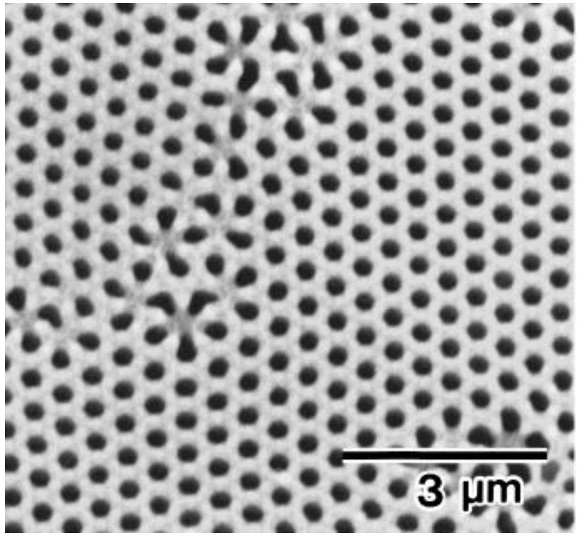


Anodic Aluminum Oxide (AAO) as metamaterial, photonic crystals







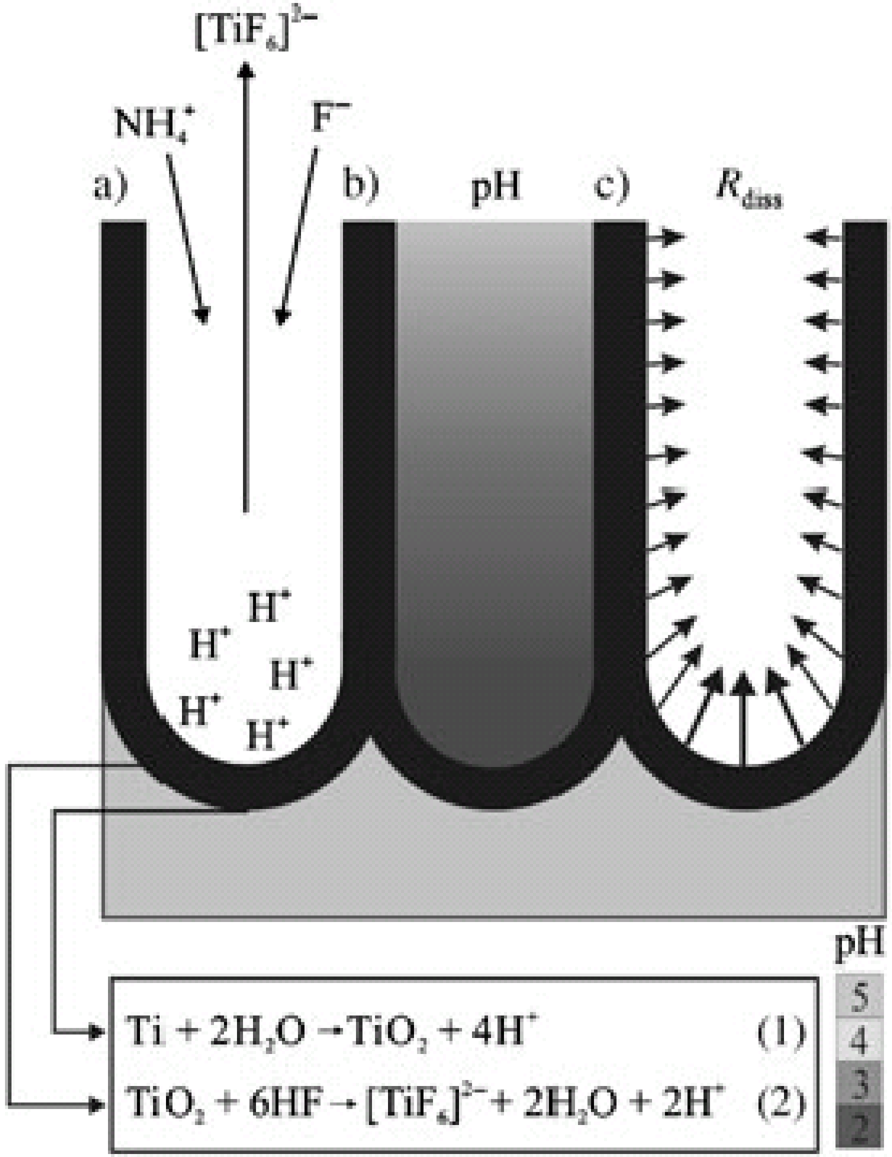


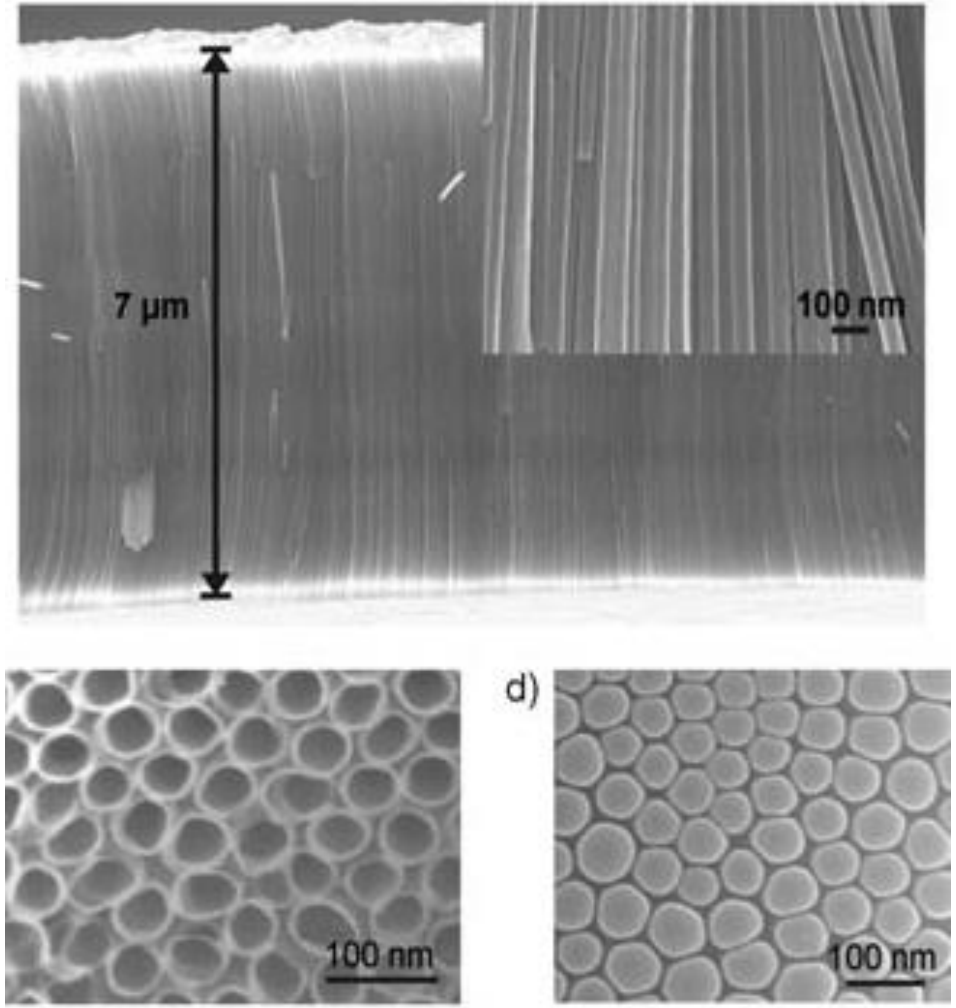
Problems:

- **domains disorder;**
- **misorientation inside domain.**

Jpn. J. Appl. Phys. 40 (2001) L 1217

The closest analogy of AAO: TiO_2 nanotubes



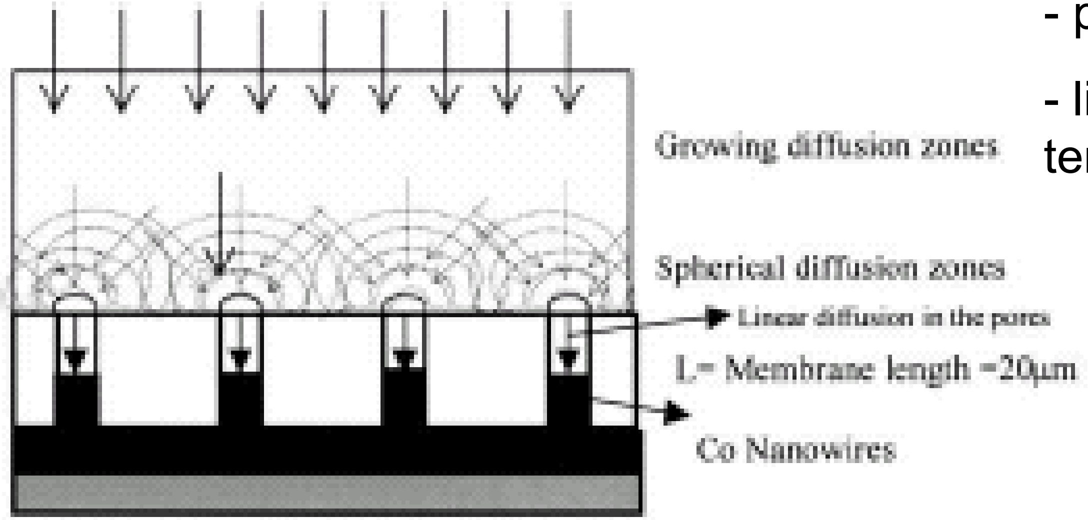


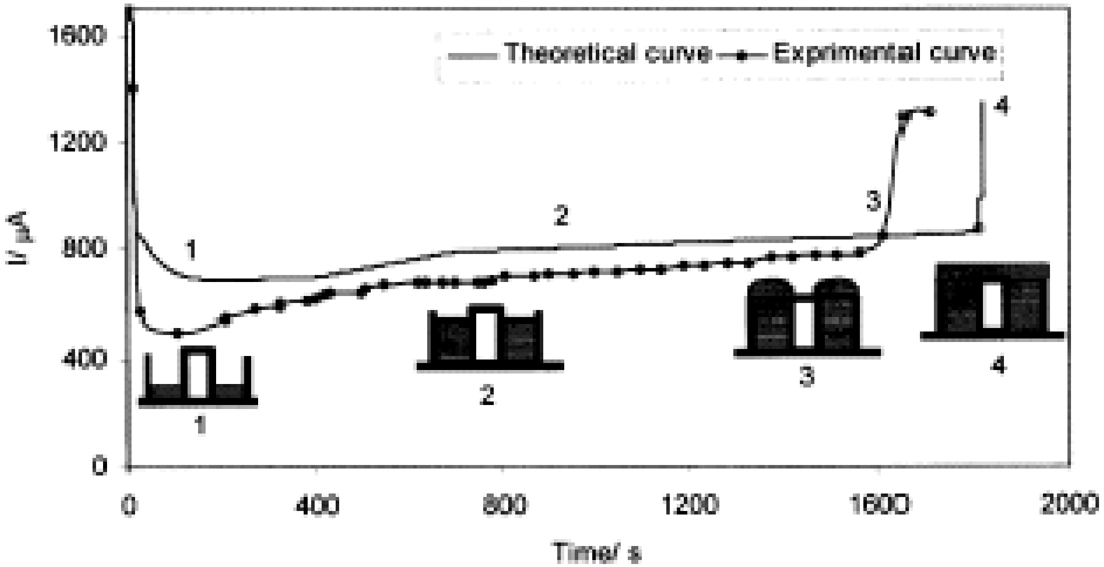
External surface

Bottom

Angew. Chem. Int. Ed. 44 (2005) 7463

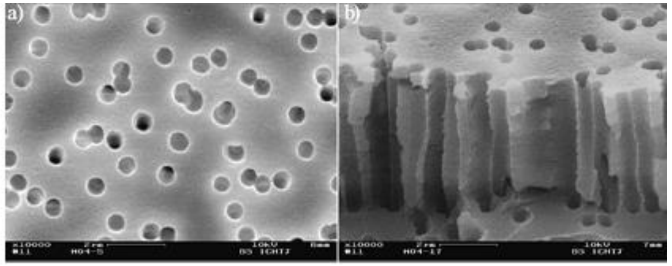
Templated deposition into pores

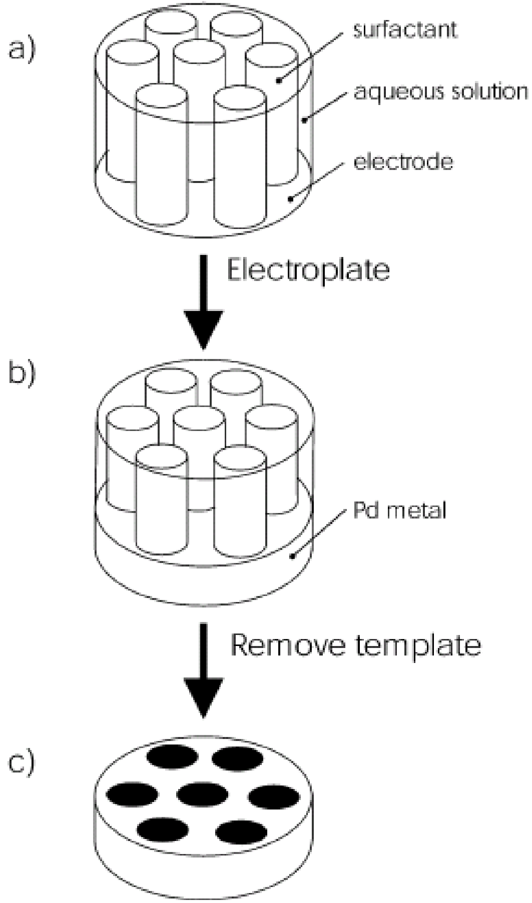




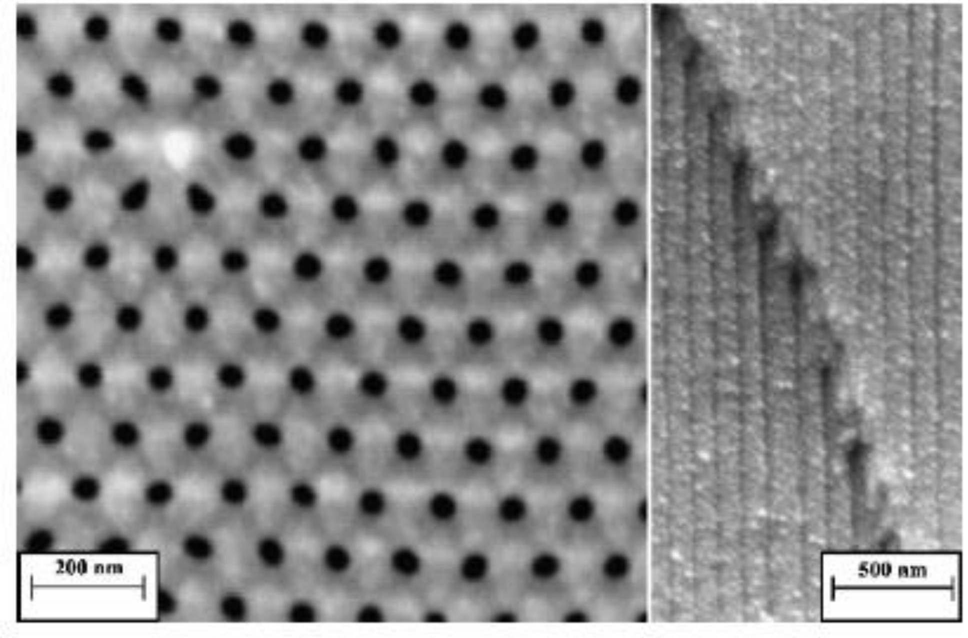
Templates:

- solid, inorganic (like AAO)
- polymer (track membranes)
- liquid crystals (reverse templates)



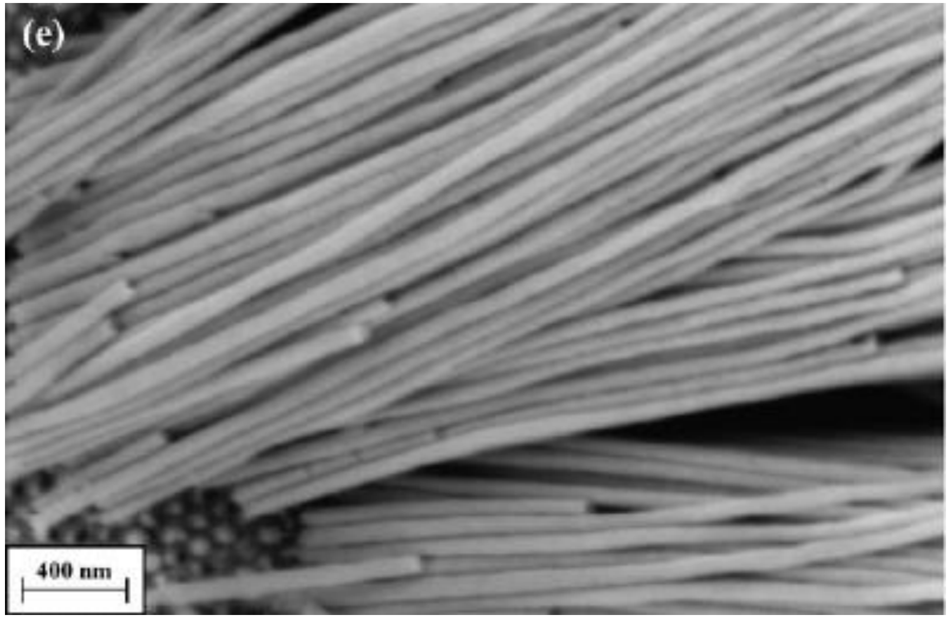


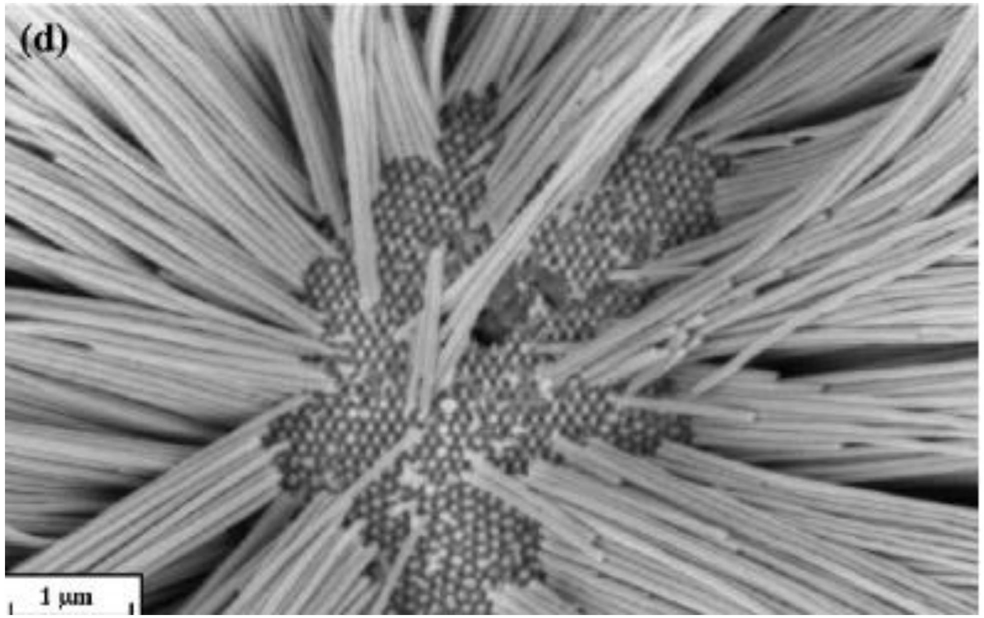
Wires growth in AAO templates



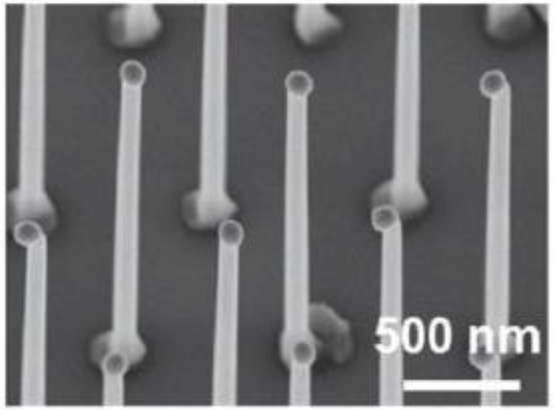
Wires diameters: 15 – 150 nm

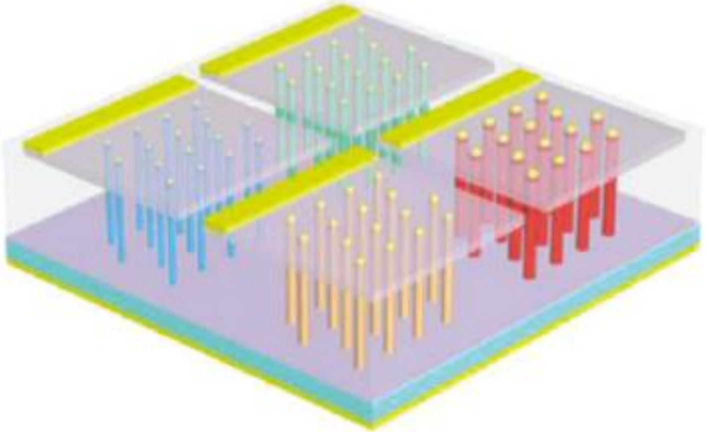
Wires length: up to 100 -200 μm



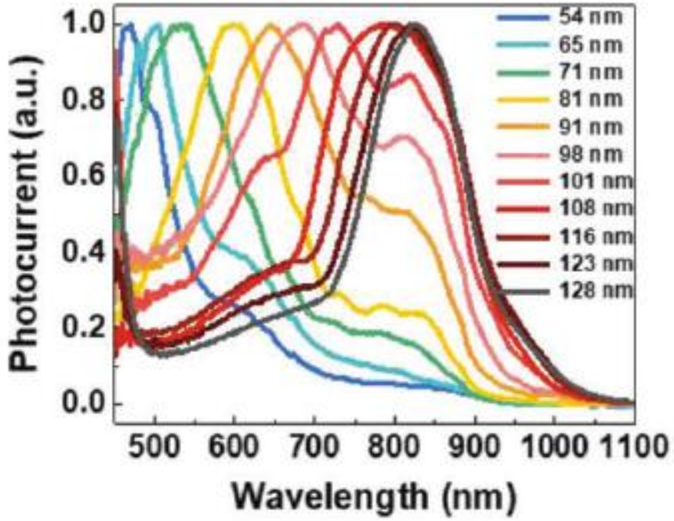


Wires in devices



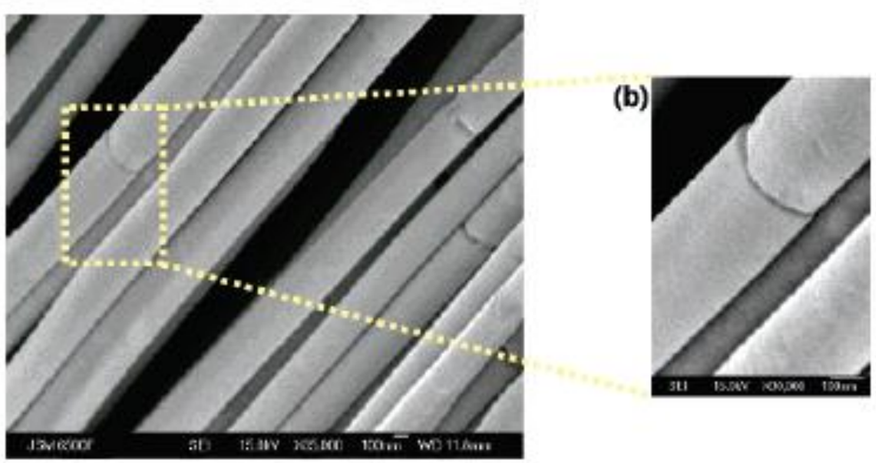


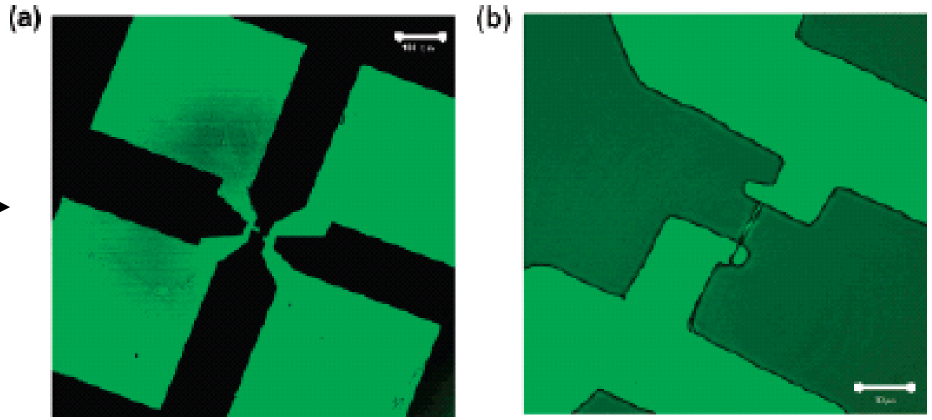
Nano Lett. 21 (2021) 7388



GaAsSb

Photoluminescence



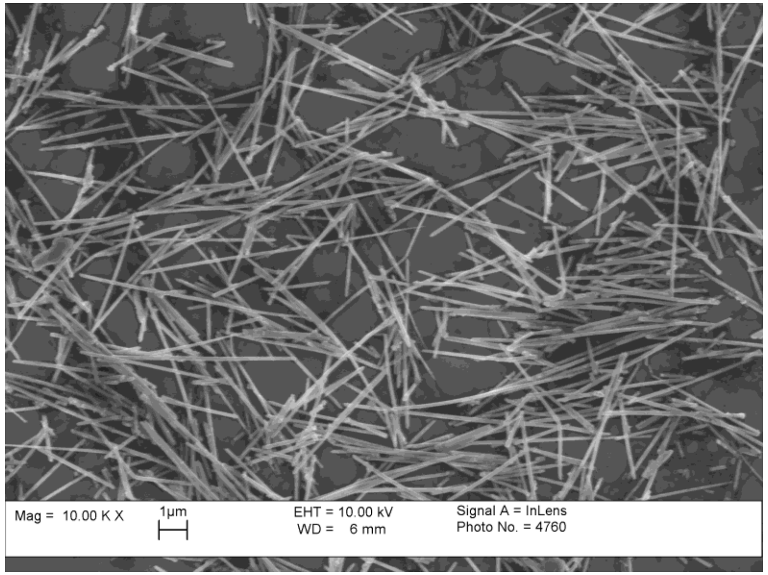


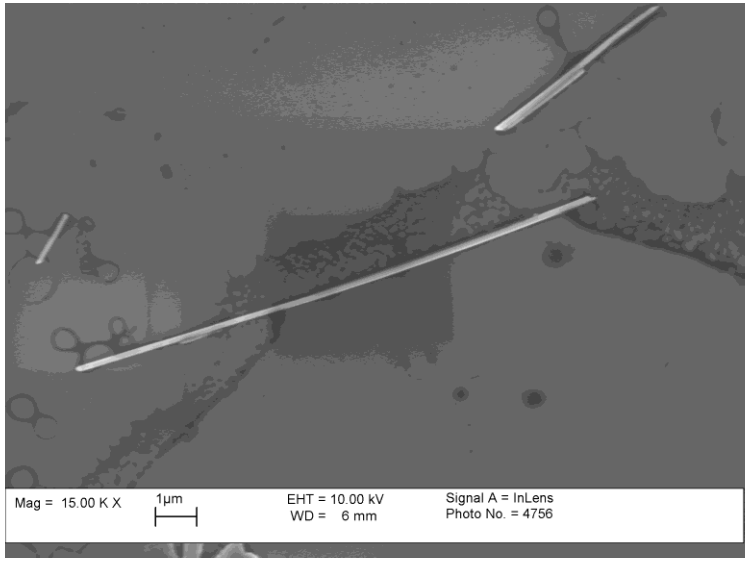
Anal. Chem. 78 (2006) 951

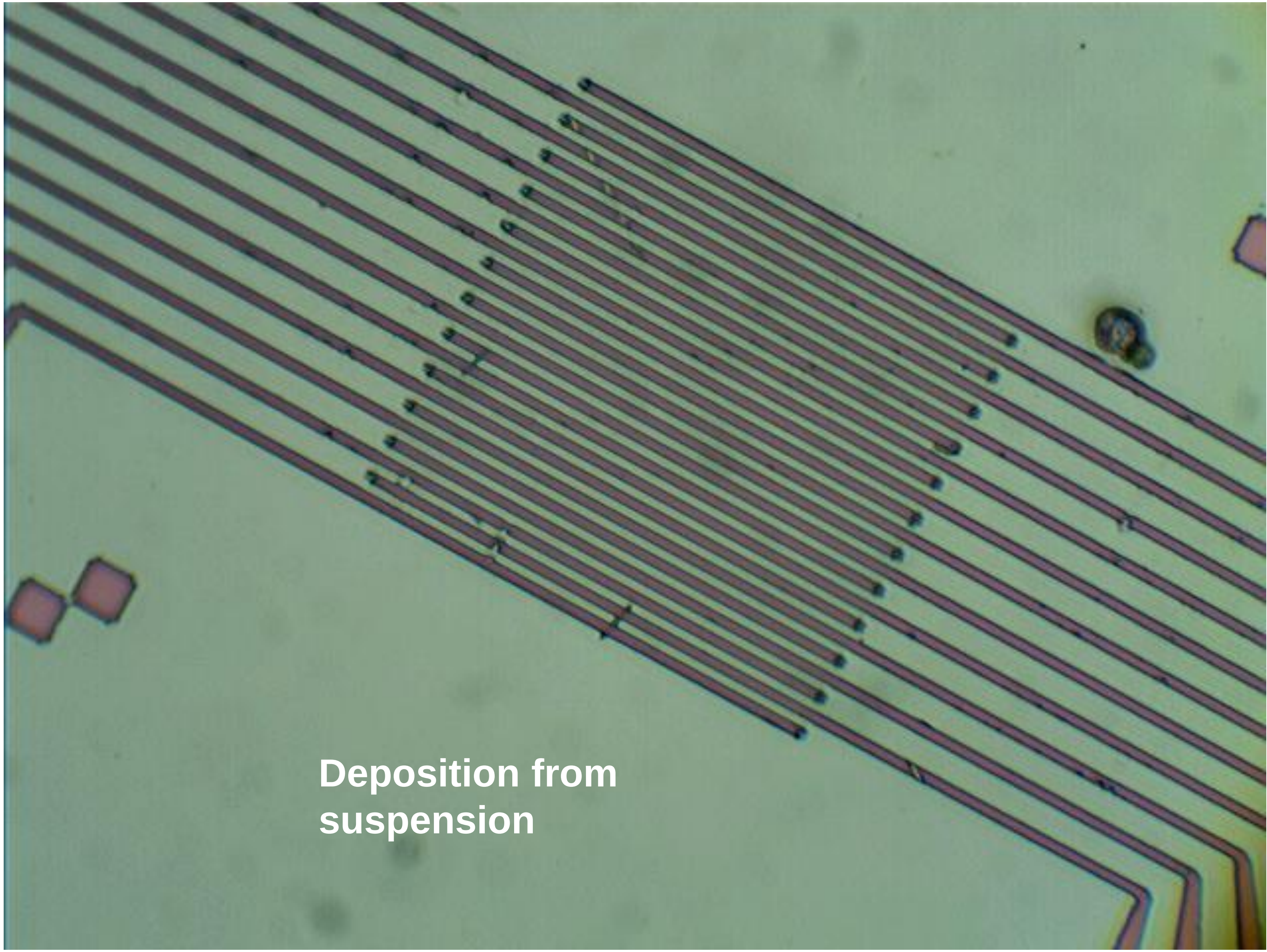
Au/Ag/Au wire (thin Ag later is dissolved to provide molecular-size gap)

Contacts for a single molecule

Single wires with contacts

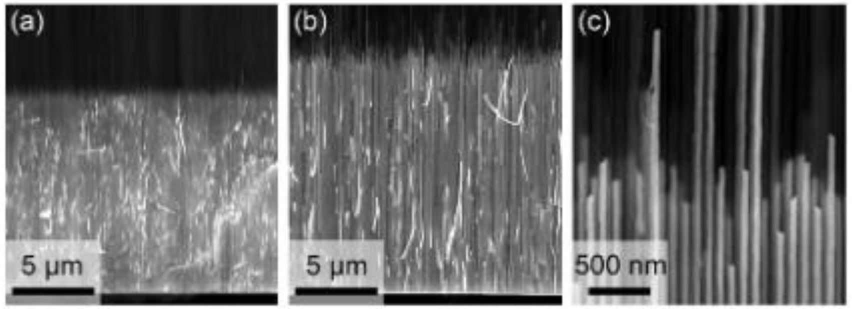


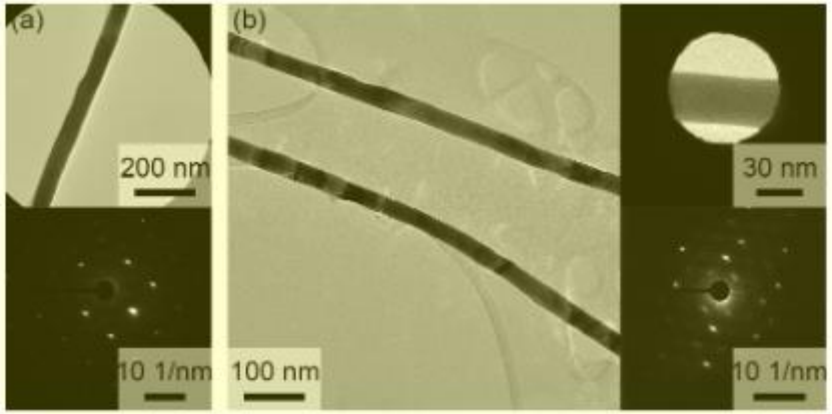




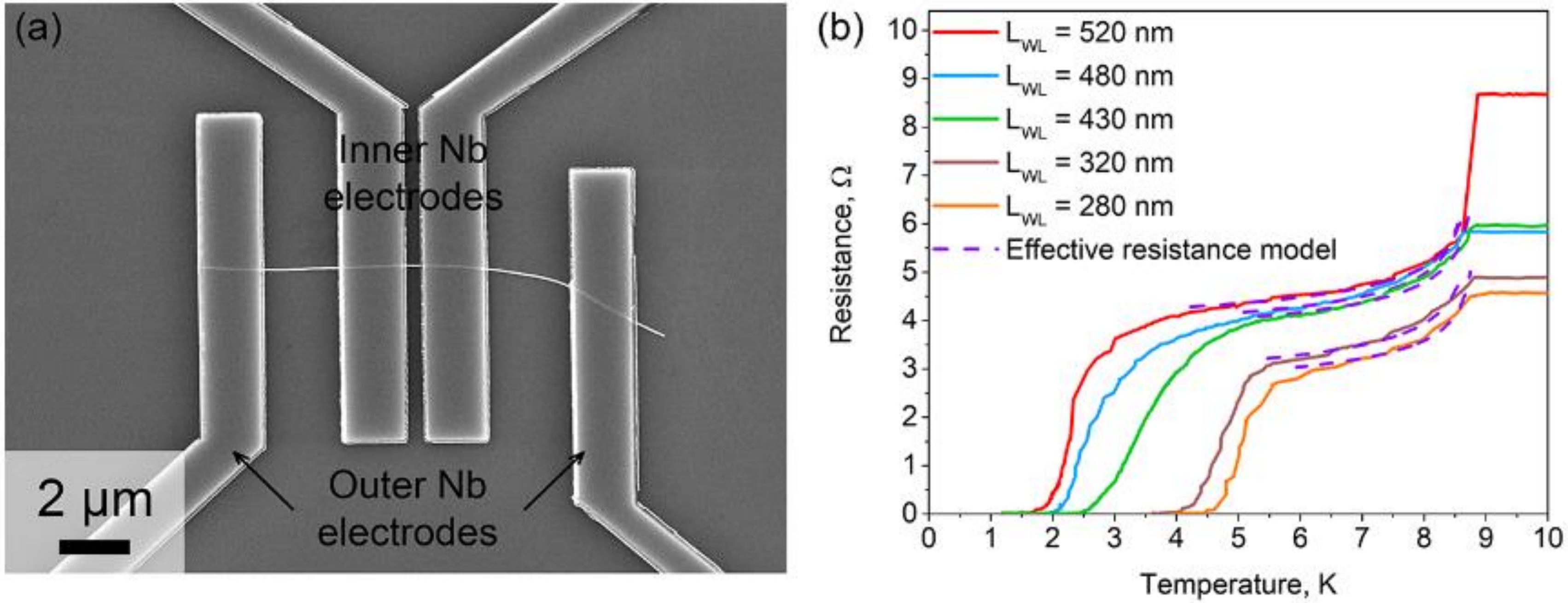
Deposition from suspension

Josephson junction with Au wire as a weak link





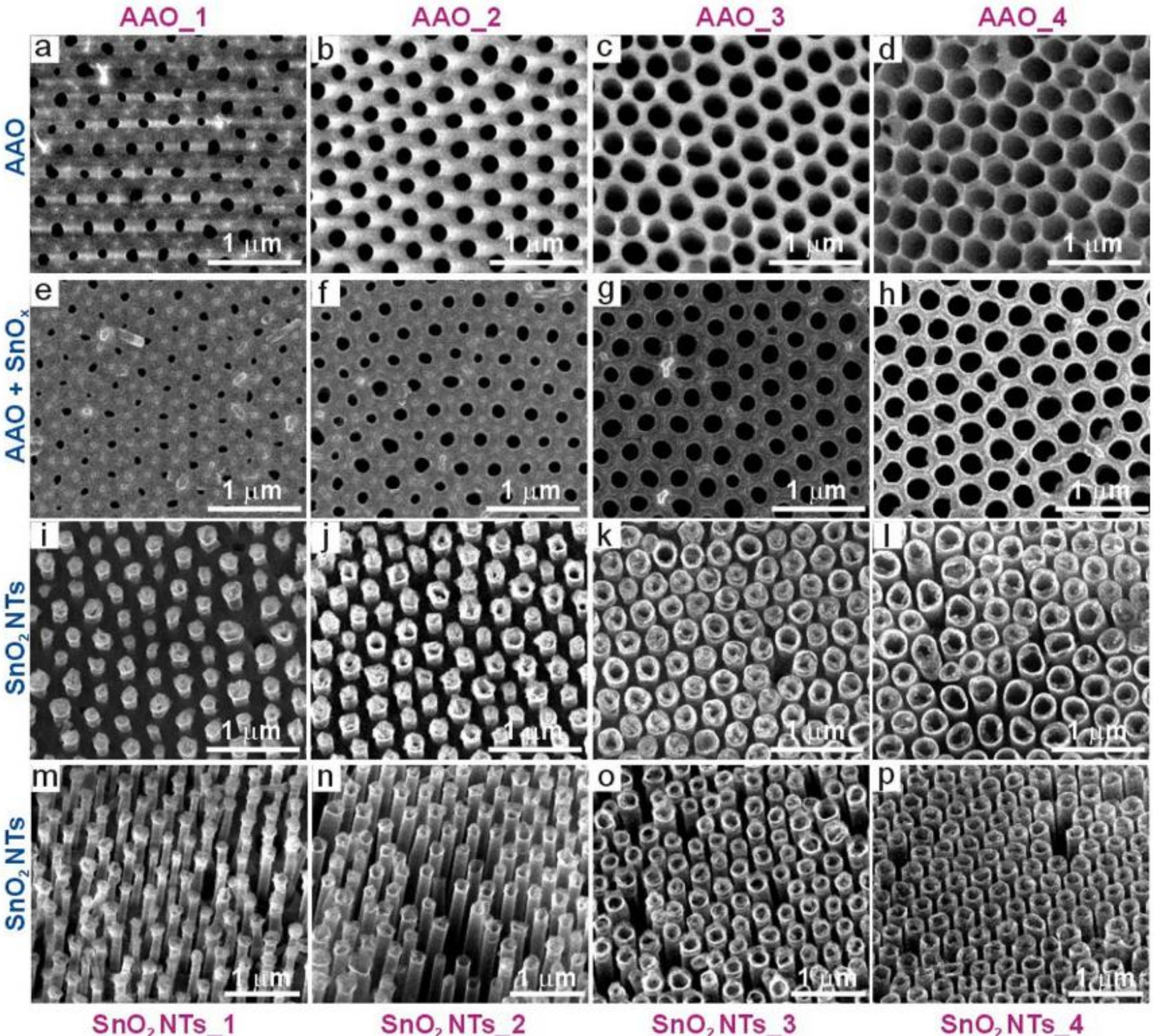
ACS Appl. Nano Mater.
5 (2022) 17059



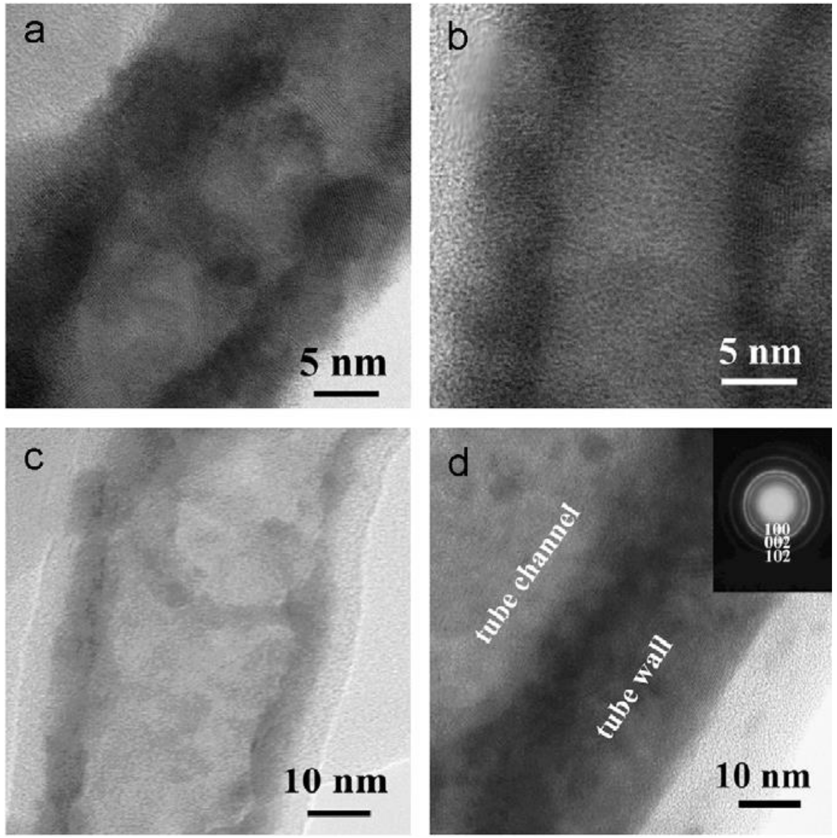
Templating of nanotubes is also possible

SnO_x in AAO

Mater. Charact. 136 (2018) 52



CdS in track membranes

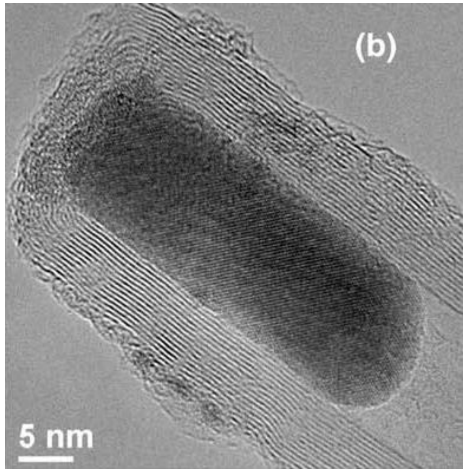


J. Crystal Growth 310 (2008) 612

Chemical vapor deposition (CVD) of carbon nanotubes (CNT)

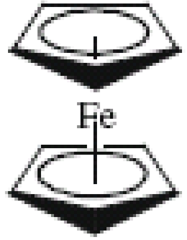
Catalytic CVD:

two-step CVD



Fe catalyst near the bottom of carbon nanotube

OR continuous-feed CVD

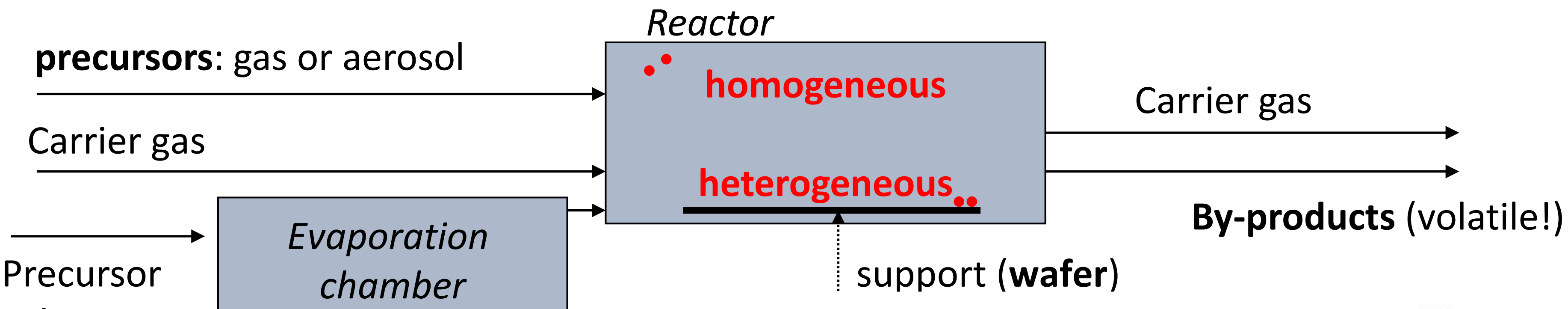


Ferrocene, precursor for both iron and carbon

Carbon 47 (2009) 384-395

Pyrolysis (thermal decomposition of a single reagent) $CH_4 \rightarrow C + H_2$

Disproportion (two products from one reagent) $CO \rightarrow C + CO_2$



Reactor

precursors: gas or aerosol

Carrier gas

homogeneous

heterogeneous

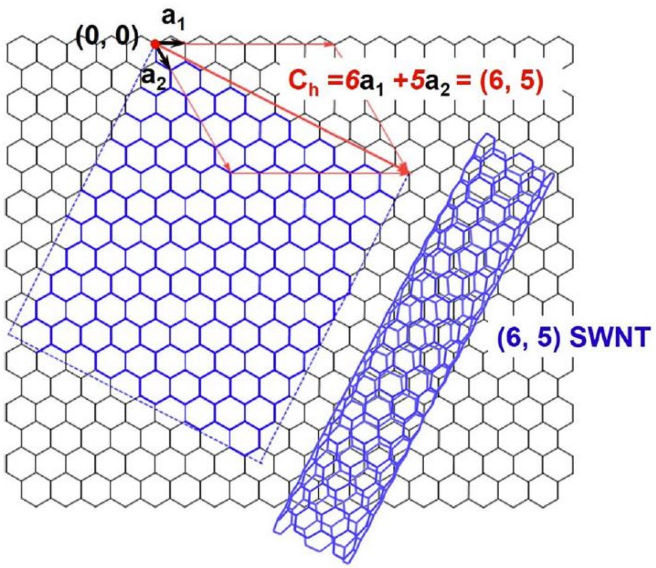
Carrier gas

By-products (volatile!)

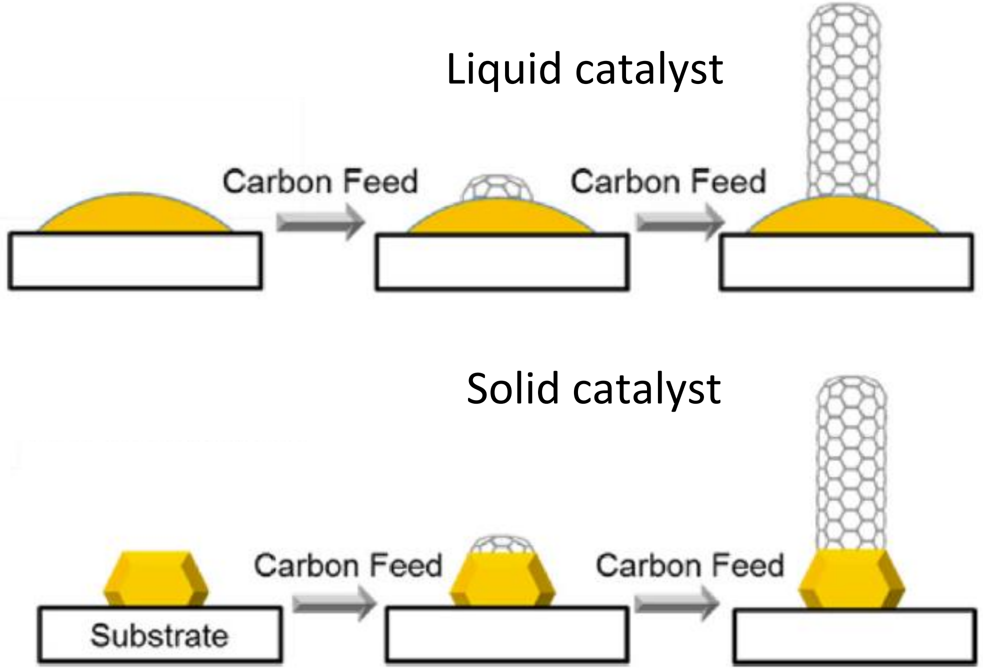
Evaporation chamber

Precursor solutions

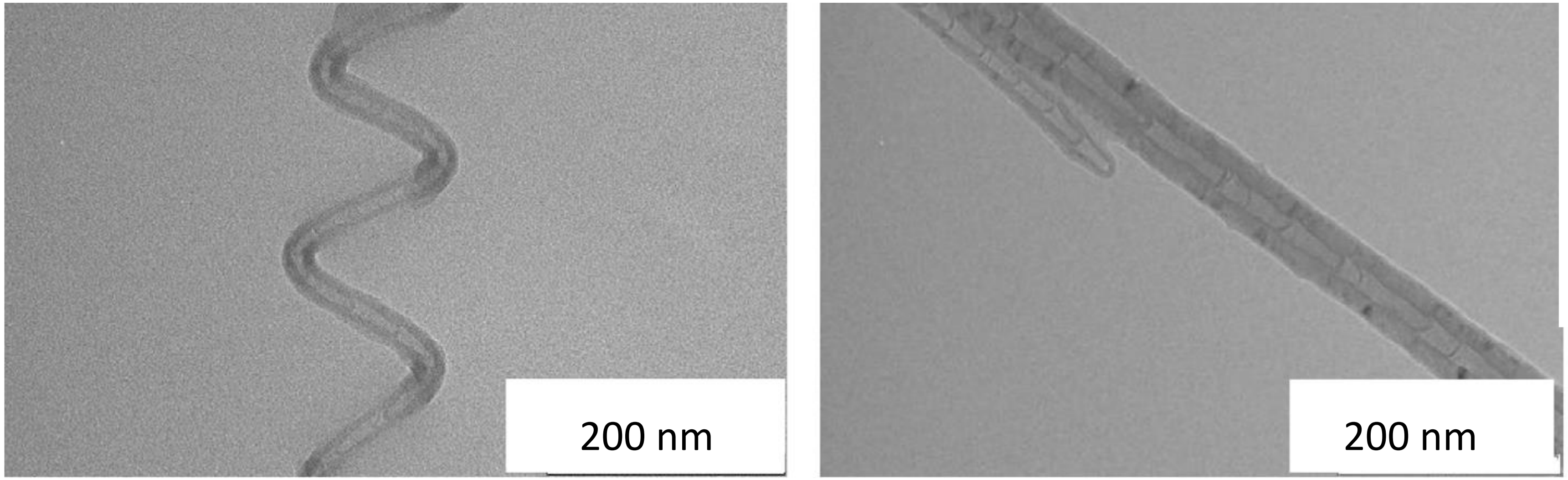
support (**wafer**)



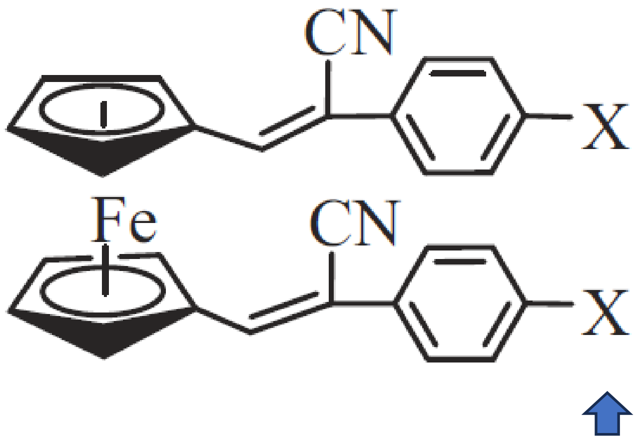
Top. Curr. Chem. (Z) 375 (2017) No 29



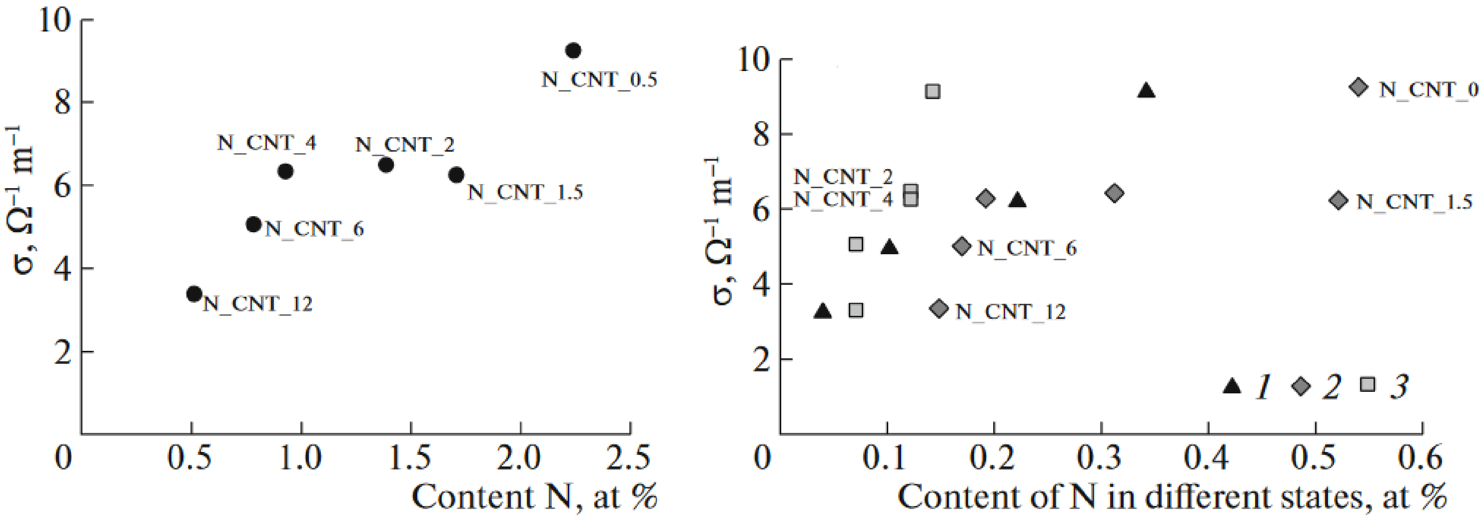
Carbon nanotubes doped with foreign elements (example for nitrogen)



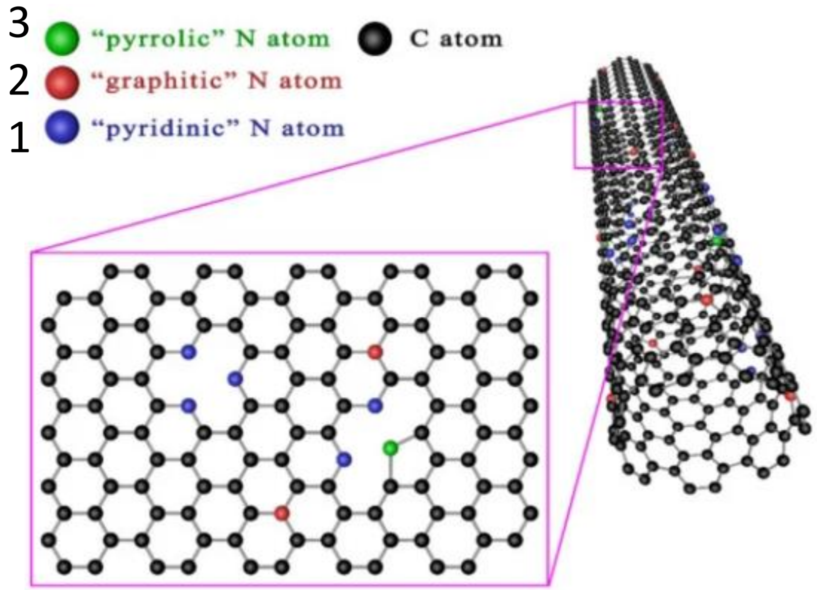
J. Solid State Chem. 235 (2016) 202



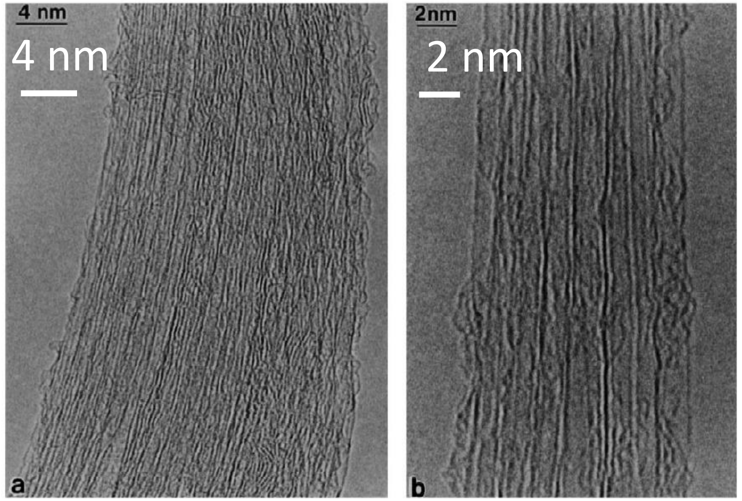
X=CN, or can contain another doping element



Russ. J. Phys. Chem. A 93 (2019) 1952

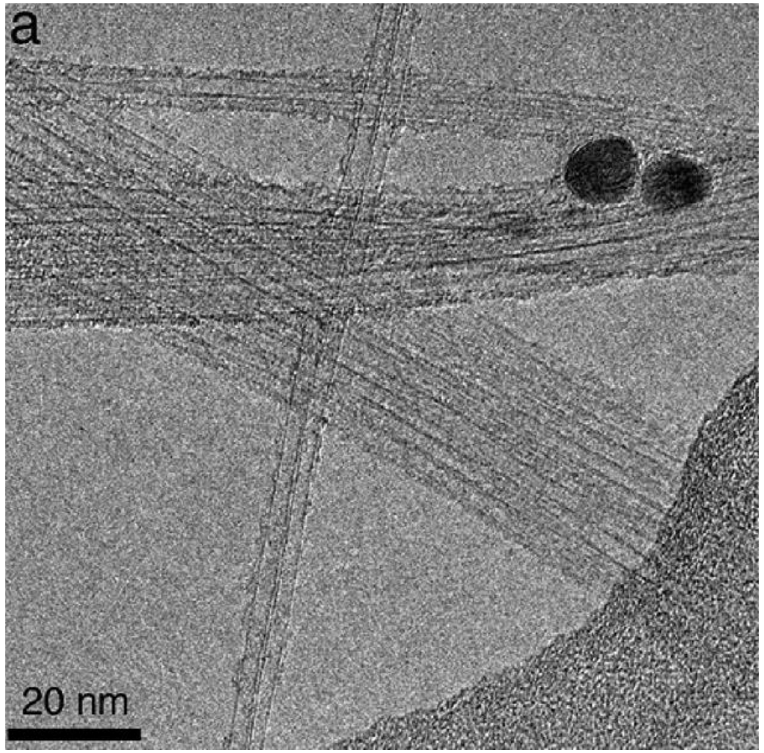


Problems with single nanotubes: bundles and residual catalyst



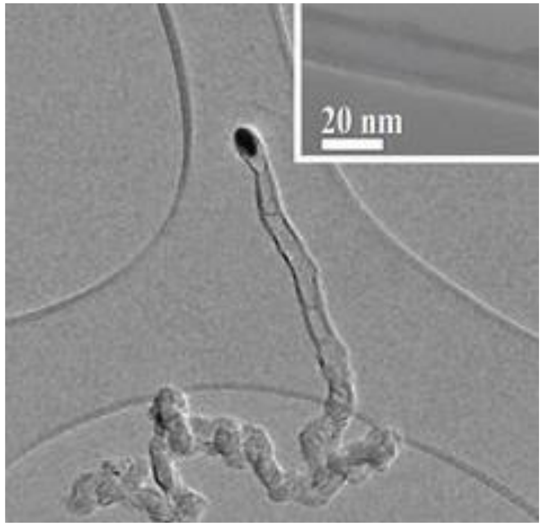
Carbon 38 (2000) 2017

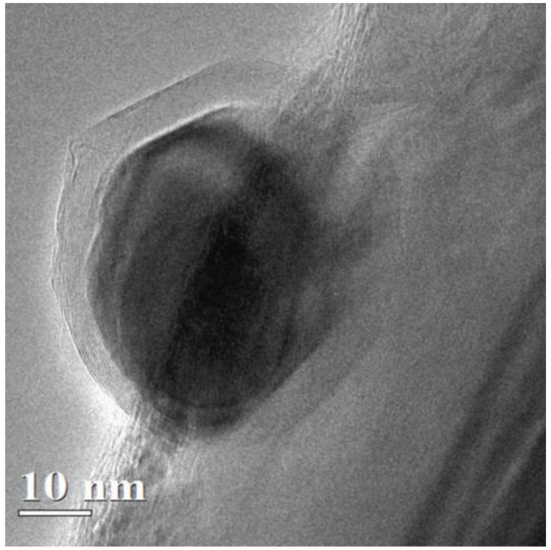
Can be separated by ultrasound treatment in presence of adsorbing substances.



Carbon 100 (2016) 501

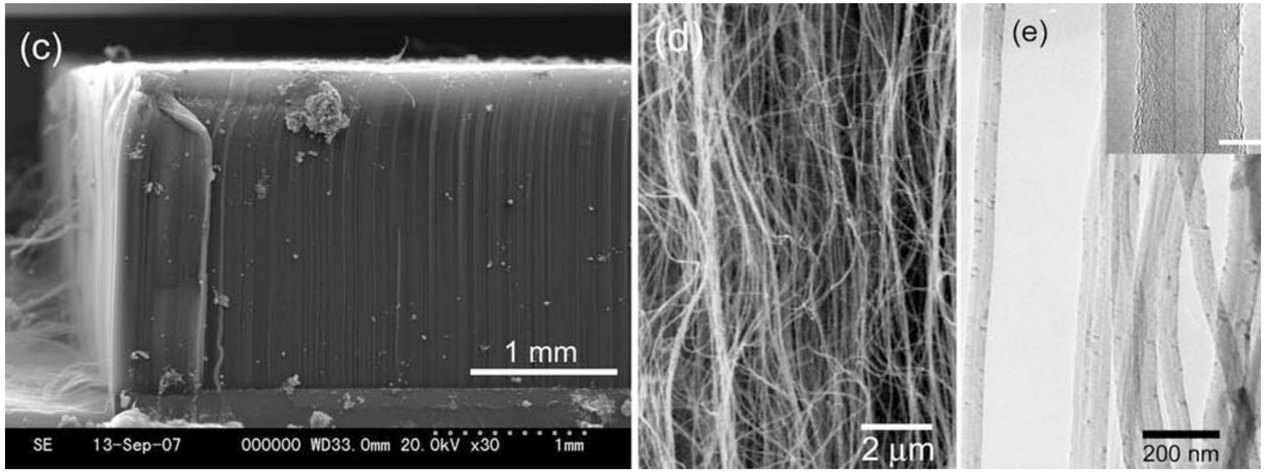
Can be purified by acidic chemical treatment (e.g., HCl). However incapsulated catalyst remains undissolved.



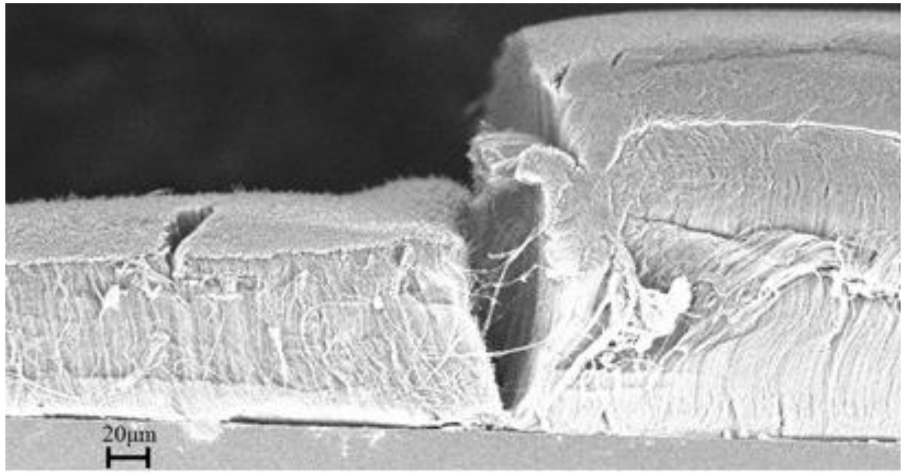


J. Nanomater. (2014) 586241

Forests of nanotubes: ordered compact materials

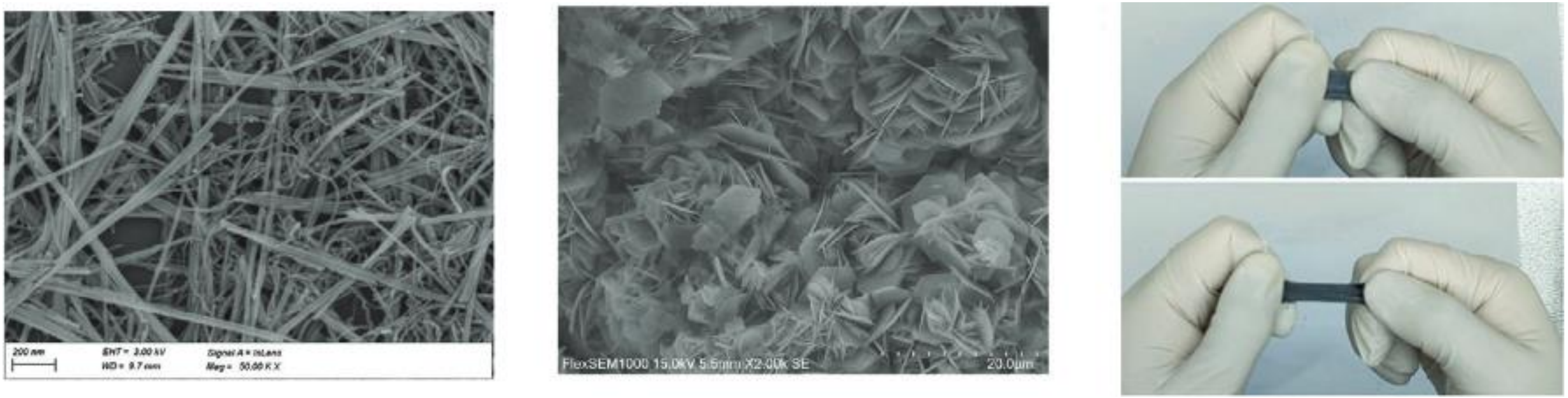


Appl. Phys. Lett. 92 (2008) 213113



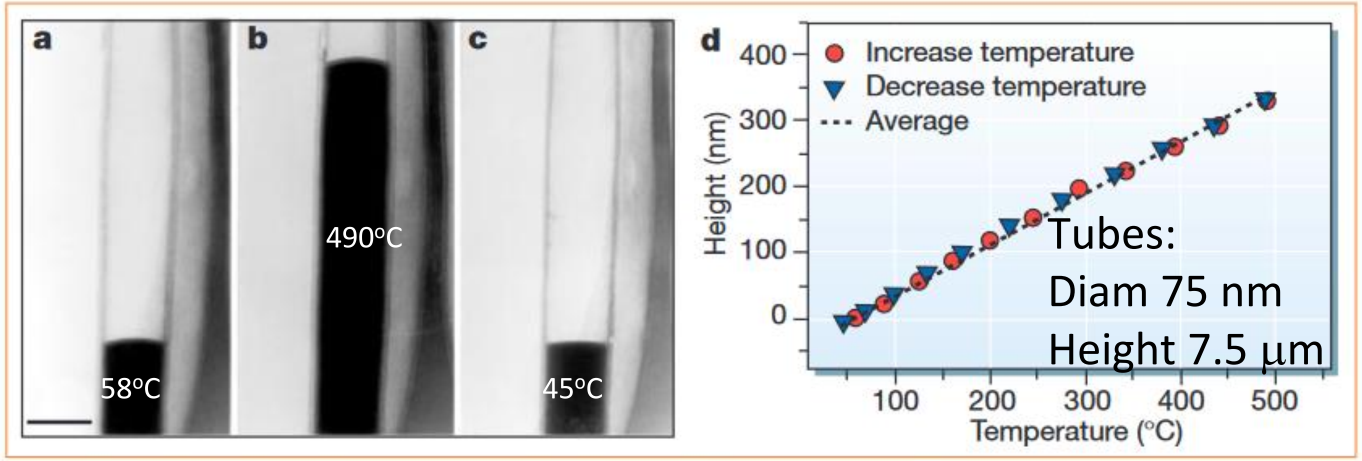
Appl. Mechan. Mater. 496-500 (2014) 536

CNT-based flexible materials



Macromol. Rapid Commun. 44 (2023) 2200795

Metal filled carbon nanotubes: gallium thermometer



Expansion of gallium inside a carbon nanotube with increasing temperature. **a–c,** Changing level of the gallium meniscus at 58 °C (**a**), 490 °C (**b**) and 45 °C (**c**); scale bar, 75 nm. **d,** Height of the gallium meniscus plotted against temperature, measured in steps of 30–50 °C; results are averaged (green curve) from closely similar measurements obtained during heating (red) and cooling (blue).

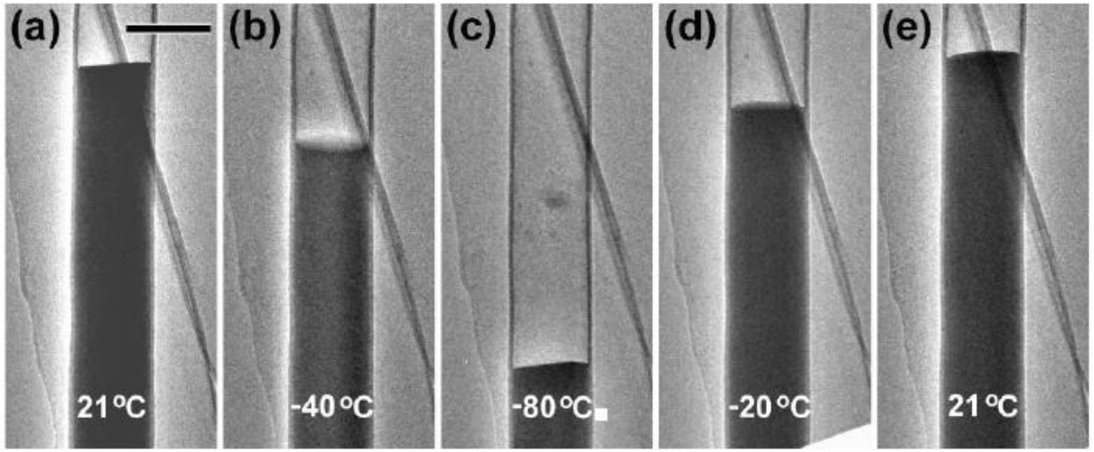
Nature 415 (2002) 599

There are many important findings for bulk composite materials containing CNT (especially related to thermal conductivity).

There are many other nanowires already actively applied in various devices (especially Si, Ge, Ag).

Assemblies of nanowires will be also discussed in subsequent parts of this course, as related to 2D in combination with lithography.

Phys. Rev. Lett. 93 (2004) 095504



TEM micrographs showing Ga volume contraction and expansion inside a carbon nanotube upon cooling and heating. The background feature is a carbon film. Scale bar = 100 nm. (a) At room temperature, 21 °C, before cooling. (b) At −40 °C. (c) At −80 °C, solidification occurred. (d) The crystallized Ga was melted at −20 °C. (e) Reheated to room temperature, 21 °C.

	α-Ga	β-Ga	γ-Ga
Symmetry	orthorhombic	monoclinic	orthorhombic
Melting point	29.8 °C	−16.3 °C	−35.6 °C

1D material: books and reviews

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