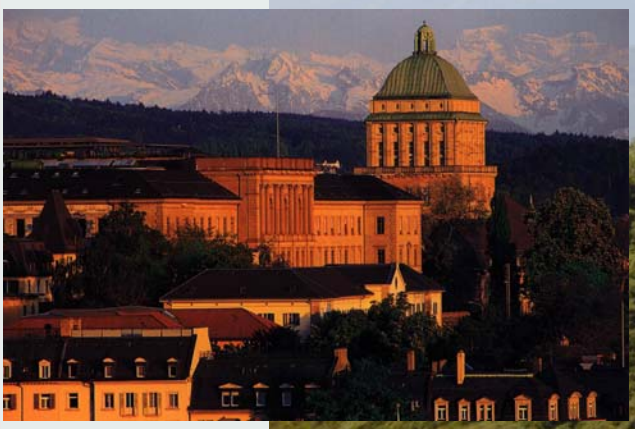
Nanochemistry Course Oslo University

R. NESPER ETH ZÜRICH & COLLEGIUM HELVETICUM



30.10.2006

Nanochemistry Course Oslo University

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Synthesis, Structures, Properties & Applications

- World & Nanoworld - philosophy, general definitions, hopes, challenges
- Physico-Chemical Considerations
  band structures, typical “nano effects”
- Colloids + General Syntheses of Nanoparticles
- Fullerenes, C-nanotubes and other carbon-related matter
- Oxidic nanotubes and nanofibers
- Future Energy and Nanosciences
- Other Inorganic Nanotubes + Fibers
- Nano Clusters
- Bio-Nano Aspects
- Risk Discussion

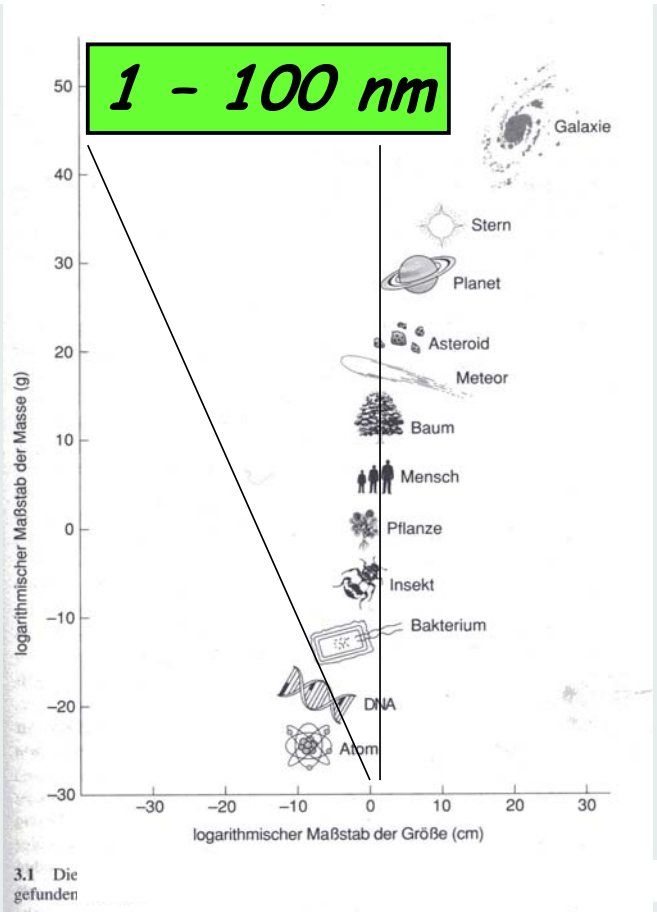
Where are We

and

where is the Nano World?

30.10.2006

1 – 100 nm



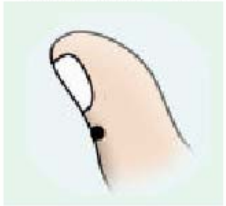
3.1 Die gefunden

The Nano World

The Incredible Tininess of Nano

Billions of nanometers
A two meter tall male is two billion nanometers.

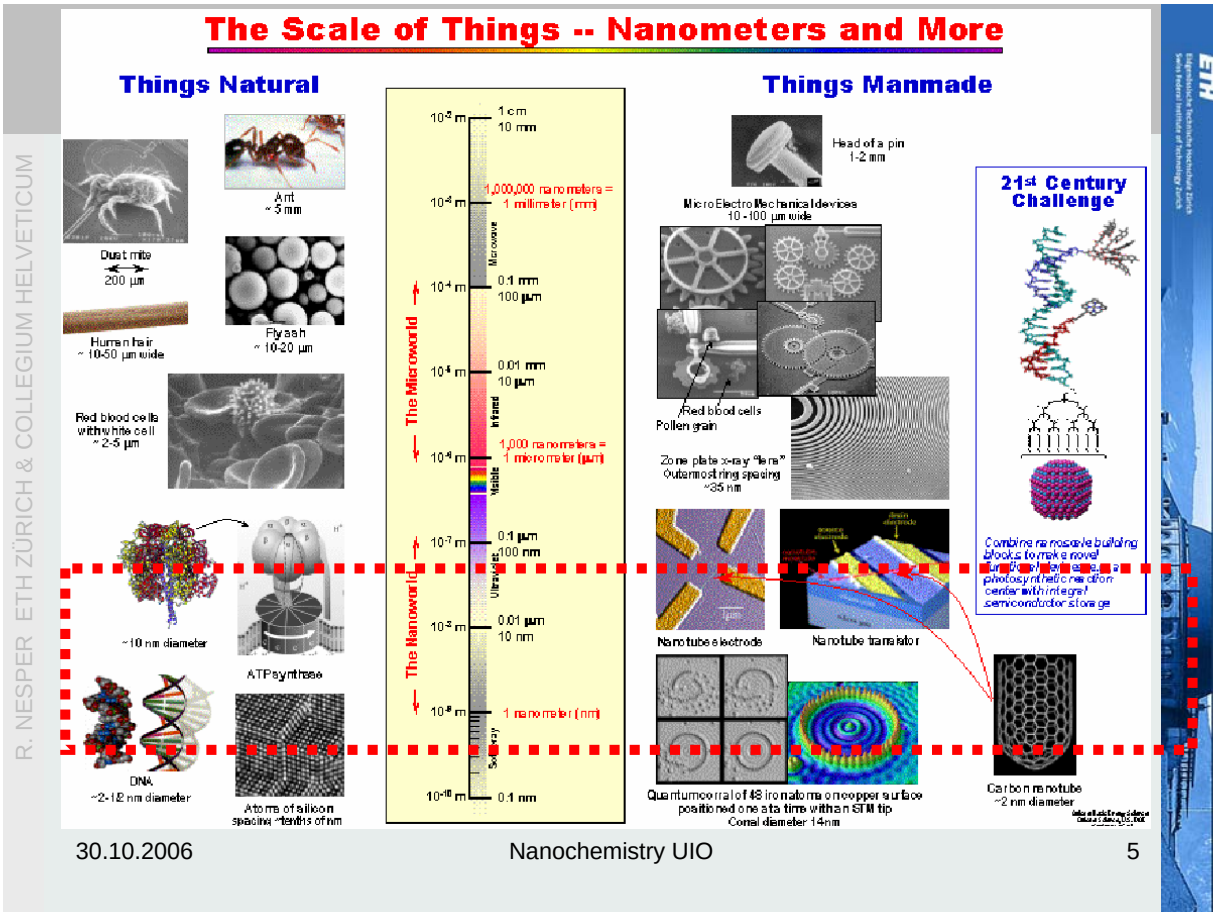
A million nanometers
The pinhead sized patch of this thumb is a million nanometers across.



Thousands of nanometers
Biological cells have diameters in the range of thousands of nanometers.

Nanometers
Ten shoulder-to-shoulder hydrogen atoms span 1 nanometer. DNA molecules are about 2.5 nanometers wide.

Less than a nanometers
Individual atoms are up to a few tenths of a nanometer, in diameter.


The Scale of Things -- Nanometers and More
Things Natural
Things Manmade
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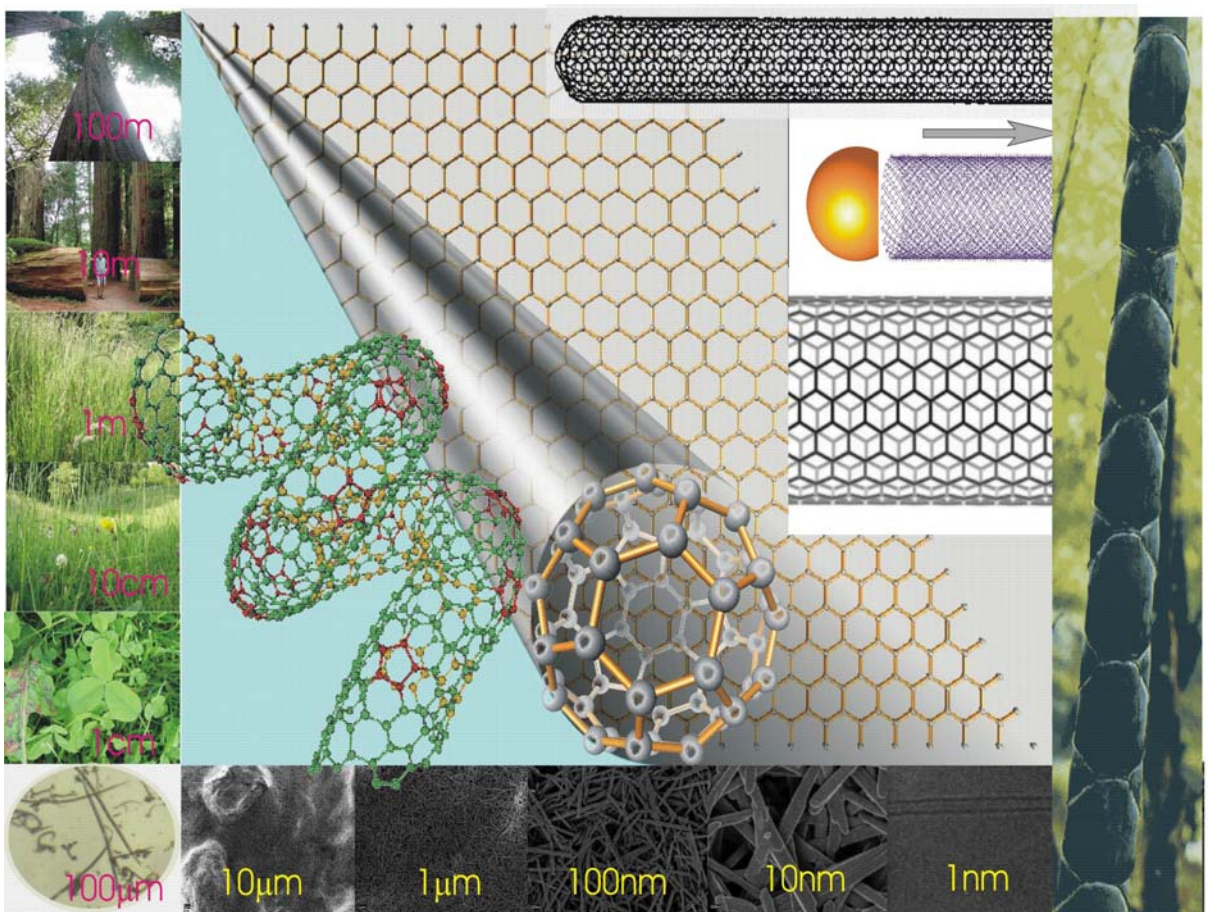
Dust mite
200 µm
Ant
~ 3 mm
Human hair
~ 10-50 µm wide
Fly ash
~ 10-20 µm
Red blood cells with white cell
~ 2-5 µm
~10 nm diameter
ATP synthase
DNA
~2-12 nm diameter
Atoms of silicon
spacing ~tenths of nm
The Microworld
The Nanoworld
1 cm
10 mm
1,000,000 nanometers = 1 millimeter (mm)
0.1 mm
100 µm
0.01 mm
10 µm
1,000 nanometers = 1 micrometer (µm)
0.1 µm
100 nm
0.01 µm
10 nm
1 nanometer (nm)
0.1 nm
Microwave
Infrared
Visible
Ultraviolet
Soft X-ray
Head of a pin
1-2 mm
Micro Electro Mechanical devices
10 - 100 µm wide
Red blood cells
Pollen grain
Zone plate x-ray "lens"
Outermost ring spacing
~35 nm
Nanotube electrode
Nanotube transistor
Quantum corral of 48 iron atoms on copper surface positioned one at a time with an STM tip
Corral diameter 14 nm
21st Century Challenge
Carbon nanotube
~2 nm diameter


100m
10m
1m
10cm
1cm
100µm
10µm
1µm
100nm
10nm
1nm

Nano World ➔

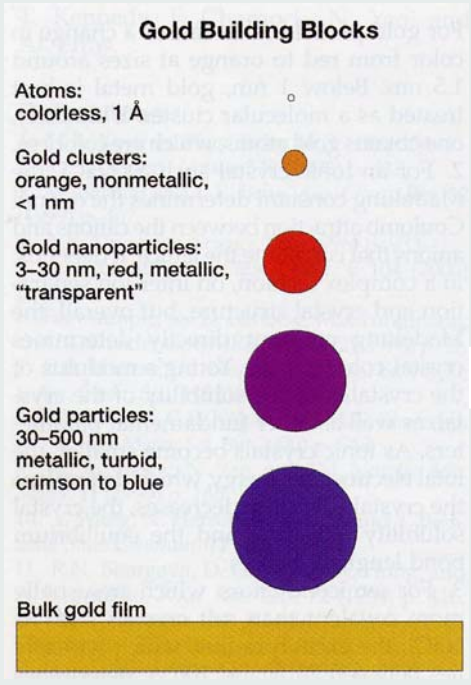
part of colloid world

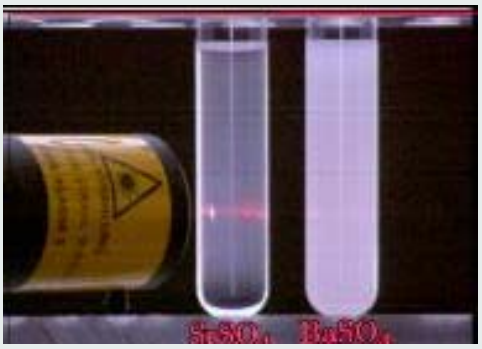
1 - 100 nm

Gebiet definierter Größenordnung	Heterogene Systeme Grobe Diskonti-nuitäten	**Kolloide: 1 nm - 500 nm**	Homogene Systeme kleine Moleküle Ionen
Beispiel	Makroemulsionen, Dispersionen	Metallsole, Biokolloide, geknäuelte Makromoleküle Mizellen, Mikroemulsionen	Wasser, Benzen, La^{3+}
Optische Auflösungs-bereiche	Lupe → Mikroskop	→ Ultra-mikroskop → Elektronen-mikroskop	
Dimensionen	cm 10^{-1}	10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8}	
	1 mm	100 µm 10 µm 1 µm 100 nm 10 nm 1nm 1 Å	

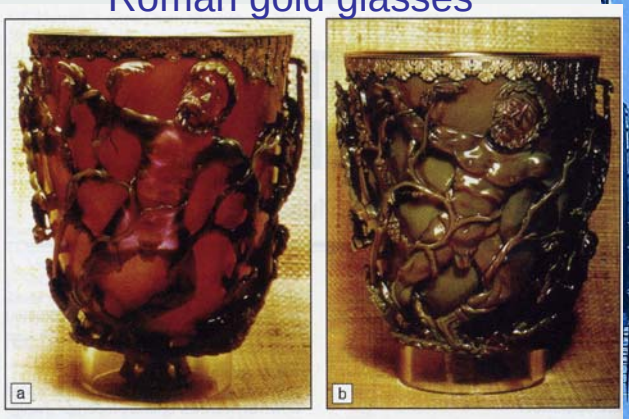
Abb. 1-1 Abgrenzung der Dimension des kolloiddispersen Zustandes von den Dimensionen kleinerer Moleküle und grober Diskontinuitäten.

Colloids



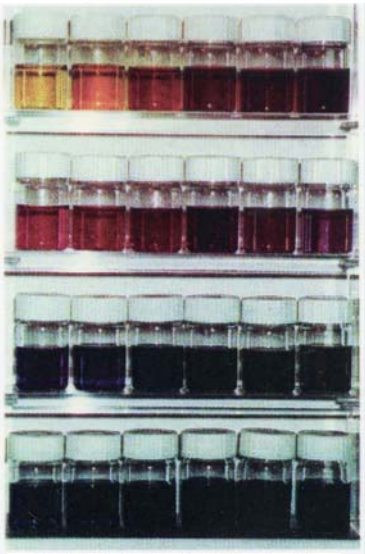


Roman gold glasses

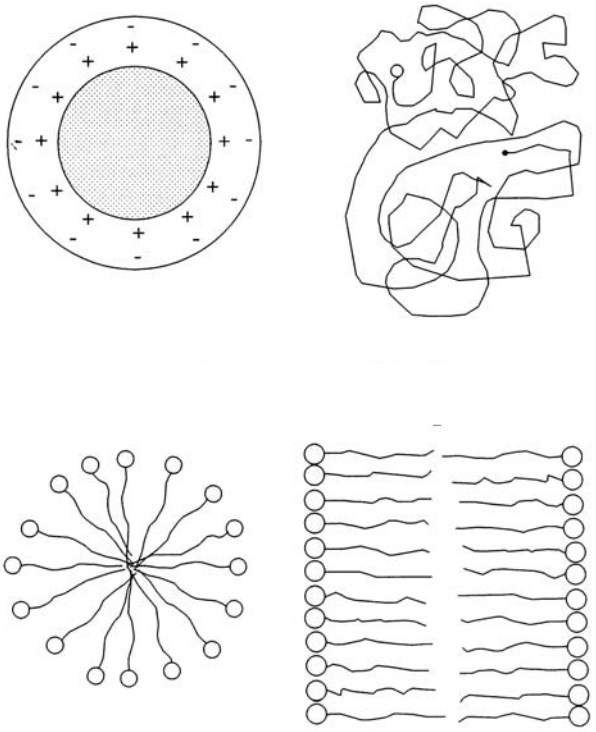


Colloids

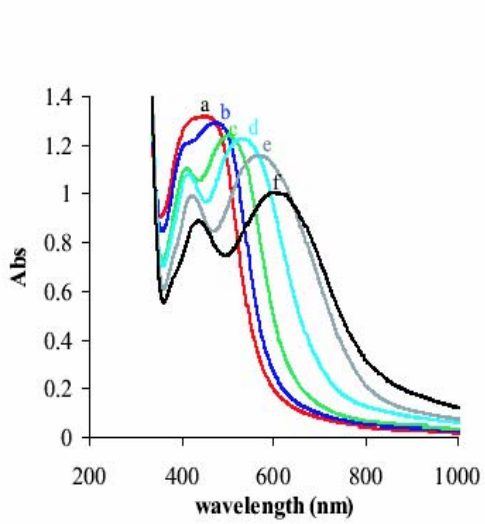
M. Faraday:
Reduktion von Goldsalzen $[AuCl_4]^-$
3-30 nm
(Phil. Trans. Roy. Soc. 1857)



Gold-Kolloide in Polystyrol-sulfonat-Mikrogelen
(M. Antonietti et al. Angew. Chem. 1997)



Size-dependent Properties



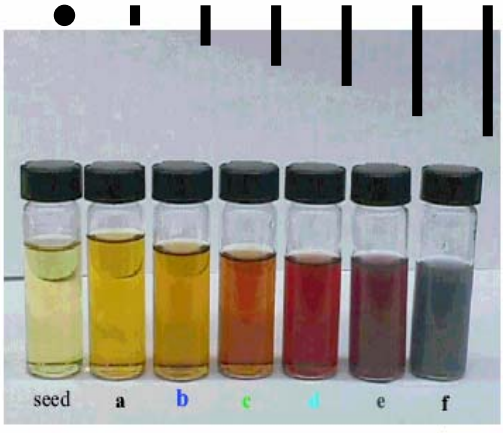
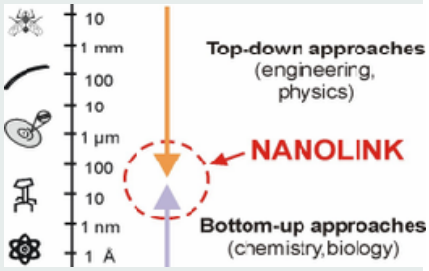
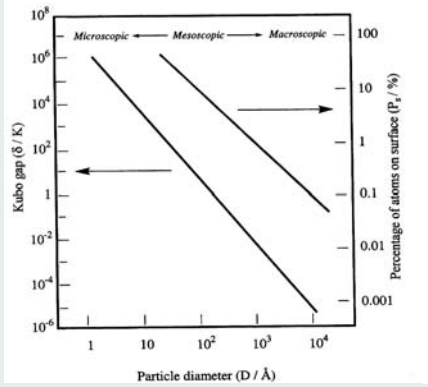


Fig. 1. Aqueous solutions of silver nanoparticles show a beautiful variation in visible color depending on the aspect ratio of the suspended nanoparticles: far left in the photograph, silver nanospheres 4 nm in diameter that are used as seeds in subsequent reactions; a–f) silver nanorods of aspect ratio 1–10. The corresponding visible absorption spectra for (a)–(f) are also shown.

Ways to the Nano World





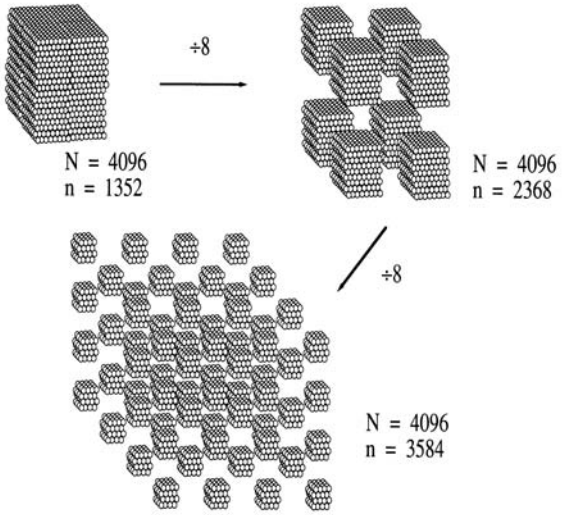
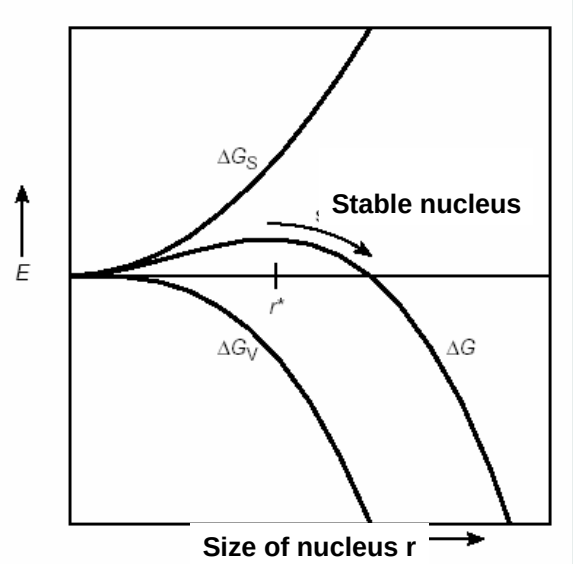
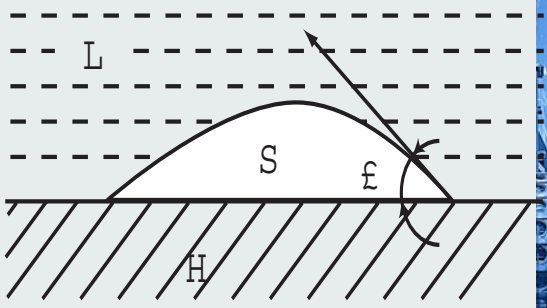


Figure 6-1. Surface statistical consequences of the subdividing of a cube with 16 atoms on a side. N = total atoms; n = surface atoms. The structural, electronic, and chemical consequences of the presence of a high proportion of surface and near-surface atoms predominate in the more highly dispersed material.

Bottom up to Nano

Nucleation processes

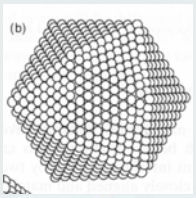




Nanoparticles and Size Effects

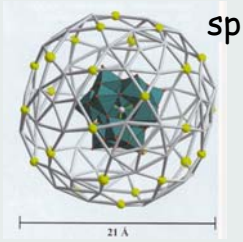
Size :	1 –100 nm
Surface to volume ratio :	critical
optical properties :	f(size)
magnetism :	f(size)
electronic properties :	f(size)
cooperative properties :	f(size)

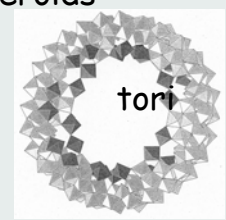
integration density of functions : very large



clusters

hollow spheroids





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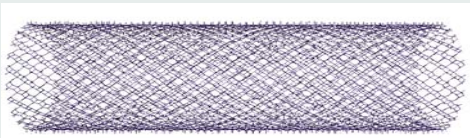


tubes

Nano Particles

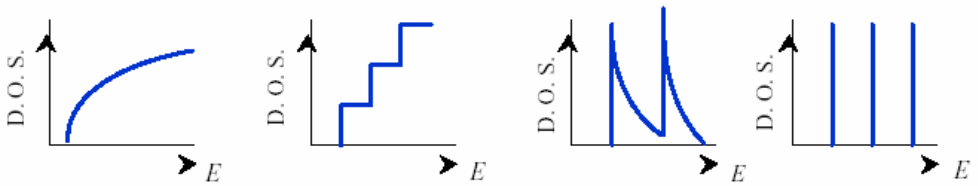
Tab. 1.1. Examples of nanomaterials.

	Size (approx.)	*Materials*
Nanocrystals and clusters (quantum dots)	diam. 1–10 nm	Metals, semiconductors, magnetic materials
Other nanoparticles	diam. 1–100 nm	Ceramic oxides
Nanowires	diam. 1–100 nm	Metals, semiconductors, oxides, sulfides, nitrides
Nanotubes	diam. 1–100 nm	Carbon, layered metal chalcogenides
Nanoporous solids	pore diam. 0.5–10 nm	Zeolites, phosphates etc.
2-Dimensional arrays (of nano particles)	several nm2–μm2	Metals, semiconductors, magnetic materials
Surfaces and thin films	thickness 1–1000 nm	A variety of materials
3-Dimensional structures (superlattices)	Several nm in the three dimensions	Metals, semiconductors, magnetic materials

Electrons and Dimensions

- Nanostructures (< 30 nm) have become an exciting research field
  - New physics phenomena affect physical properties
  - Unusual quantum effects and structural properties
  - Promising applications in optics, electronics, thermoelectric, magnetic storage, NEMS (nano-electro-mechanical systems)

- Low-dimensional systems are realized by creating nanostructures that are quantum confined in one or more directions



Examples: Nano-Silicon

The powders obtained as described above were dispersed in methanol using mild sonication, then etched with solutions of 0.5–4% HF and 20–30% HNO3 in water to reduce the particle size and passivate the particle surface. Acid solutions were prepared from 49 to 51 wt% HF, 70% HNO3, and DI water in the necessary proportions. After etching, the particles were collected on polymeric membrane filters and washed with water and methanol.

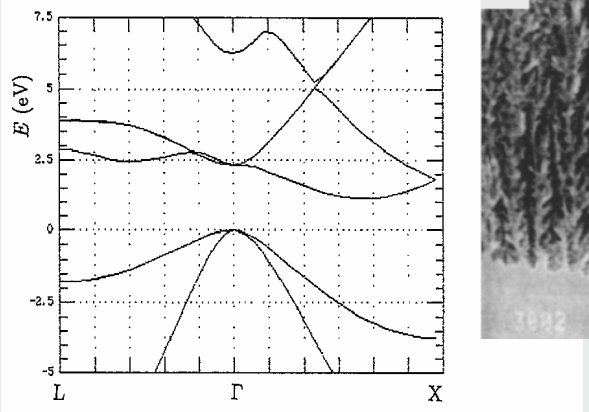
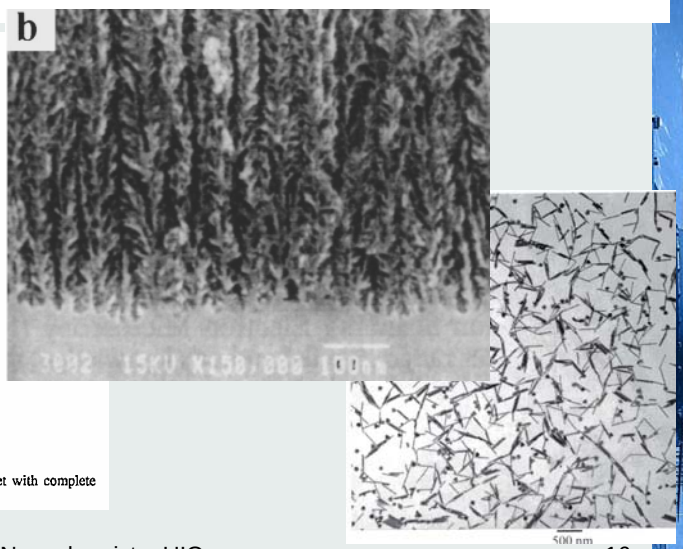


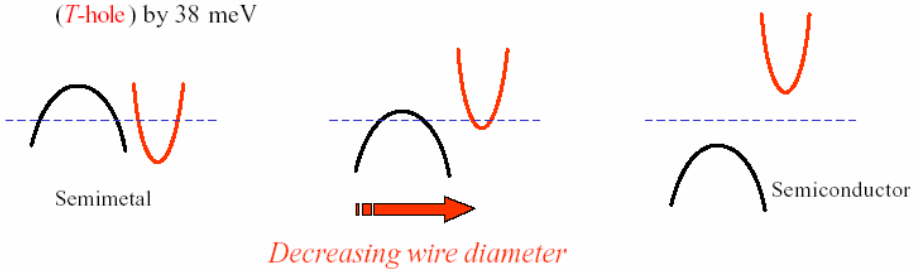
Figure 3. The band structure of silicon calculated with a (3s, 3p, 3d) basis set with complete configuration self-consistency.



The Nano World

Quantum Confinement Produces New Materials Classes

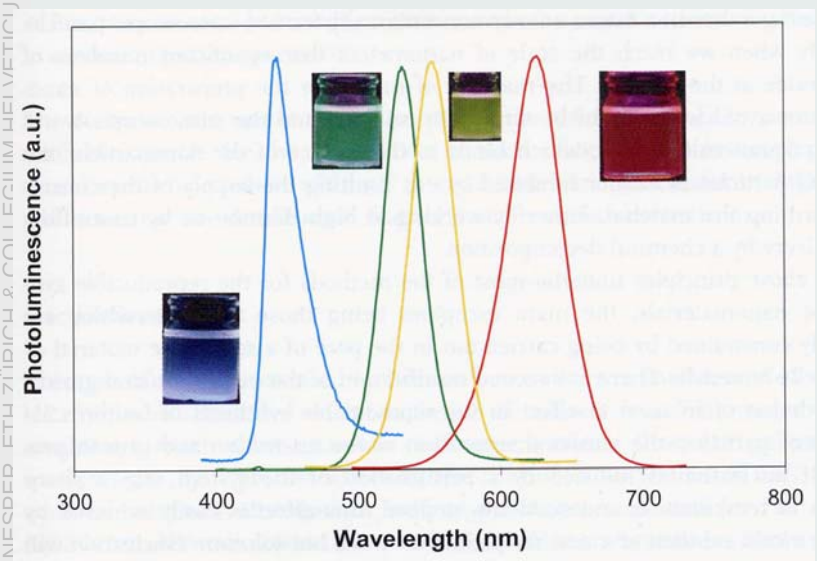
- Bi
  - Group V element
  - Semimetal in bulk form
  - The conduction band (*L*-electron) overlaps with the valence band (*T*-hole) by 38 meV
- Bi nanowire
  - Semimetal-semiconductor transition at a wire diameter about 50 nm due to quantum confinement effects

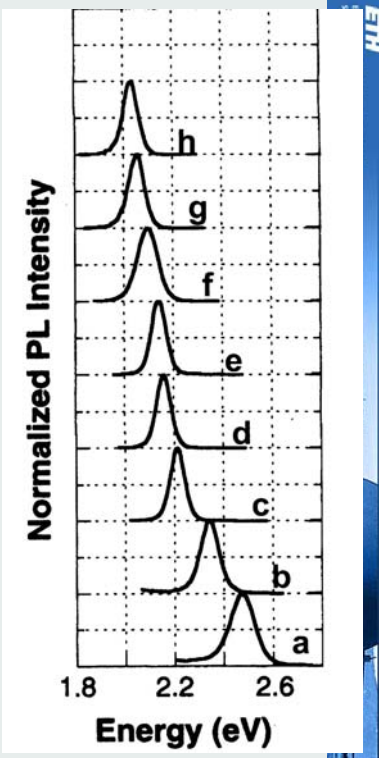


Decreasing wire diameter

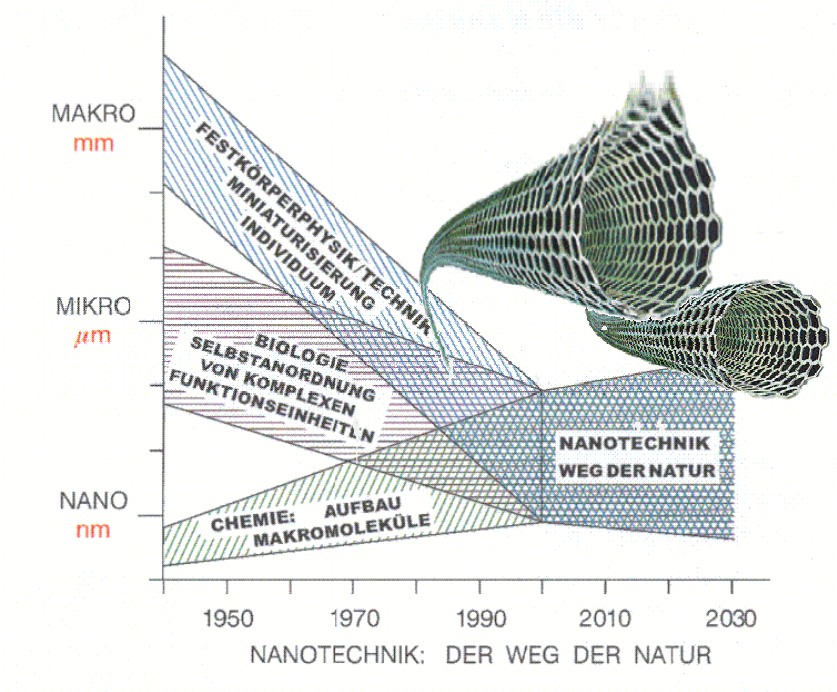
Semimetal-Semiconductor Transition

Size of Nano Particles and Luminescence





Nanotechnology



Development of Nanotechnology

Current applications	1-5 Years	6-10 Years	10– 30Years
Cosmetics	• Security application	• Flat panel displays	• light emitting diodes
Self-cleaning windows	• Luminescent probes in biological screening applications	• Solar cells	• Single electron devices
Pigments	• Bar coding	• Date storage	• quantum computing
Stained glass windows	• Chemical\biological sensors		
Sunscreen	• Coloured lighting		

Nanotechnology – quo vadis?

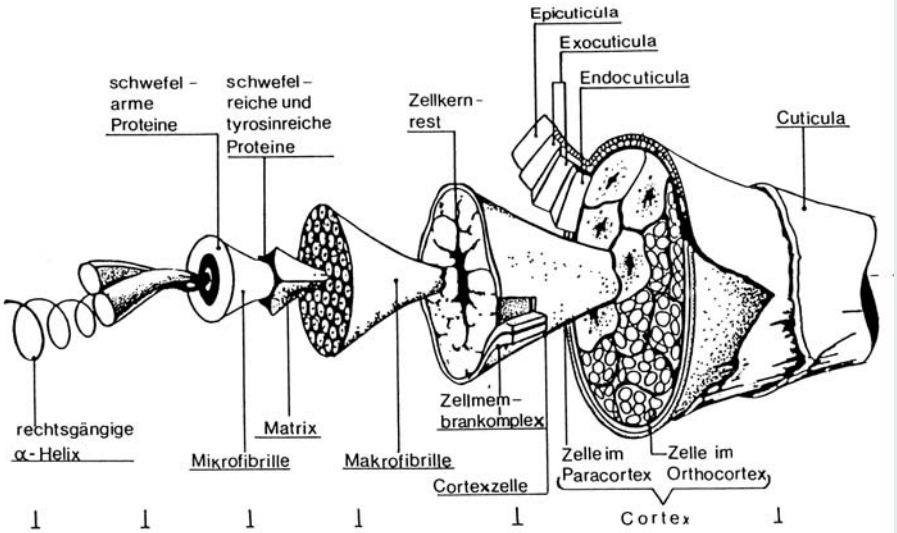


Abb. 2:12 Der Aufbau der Wollfaser aus anderer Perspektive: Hierarchie einer feinen Merinowollfaser (mit freundlicher Genehmigung der Division of Protein Chemistry C.S.I.R.O Parkville, Victoria)