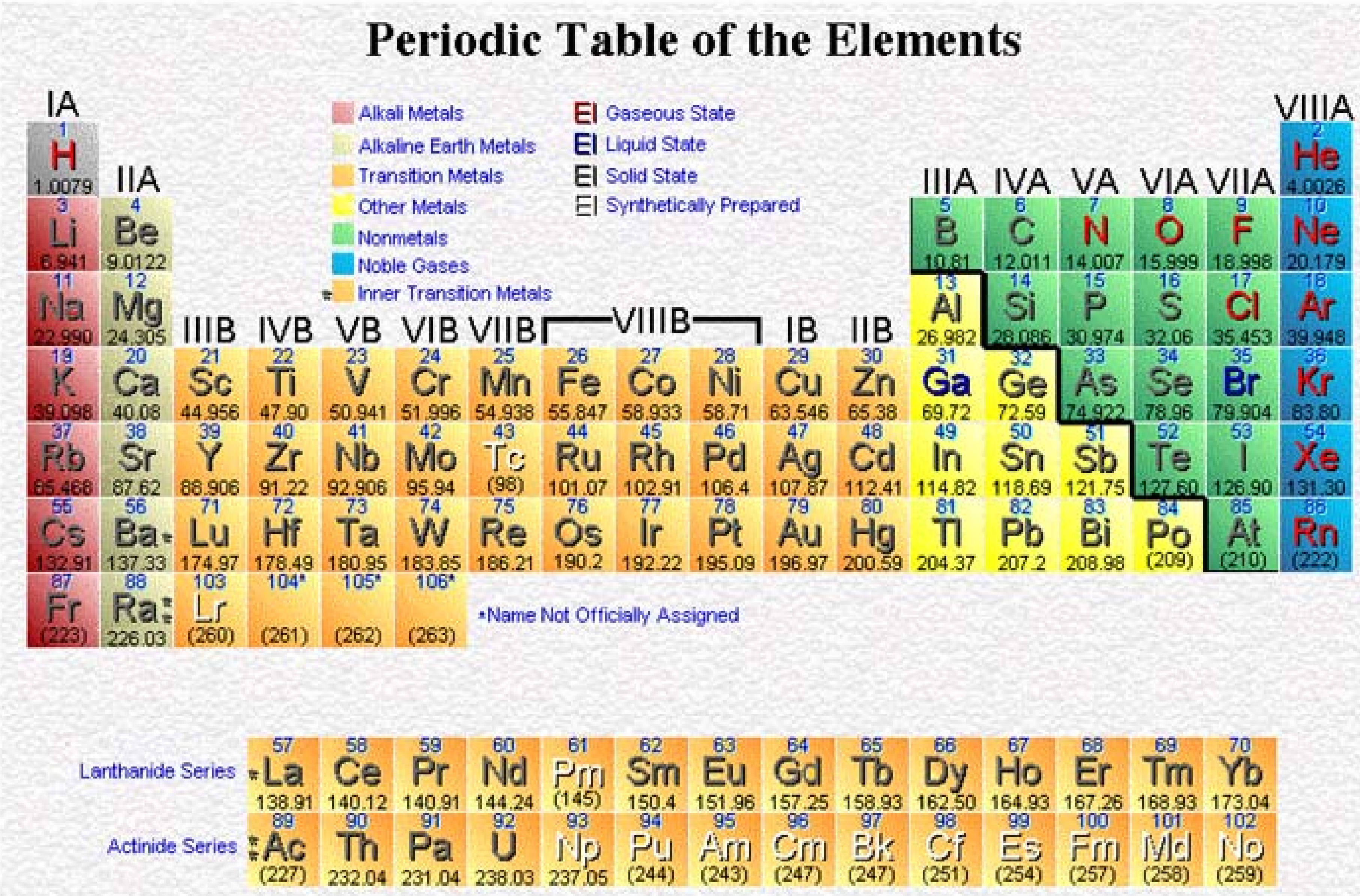
Nanomaterials

- Colloids
- Clusters
- Nanoparticles

- Dimensions
- Properties
- Synthesis
- Applications

Physical-chemical properties

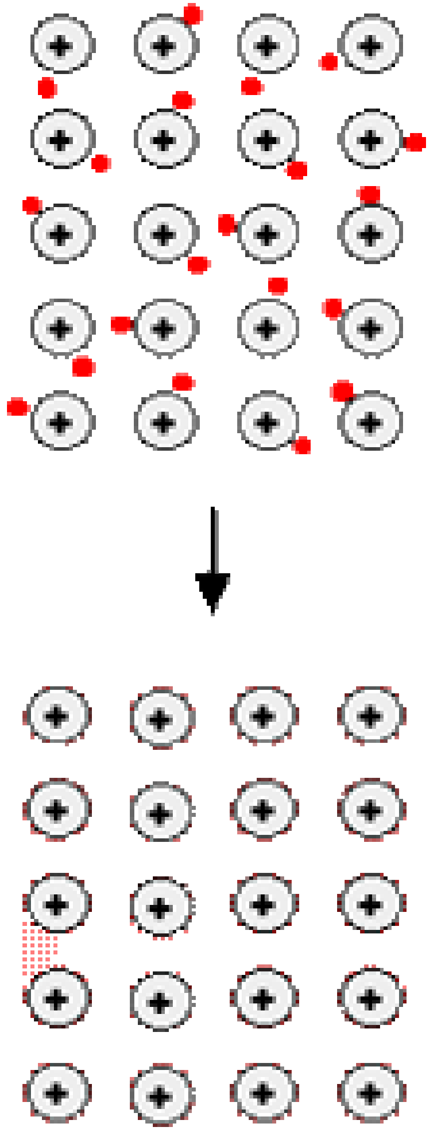


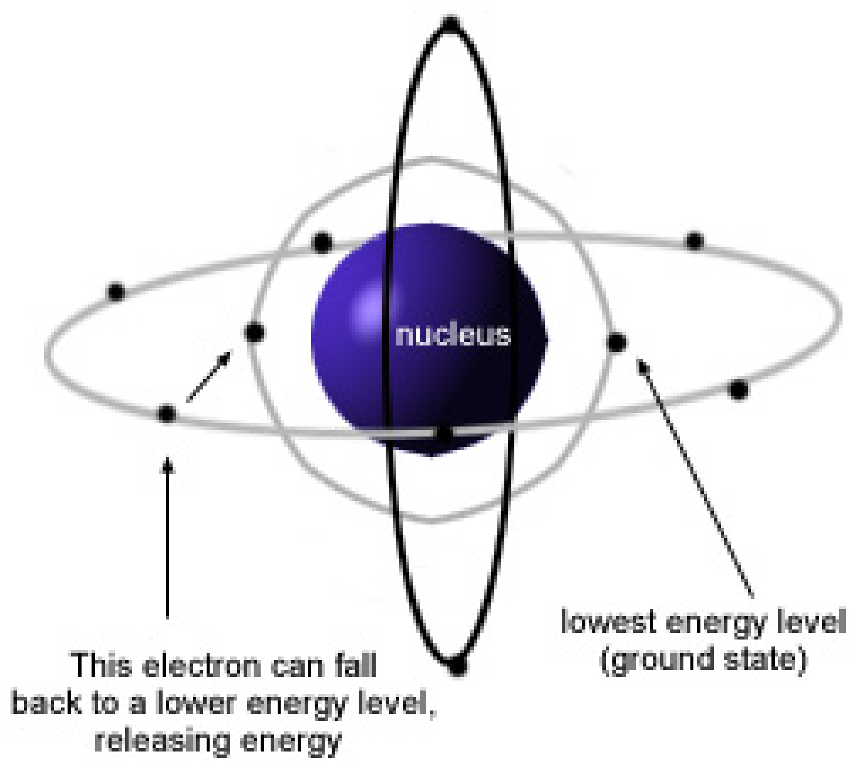
Cluster classification

- Metal: Pt, Fe…
- Covalent: C, Si…
- Ionic: CaI_2
- Hydrogen bonding: HF
- Molecule: As_4
- Van-der-Waals: He, H_2

Metallic bond

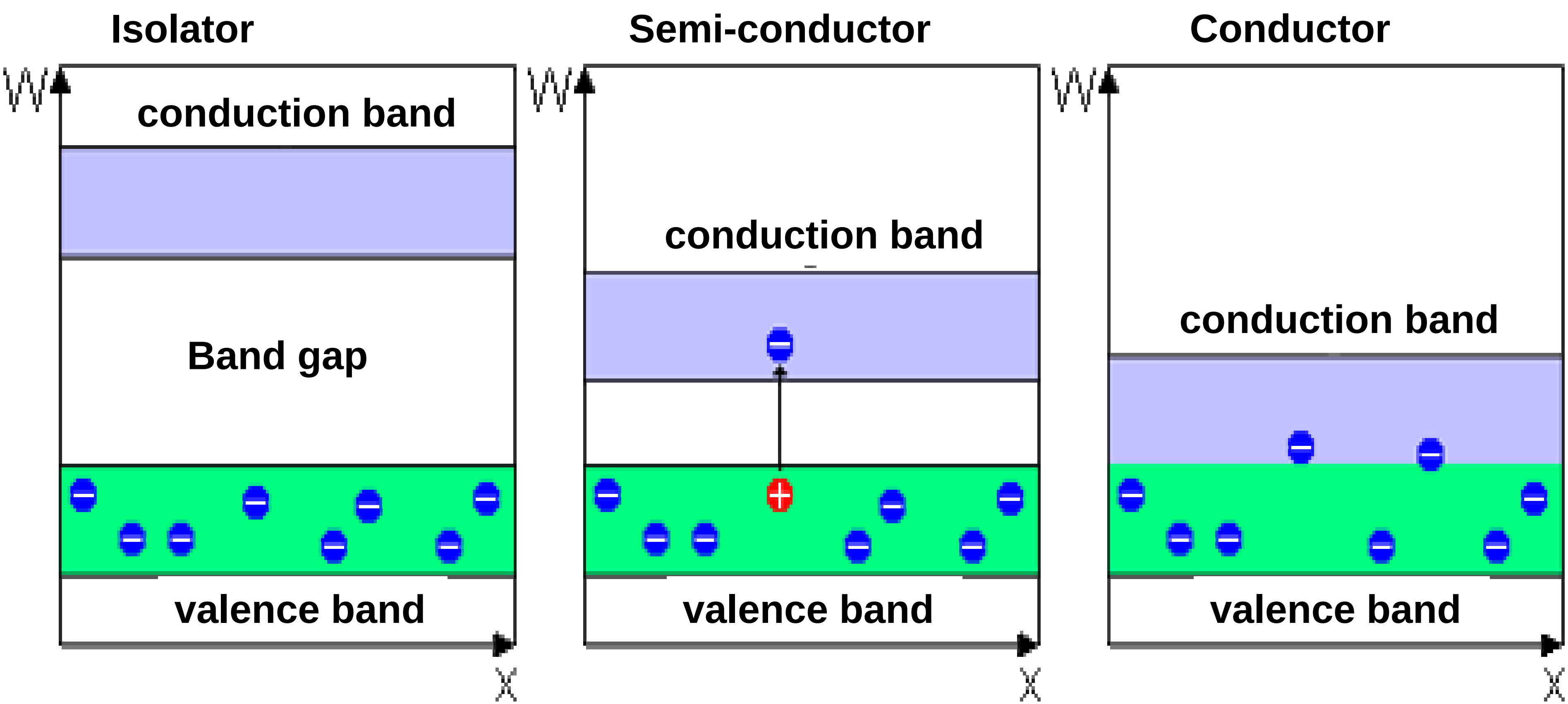
- Electron delocalization



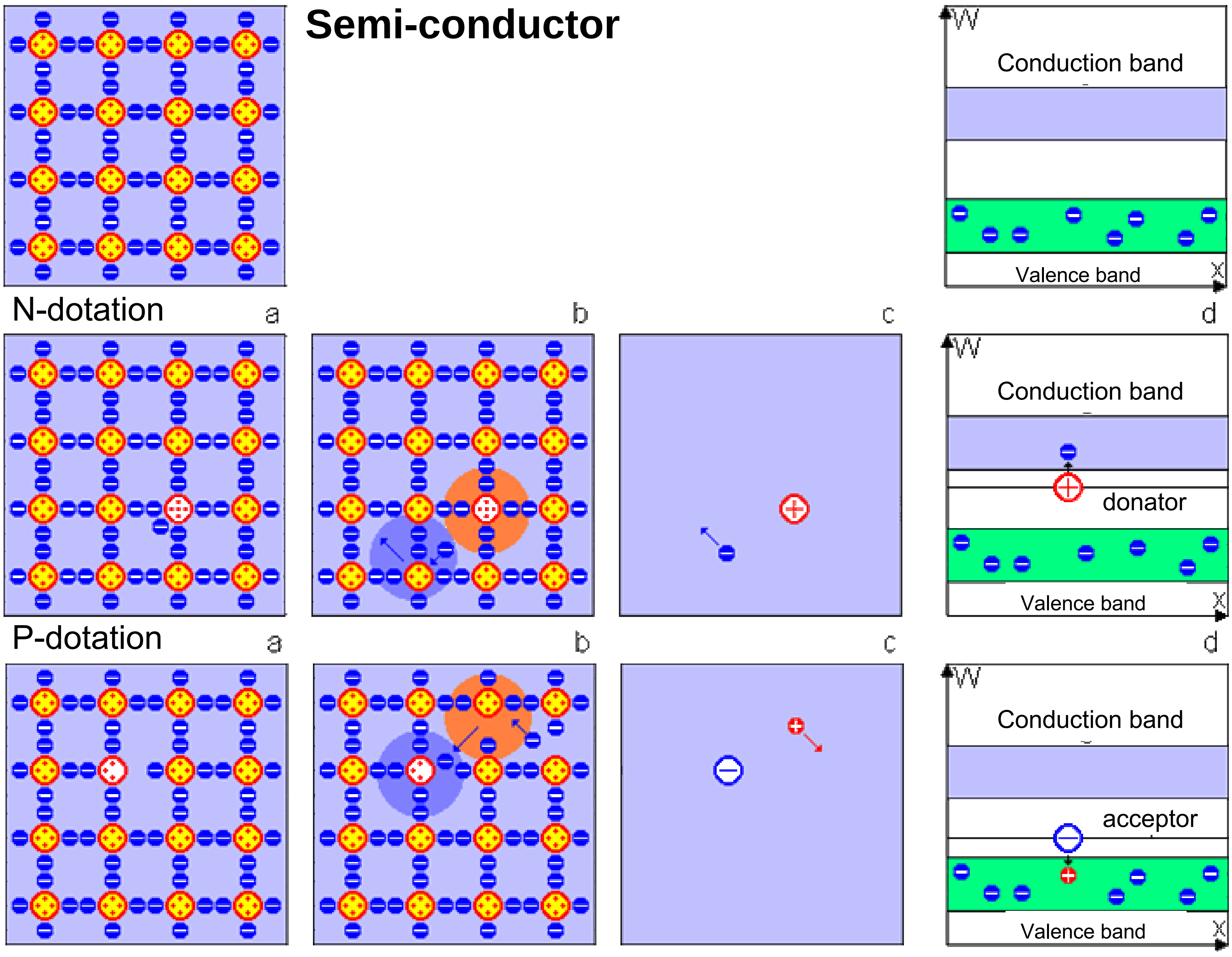


Band model

- Energy levels



Semi-conductors

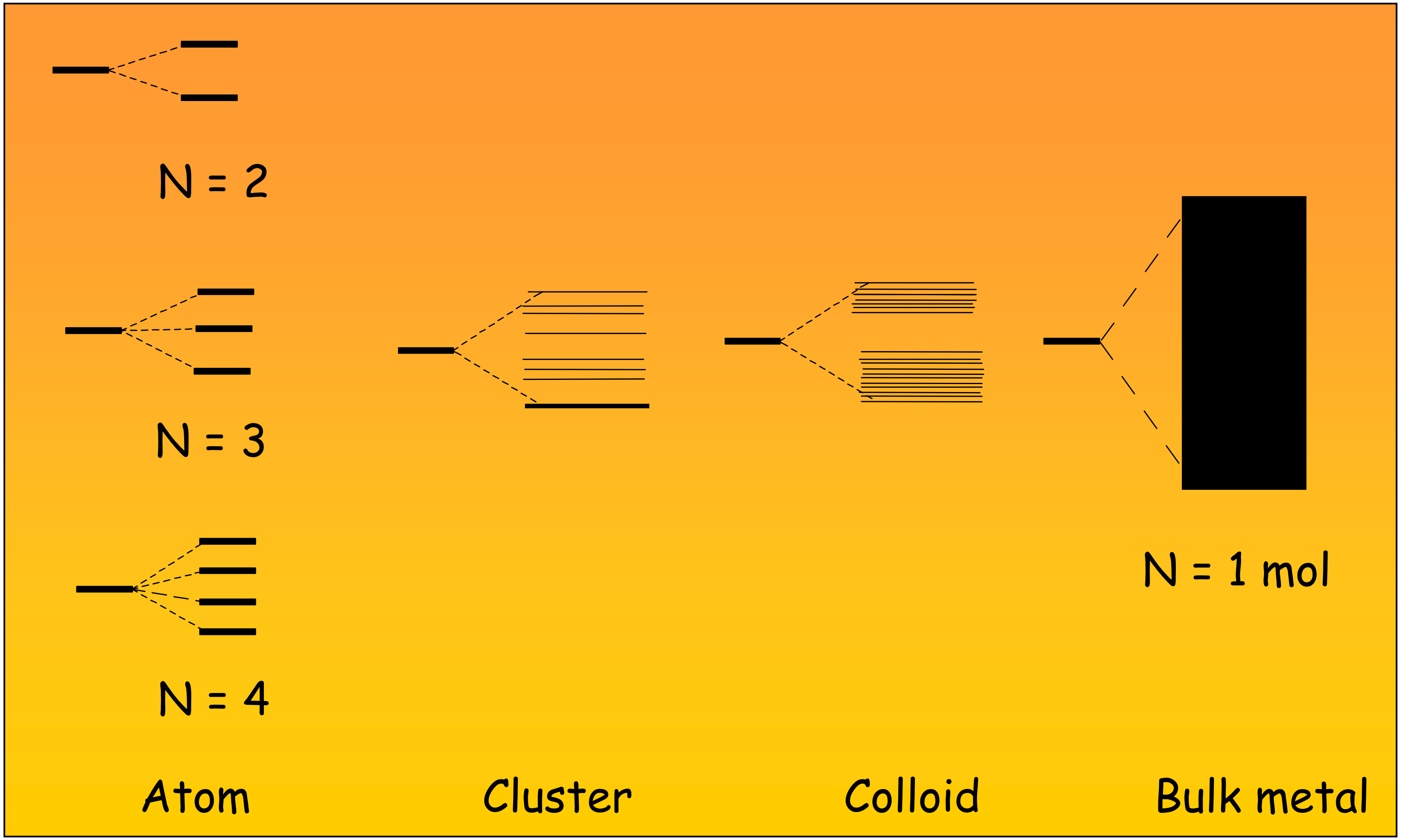


Band theory of metals

- Changing electron levels

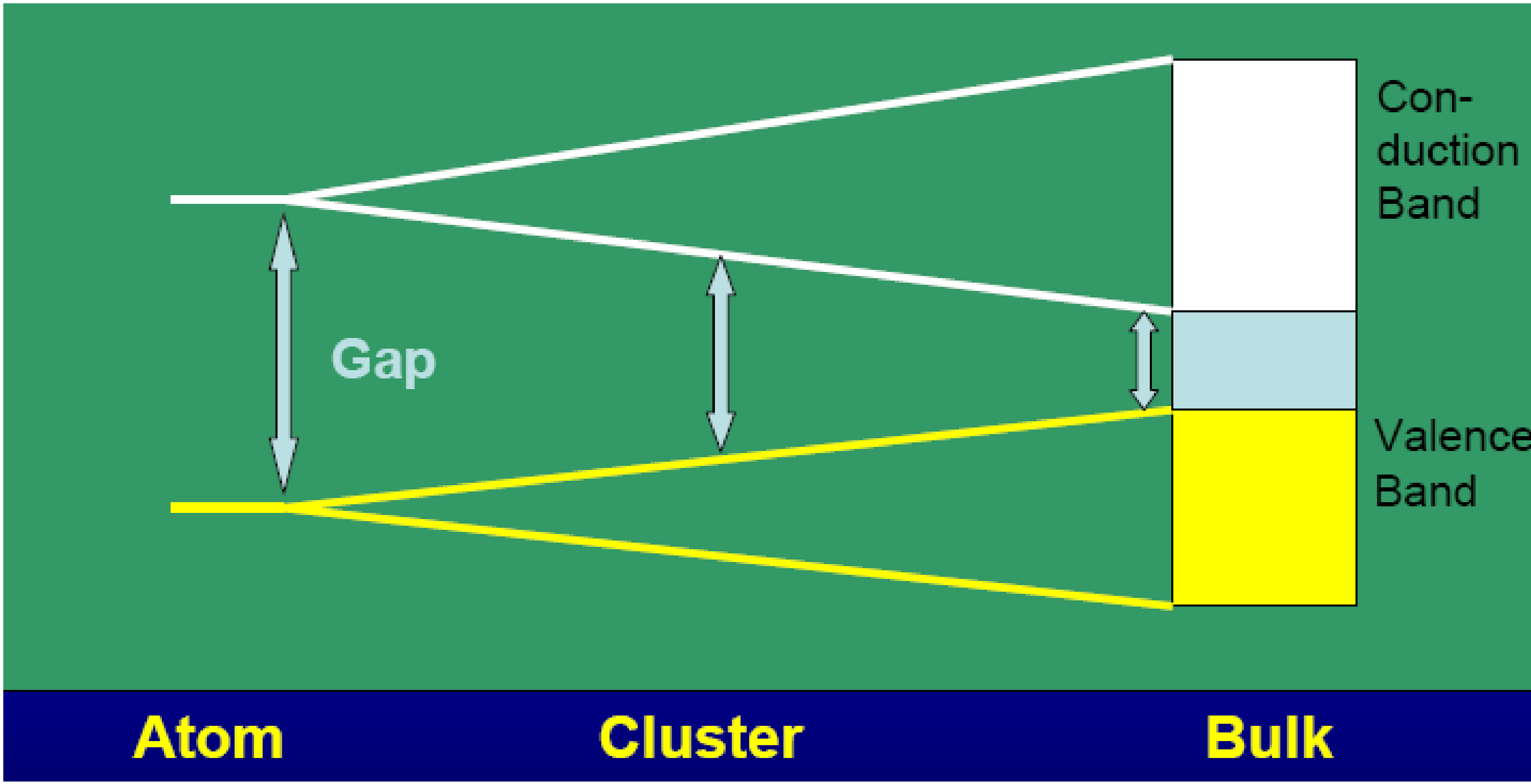
  → changed optical, electronic and catalytic properties

- Properties different from the bulk metal and molecular structures

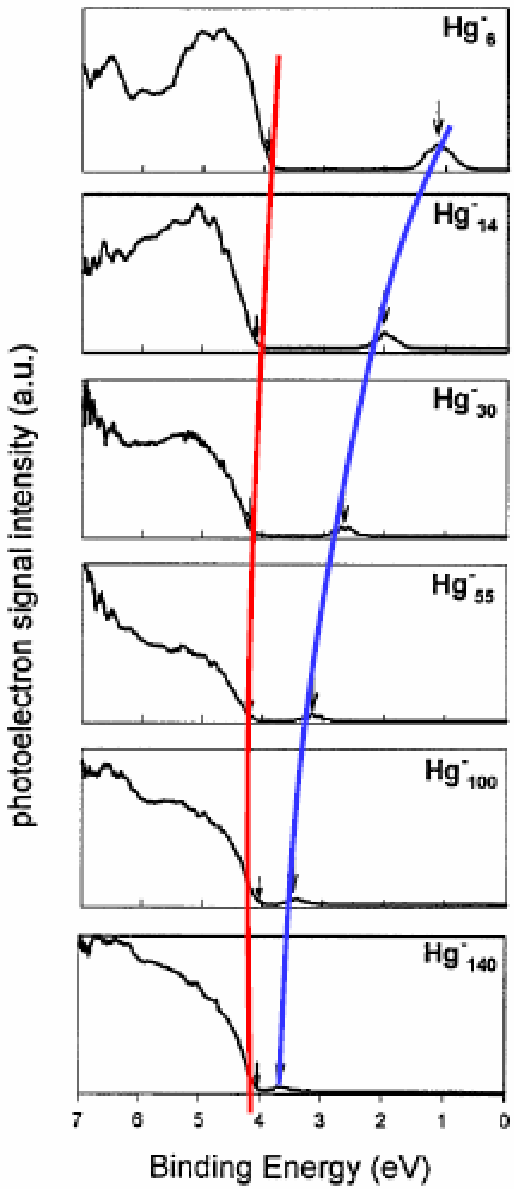


Band gap

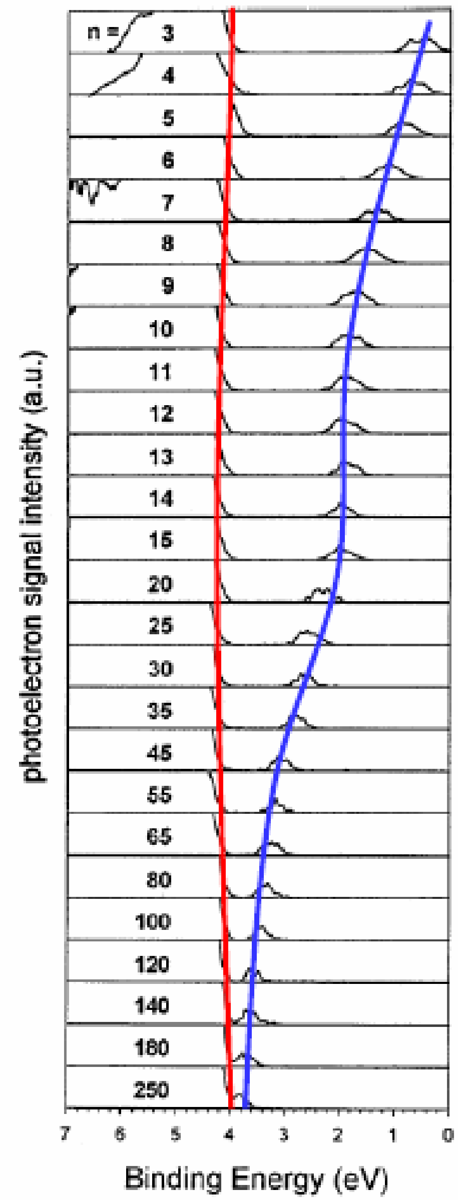
Changing metallic properties



Band Affiliation

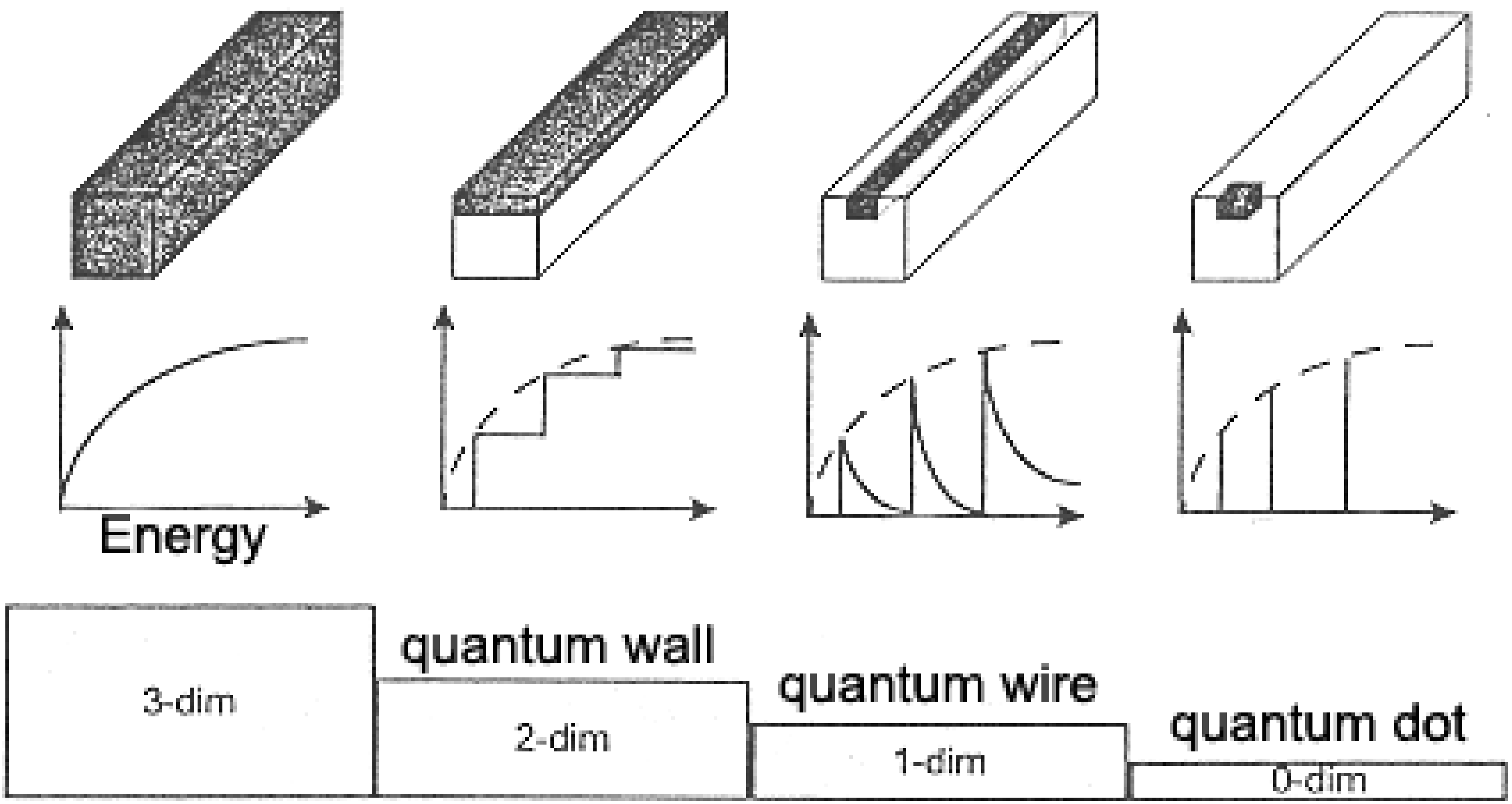


Photoelectronspectra of Hg^{-}:
6s 6p affiliation



Quantum size effect

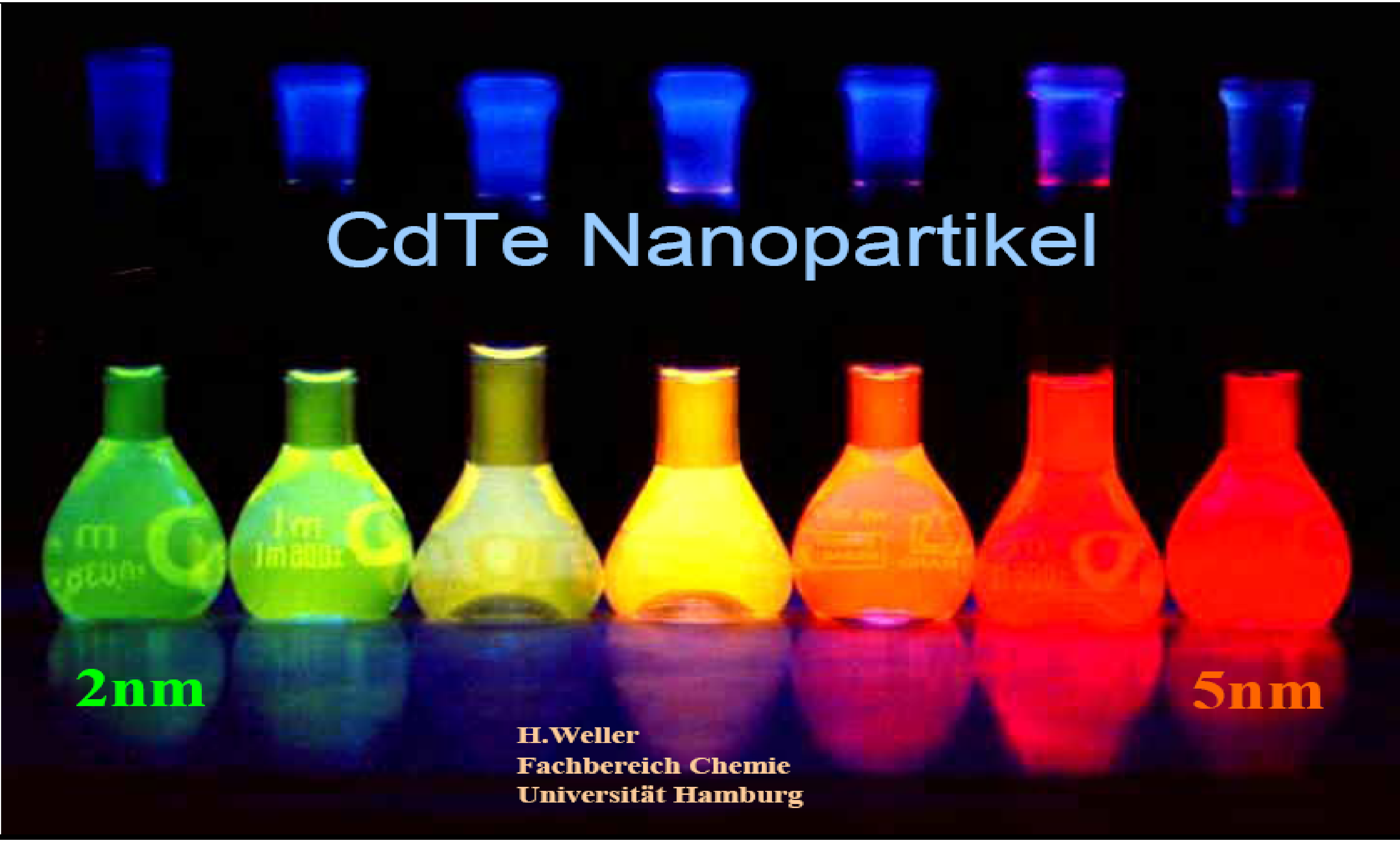
- Change of the electronic properties
- De Broglie wavelength: the freely mobile electrons are very limited in the reduced dimension



"Size Induced Metal-Insulator Transition"

Semiconductor

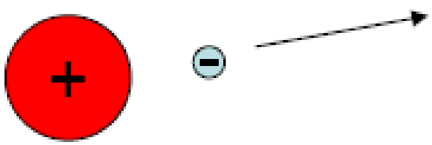
- Band gap controllable



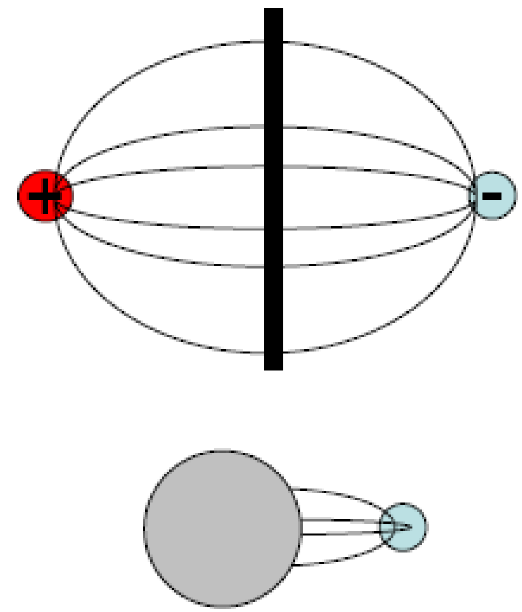
Ionization Potentials and Electron Affinities

IP: $X_n \rightarrow X_n^+ + e^-$

EA: $X_n + e^- \rightarrow X_n^-$



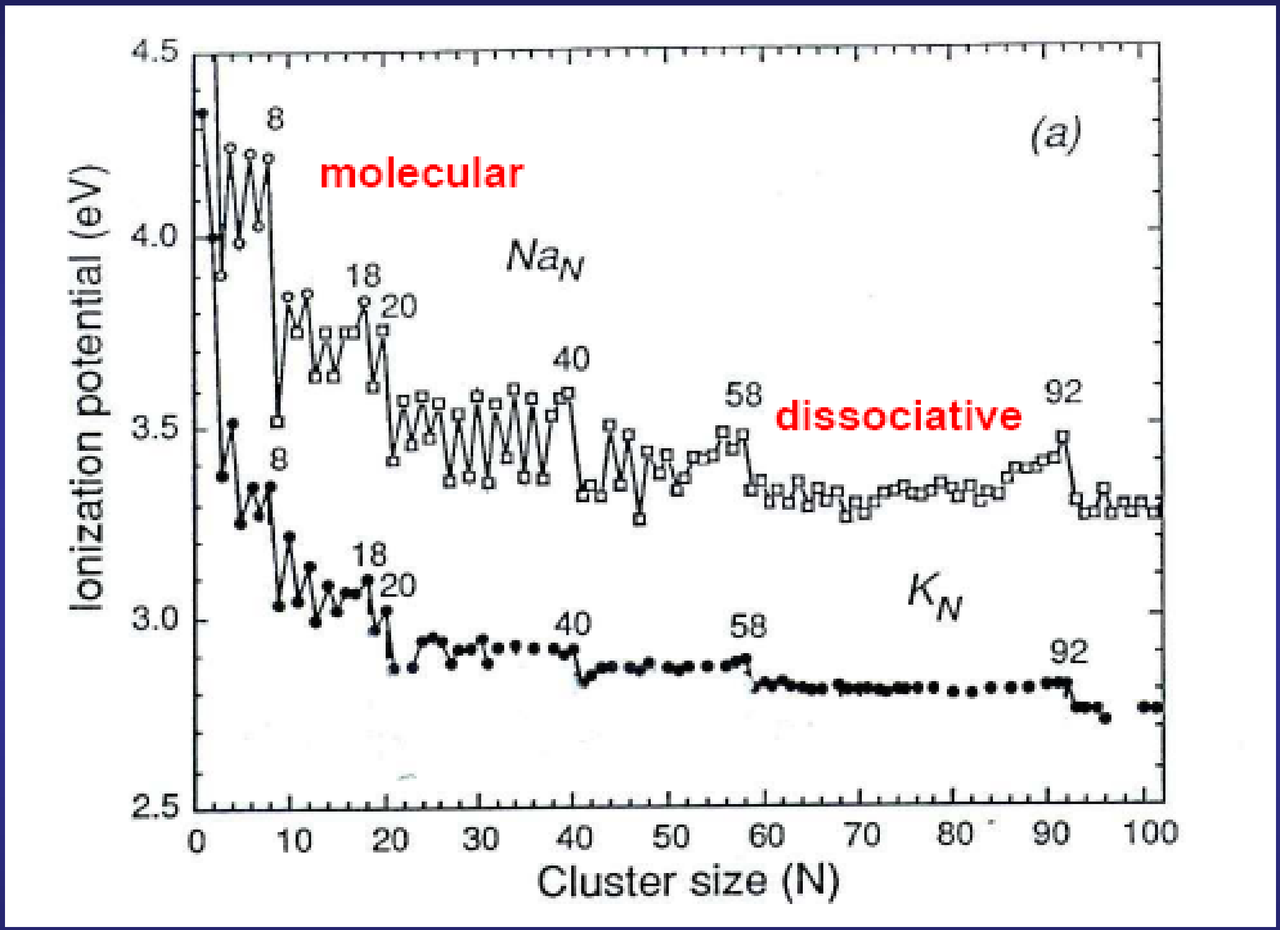
The bigger radius the less energy is necessary to remove an electron



EA is decreasing with the radius (less surface for a small cluster)

~ Electron delocalization

Ionization Potentials for Na and K



W.A.de Heer
Rev.Mod.Phys. 65, 611 (1993)

For all materials: IP (Atom) -> WF (bulk)

Hydrogen Storage

Low IP:
- H_2 dissociates
- Hydrid formation

High IP:
- Molecular chemisorption
- Hydrogen storage!!!

Transition from molecular to dissociative chemisorption

VOLUME 54, NUMBER 14 PHYSICAL REVIEW LETTERS 8 APRIL 1985

Correspondence between Electron Binding Energy and Chemisorption Reactivity of Iron Clusters

R. L. Whetten, D. M. Cox, D. J. Trevor, and A. Kaldor
Corporate Research-Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801
(Received 21 November 1984)

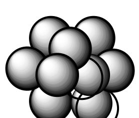
New experiments in a fast-flow reactor have uncovered a strong correlation between the reactivity of free iron clusters and cluster ionization thresholds: Clusters with low thresholds efficiently add molecular hydrogen, and the relative rates of this reaction closely follow variations in cluster-electron binding energy. This correspondence can be understood in terms of a requirement for metal-to-hydrogen charge transfer in the activation of the H_2 bond.

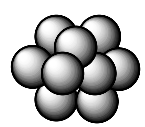
page 1494

PACS numbers: 36.40.+d

What are nanoparticles?

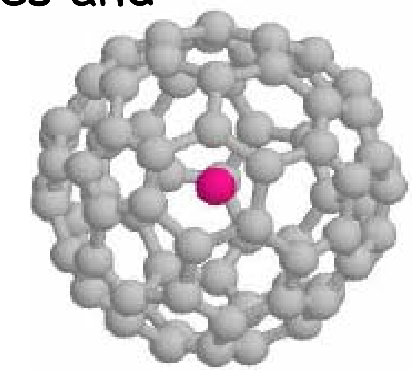
- NANO (Greek) = dwarf
- 1 nanometer = 1 nm = 10^{-9} m = 0.000000001 m
  - Some 1000 atoms or molecules
  - Cluster ≤ 1000
- Research: transition of properties from solid state to atoms
  - Different chemical and physical properties:
    - Electric conductivity
    - Chemical reactivity
    - Optical properties
- Quantum mechanic rules and not longer classical physics due to their small size
- Application in catalysis and nanoelectronics



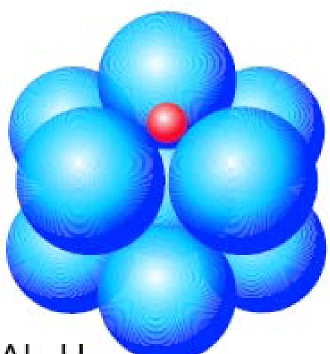


What are colloids?

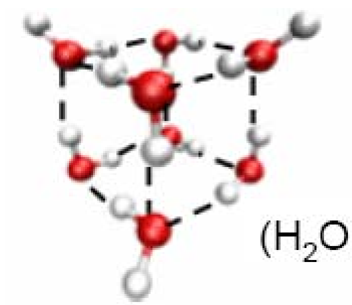
- "Colloid" (Greek: Kolla = glue) 1861 Thomas Graham
- Colloidal Systems:
  homogeneous medium and a dispersed material
- "Mesoscopic " dimension: between solid state properties and molecular effects
- Large specific surface
- New properties by functionalization and configuration



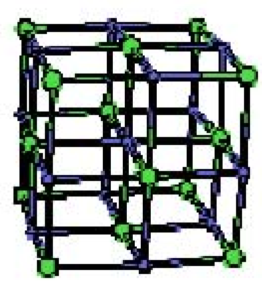
La@C_{60}



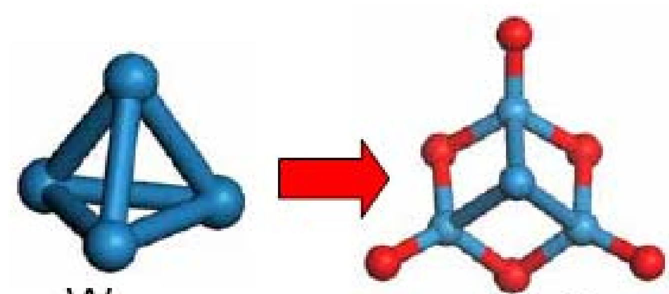
$Al_{13}H$



$(H_2O)_8$



$(NaCl)_{13}$

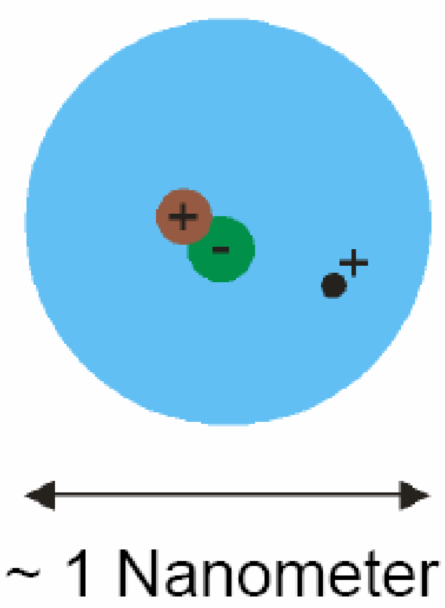


W_4 W_4O_6

Nanotube

Nanochemistry

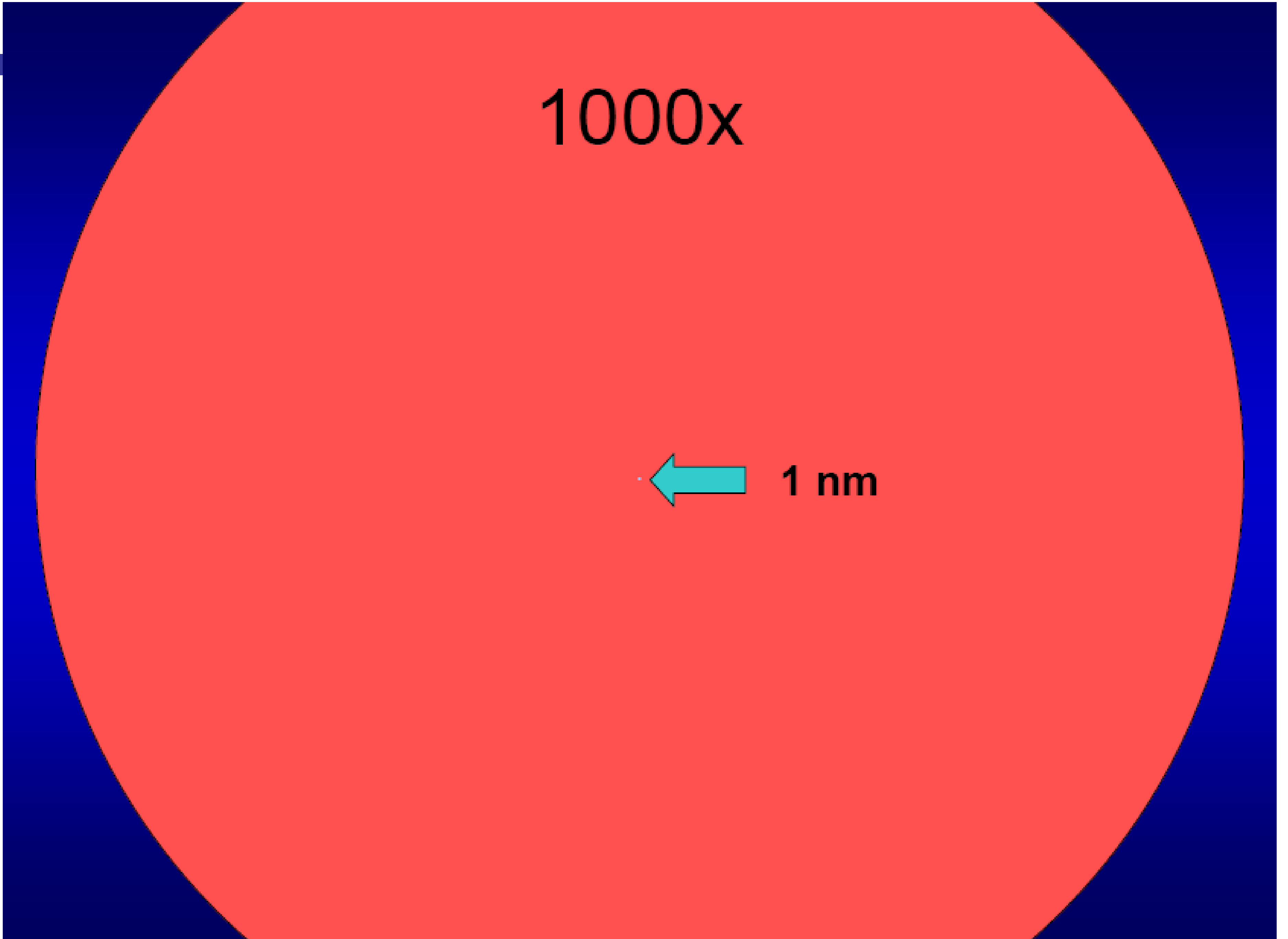
- For example: Nano-droplet
  Drop of liquid water with
  50 H_2O molecules
  Diameter = 1 nm



3.345.462.743.828.473.828.592.834

molecules

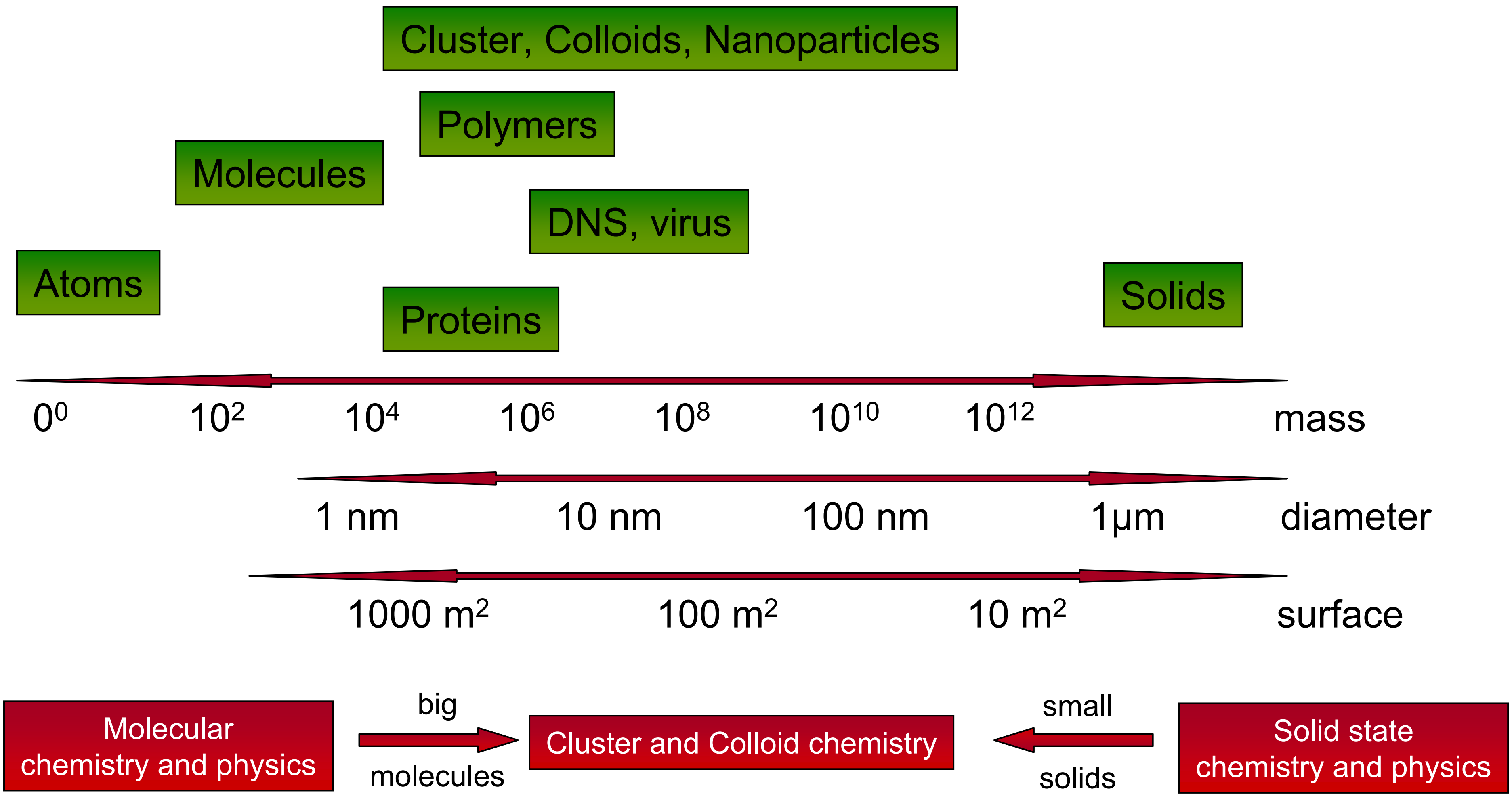
Snowflake: 1 mm


1000x
1 nm

From atoms to solids

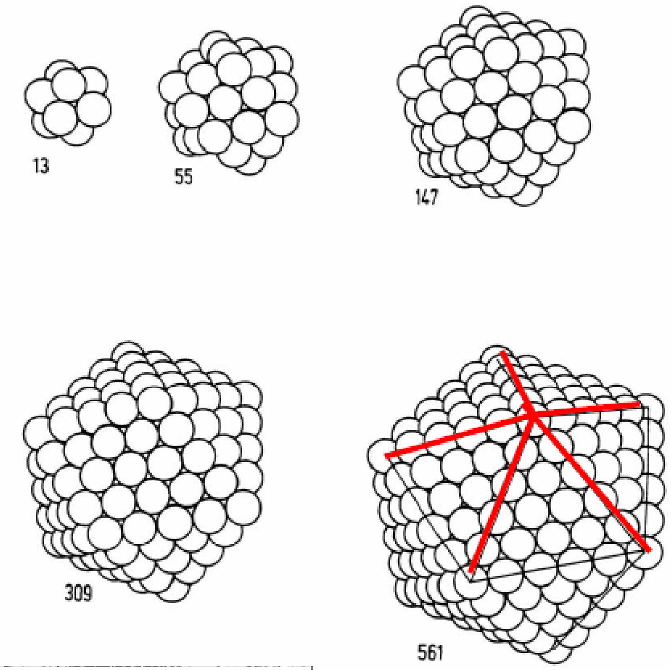
Nanometer-Scale

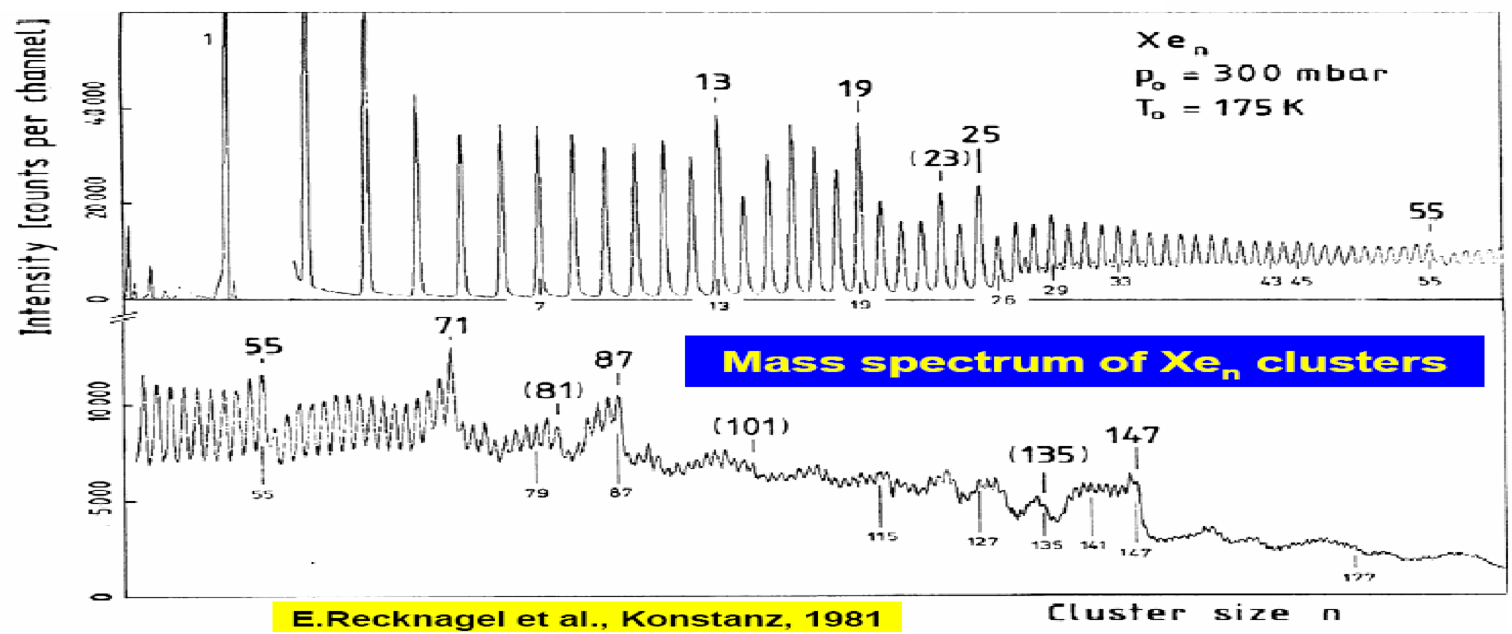
A short reminder: 1 nanometer = 1 nm = 10^{-9} m = 0.000000001 m



Rare gas clusters

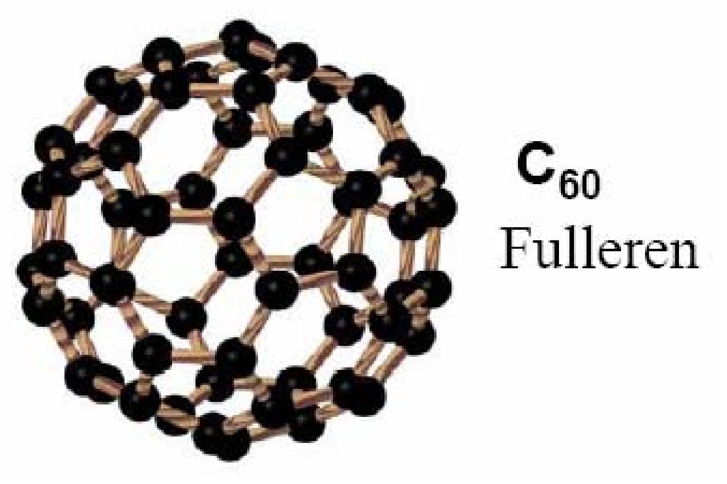
- Magic numbers of rare gas clusters in MS:
  - 13
  - 55
  - 147
  - 309
  - 561
- Geometric shell: Mackey Icosahedron
  - 5-fold symmetry axis (fcc)

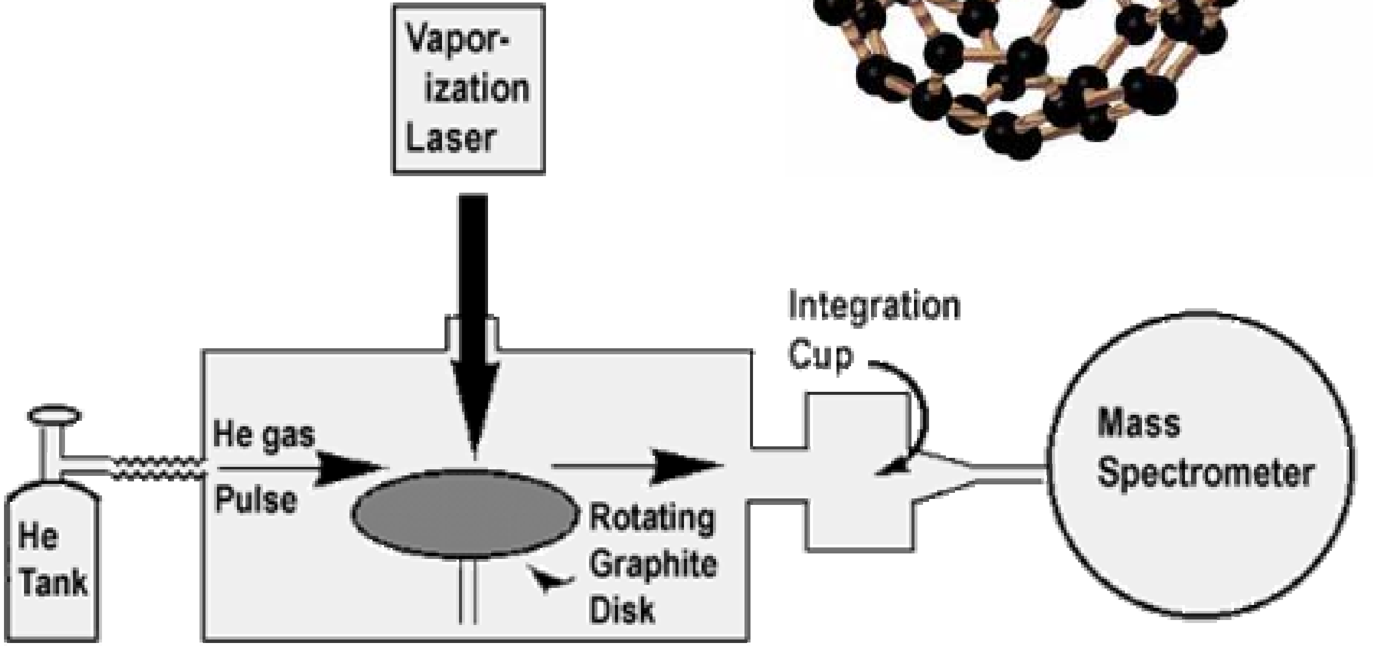


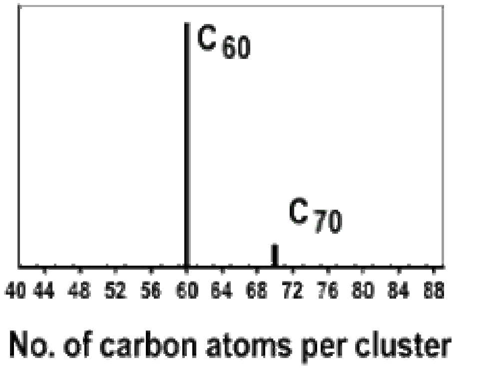


Special Nanotypes: Fullerenes

- a large current between two nearby graphite electrodes in an inert atmosphere
- the resulting carbon plasma arc between the electrodes cools into sooty residue from which many fullerenes can be isolated

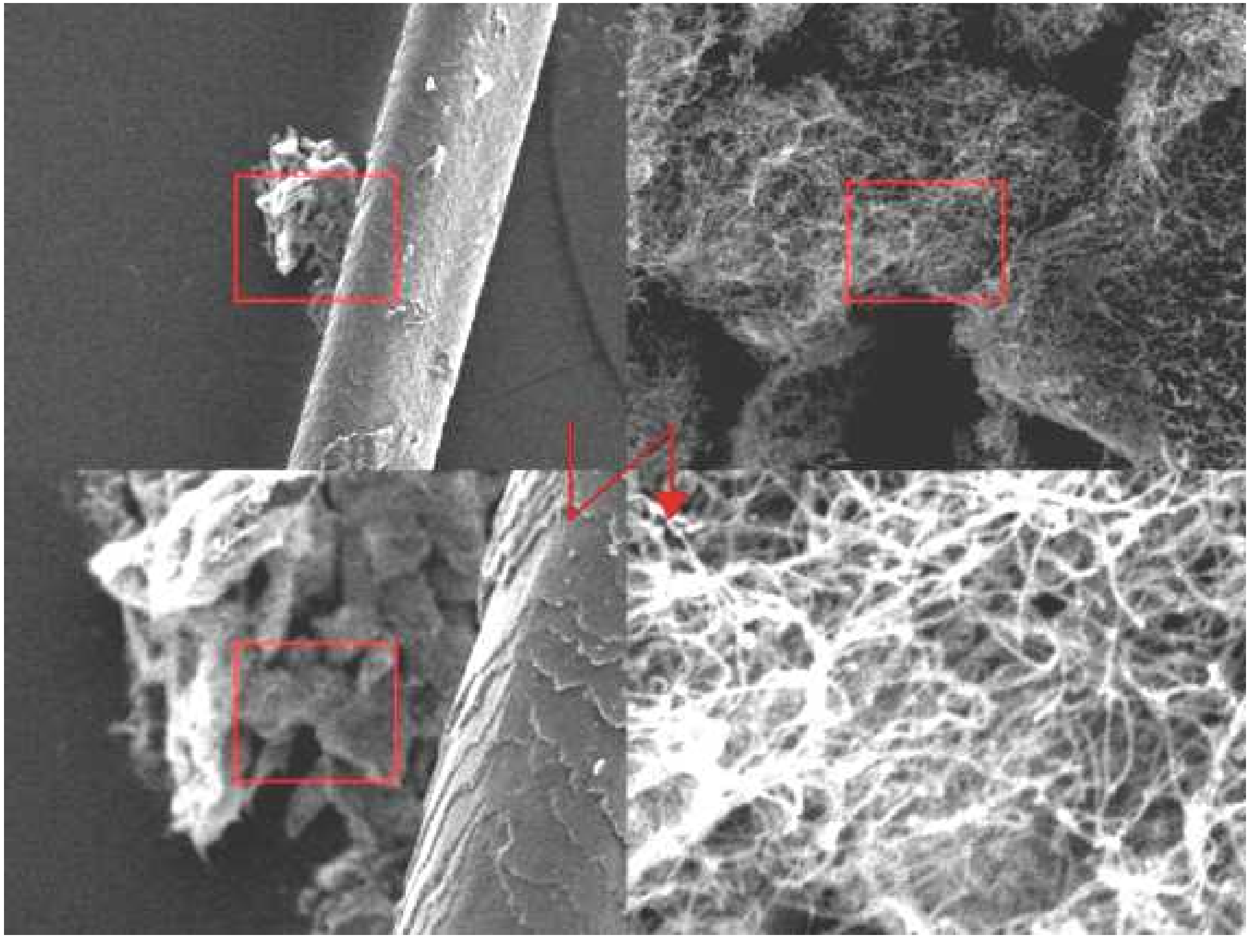


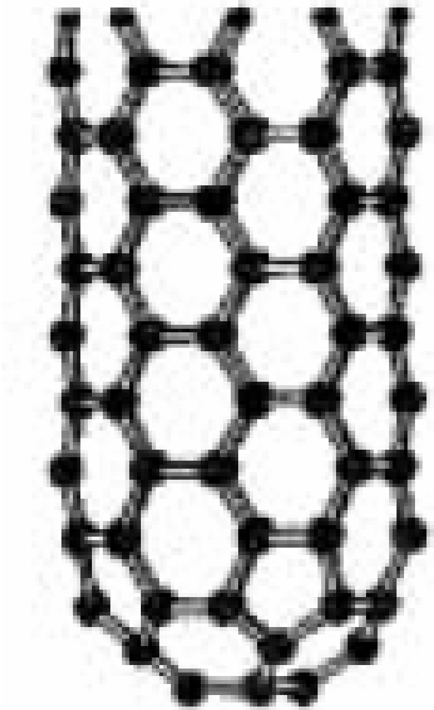




Special Nanotypes: Nanotubes

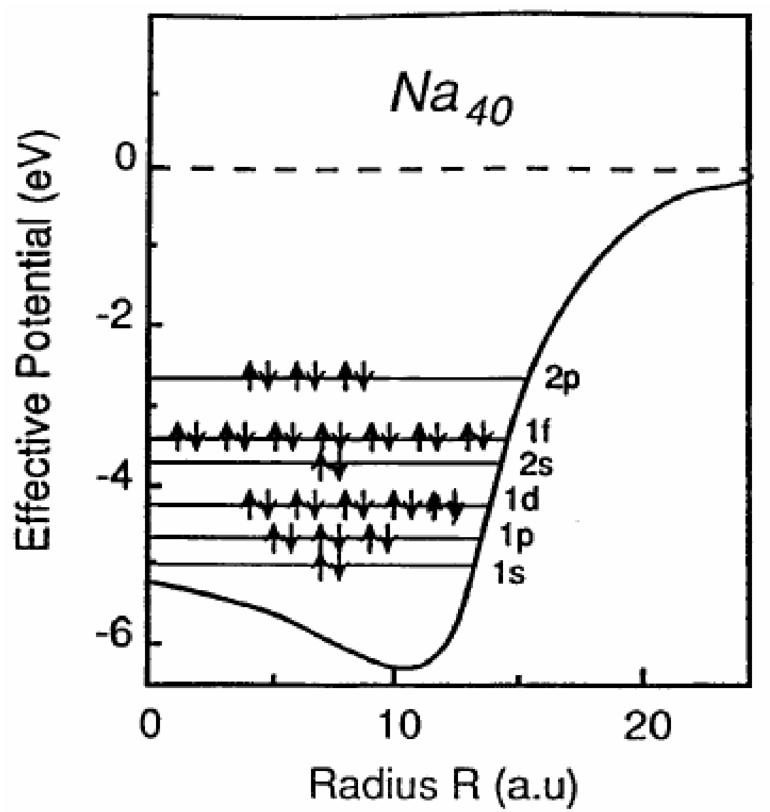
- simple carbon C !
- Diamond: four next neighbors → very stable
- plane and form a honeycomb lattice
- planes are stacked up, to form a solid body





Simple metal cluster

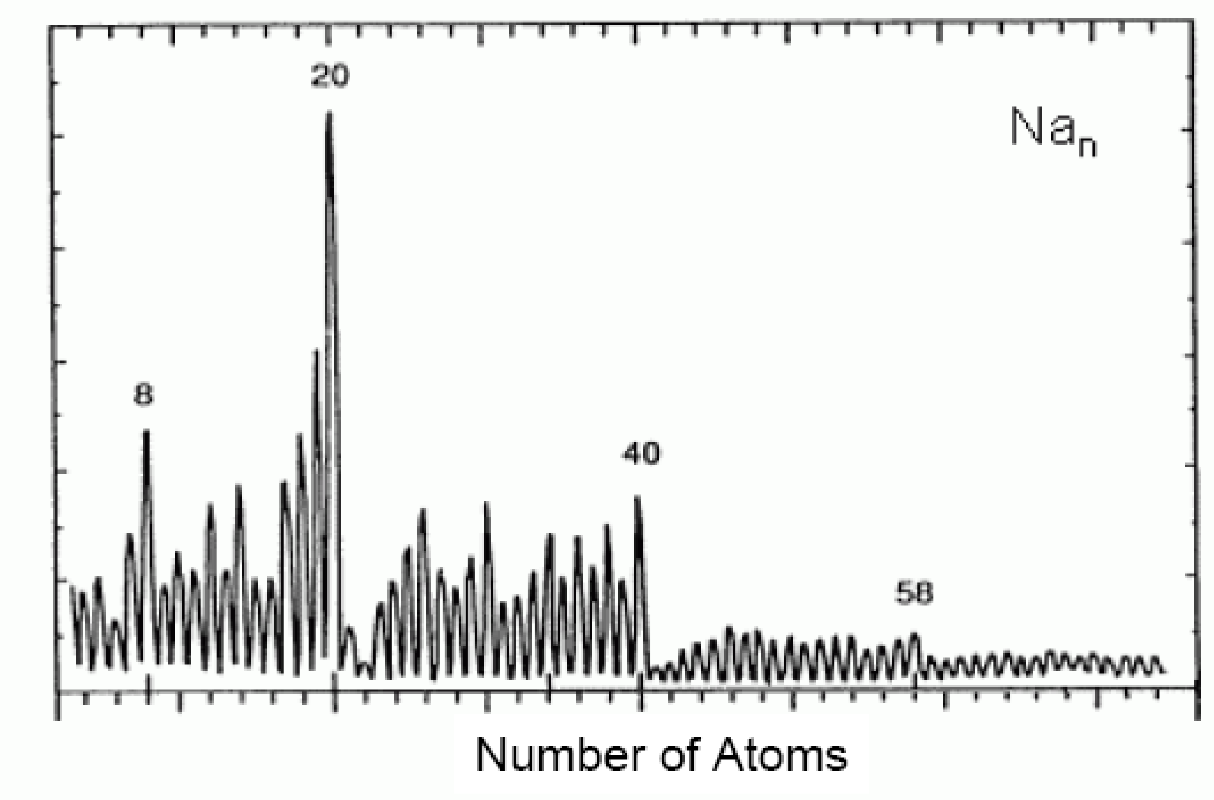
- Magic number for neutral atoms (soft metals):
  - 8
  - 20
  - 40
  - 58



W.Ekardt, Fritz-Haber Institut, Berlin

Electronic Effects

Mass spectrum of clusters of a simple (=monovalent) metal (e.g., Na, K, Cu, Ag, Au)



Walt A. de Heer, Rev.Mod.Phys. 65, 611 (1993)

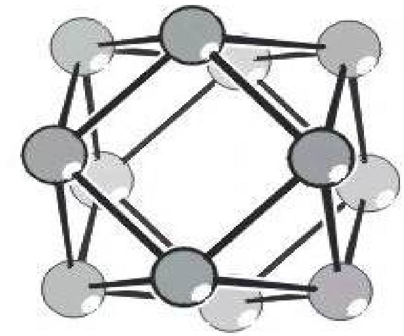
Magic numbers for neutral Clusters n= 8, 20, 40, 58, …

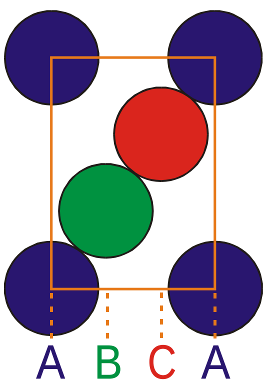
Positively charged n^+ = 9, 21, 41

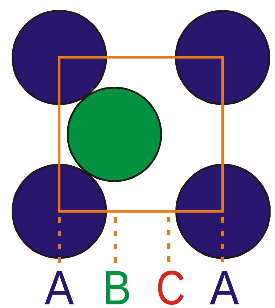
Negatively charged n^- = 7, 19, 39

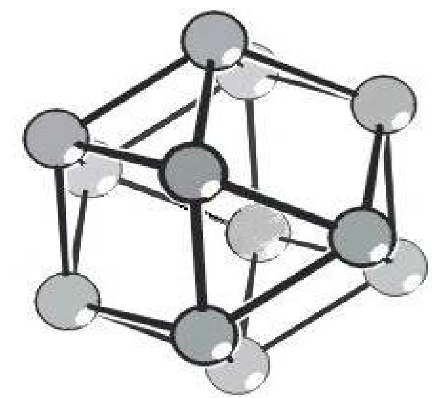
Geometric effects

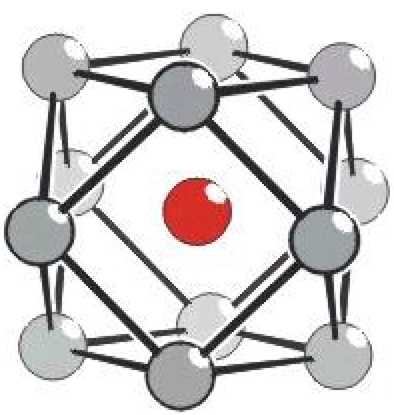
Cuboctahedron
- 6 squares and 8 triangles
- 12 corners and 24 edges
- Geometric shells
  - Cubic (ccp) or hexagonal (hcp) closed packed

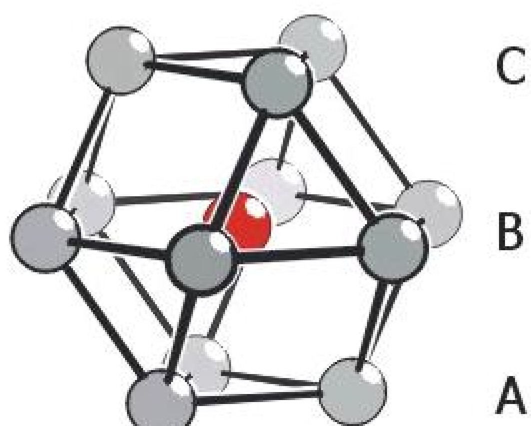












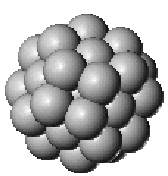
Coordination number = 12

Magic Numbers

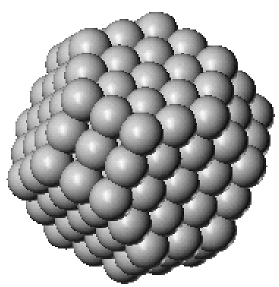
- Magic number of atoms N

  $N = 10\,n^2 + 2$ (n = number of shells)

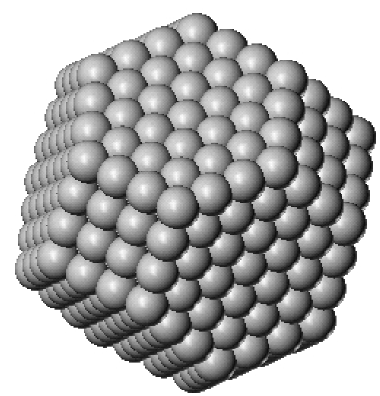
$N_{edge} = 2$



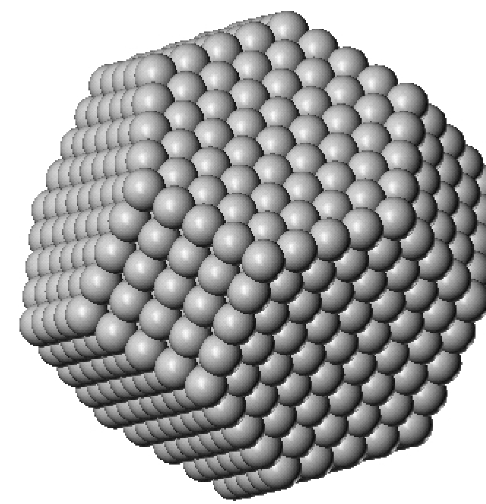
$N_{edge} = 3$



$N_{edge} = 4$



$N_{edge} = 5$



n-
N-

1-shell
13 atoms

2-shell
55 atoms

3-shell
147 atoms

4-shell
309 atoms

- 8 hexagons and 6 squares
- 36 edges and 24 corners

van Hardeveld, Hartog, *Suface Science*, 15, **1969**, 189-230.

Apparent diameters (d_N) of particles

- surface ruthenium atoms (N_s)
- total ruthenium atoms (N_t)
- density (r_N)
- molecular weight (M_N)

$d_N = (3*M_N*N_{total})/(4*\pi*N_{av}*r_N)^{1/3}$ (N_{av} is the Avogadro number)

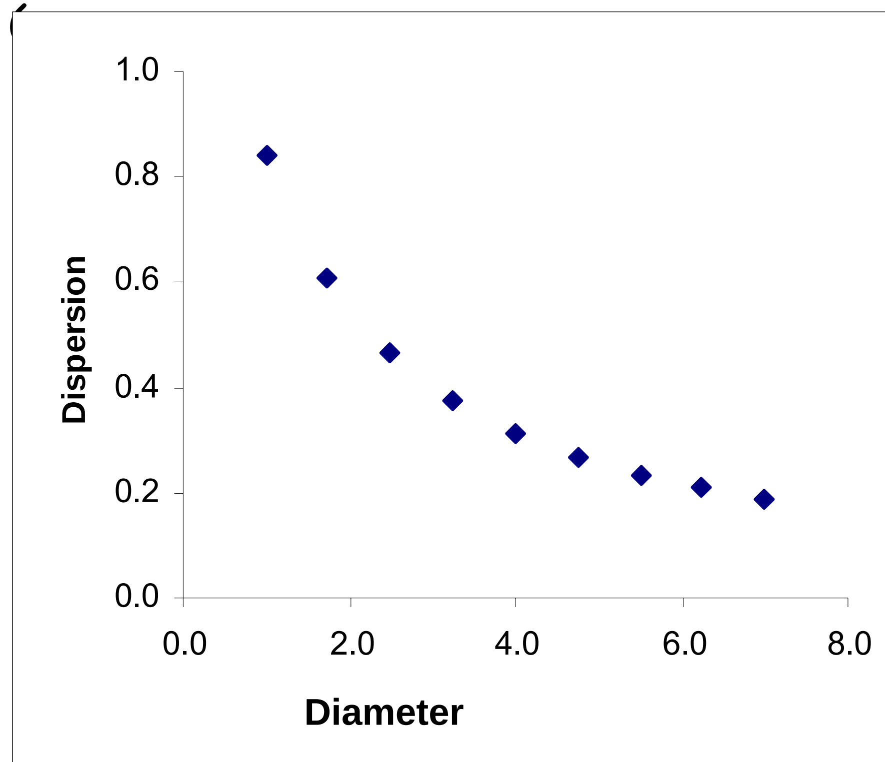
$N_t = 16\ N_{edge}^{3} - 33\ N_{edge}^{2} + 24\ N_{edge} - ($

$N_s = 30\ N_{edge}^{2} - 60\ N_{edge} + 32$

$\text{Dispersion} = N_{surface}/N_{total}$

$\text{Diameter} = 1.105\ d_{atomic}{}^{*}\ N_{total}^{1/3}$

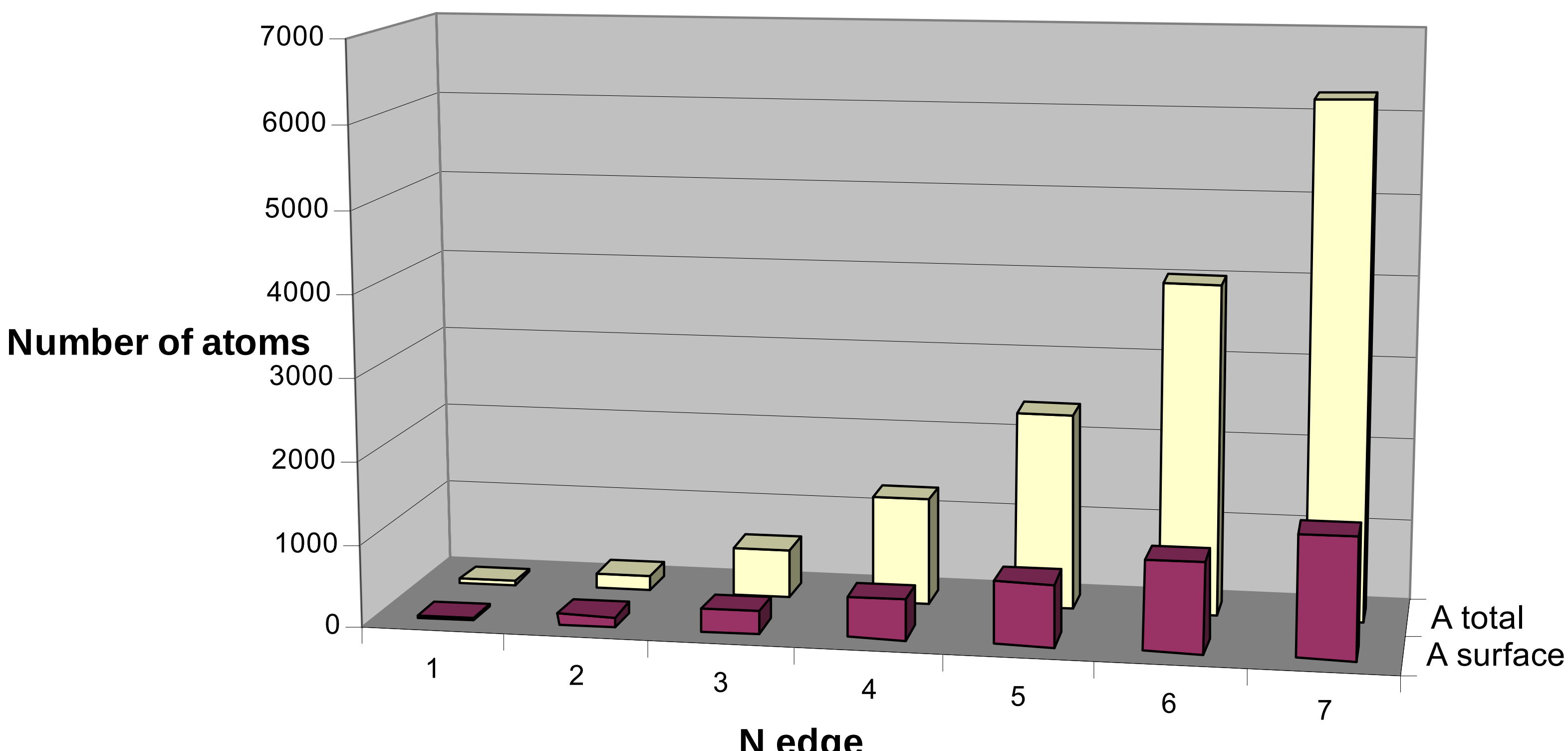
$d_{atomic} = 0.27\ \text{nm}$



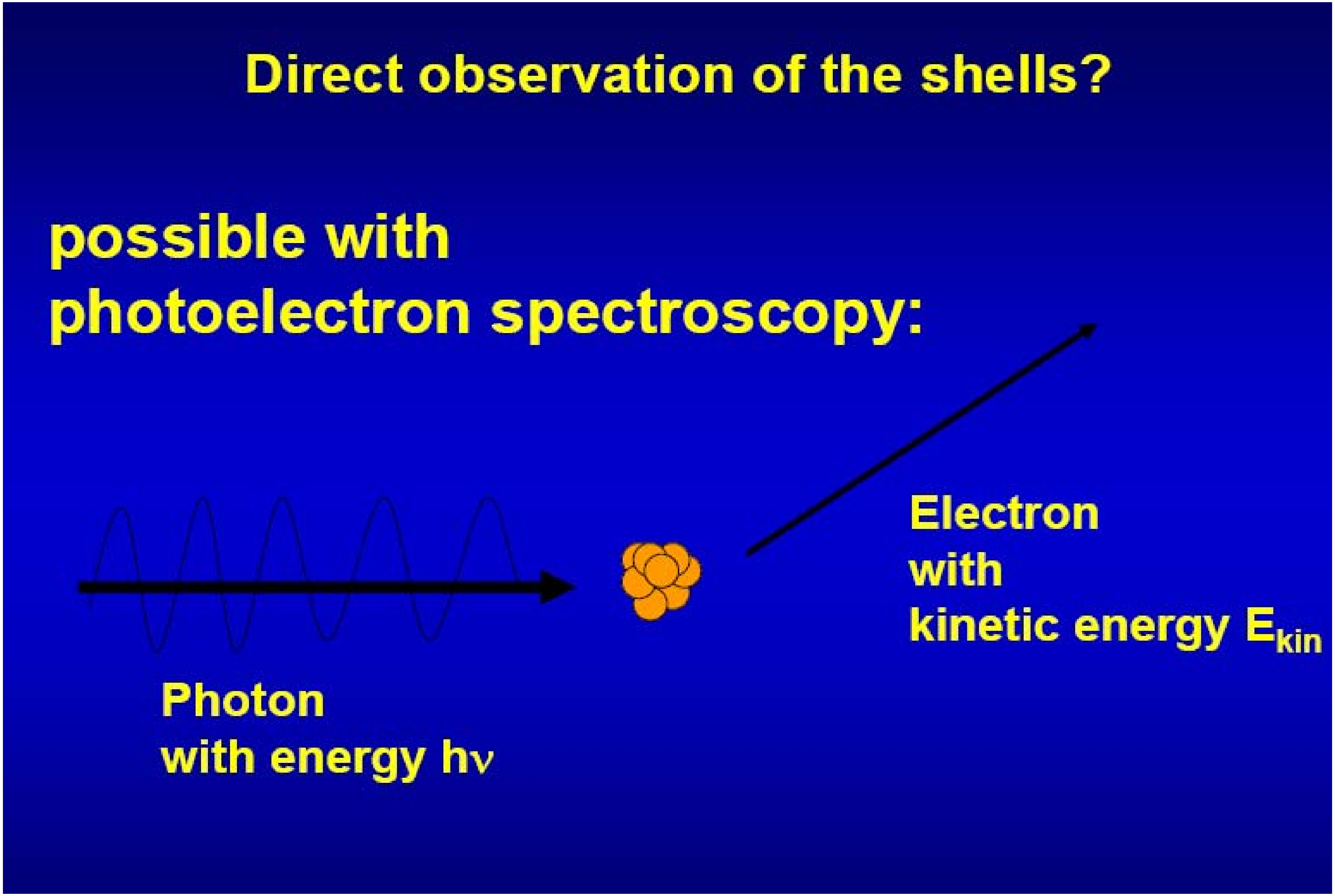
Ratio surface/total atoms

Numbers for N_s, N_t and the resulting diameter d_N for varying N_{edge}

N_{edge}	2	3	4	5	6	7	8
N_t	38	201	586	1289	2406	4033	6266
N_s	32	122	272	482	752	1082	1472
d_N	1.0	1.75	2.49	3.24	3.99	4.74	5.50



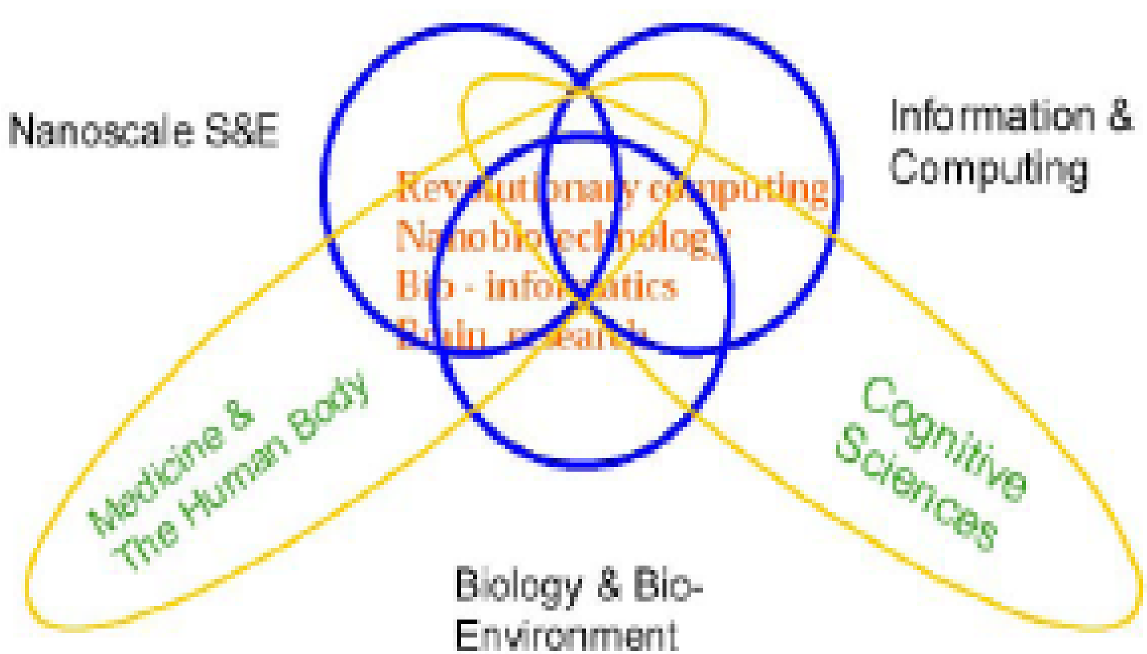
EPS: Shell observation



Application of nanomaterials

Engineered particles

- Catalysts for cars: Pt, Pd
- Pastes, glues
- Concrete
- Semi-conductor
- Photoconductor
- Microelectronic
- Nano-paints
- Pharmaceuticals
- Quantum dots
- Ceramics
- Cosmetics
- Performance chemicals



Preparation of Nanomaterials

- Lithography
- Sol-Gel-process
- Flame assisted deposition
- Gas phase deposition (CVD, PVD)
- Chemical preparation in solution e.g. reduction of different metal complexes by BH or H_2 in solution
- Self-assembled monolayers (SAM)
- Precipitation

→ Defined and narrow size distribution
Best results: Synthesis in solution and self assembly

Lithography

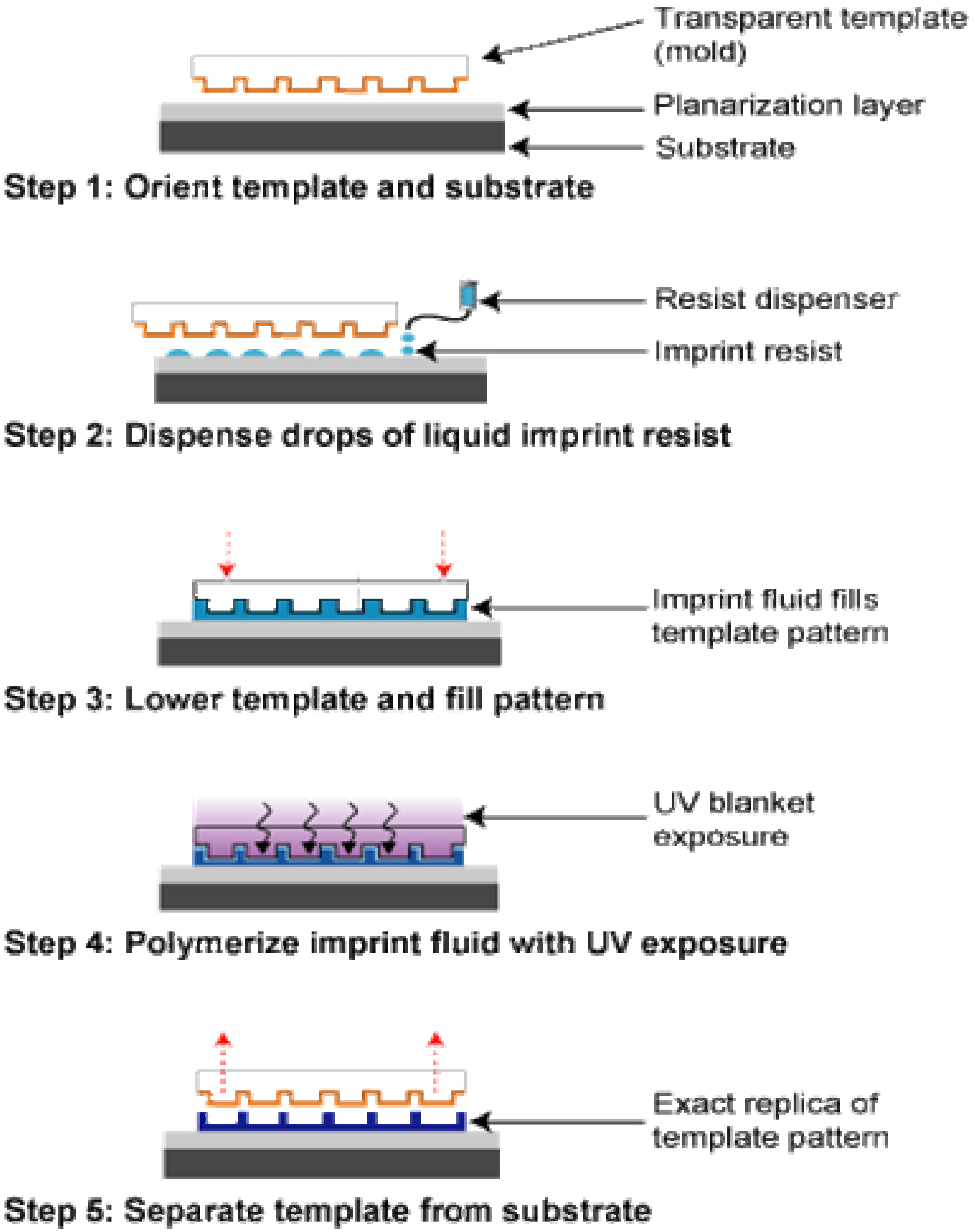
Principle

- based on the repulsion of oil and water
- image is placed on the surface with an oil-based medium
- acid 'burns' the oil into the surface
- water remains on the non-oily surface and avoids the oily parts
- a roller applies an oil-based ink that adheres only to the oily portion of the surface

Lithography

Modern technique

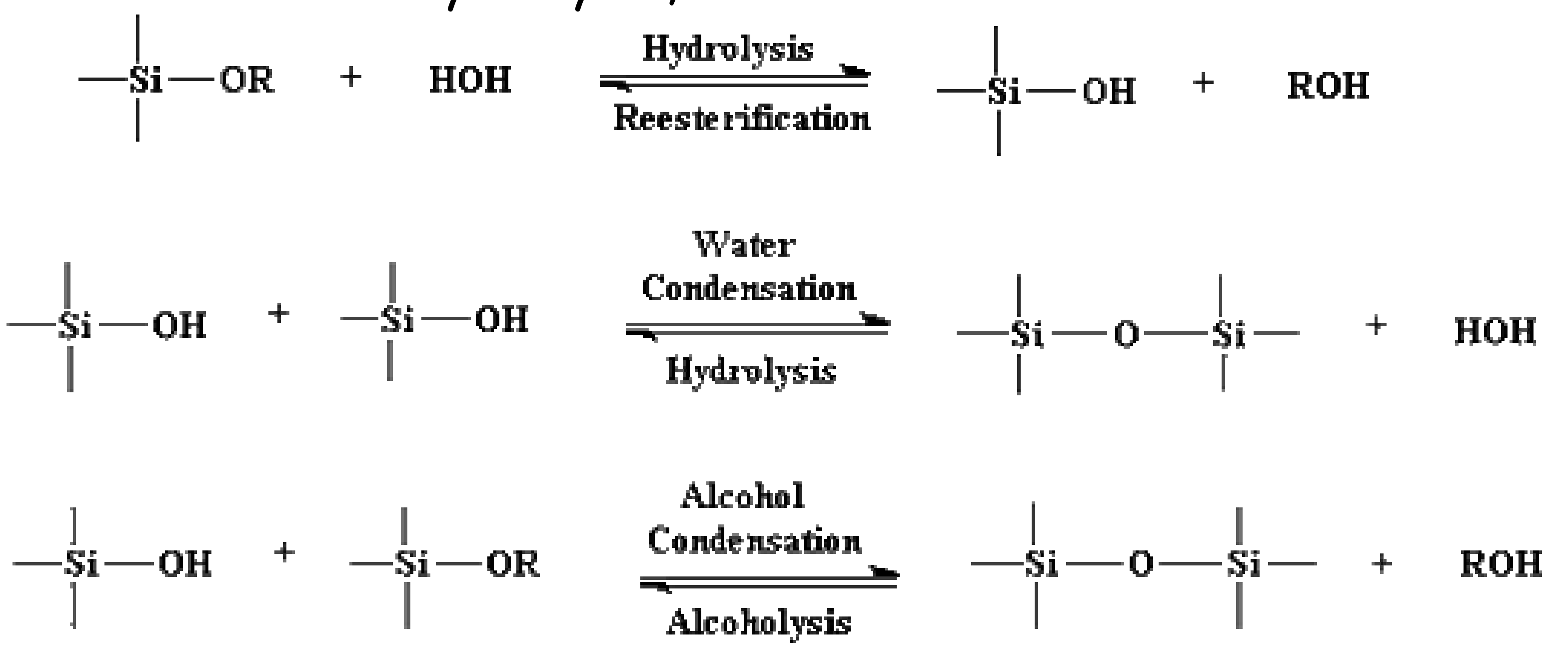
- A fused silica surface, covered with a release layer, is pressed into a thin layer of a silicon-containing monomer
- Illumination by a UV lamp polymerizes the surface into a hard material
- Upon separation of the fused silica template, the circuit pattern is left on the surface
- A residual layer of polymer between features is eliminated by an etch process
- Template fabrication process limits the resolution of the features (20 nm)



Sol-gel process

- Formation of a colloidal suspension (sol) and gelation to form a network in a continuous liquid phase (gel)
- precursors for these colloids consist of a metal or metalloid element surrounded by various reactive ligands

  Metal alkoxides: alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS).
- three reactions: hydrolysis, alcohol and water condensation



1

2a

2b

Lev, O. et al. Analytical Chemistry. 1995, 67(1), 22A-30A.
K.D. Keefer, in: Silicon Based Polymer Science: A Comprehensive Resource; eds. J.M. Zeigler and F.W.G. Fearon, ACS Advances in Chemistry Ser. No. 224, (American Chemical Society: Washington, DC, 1990) pp. 227-240.

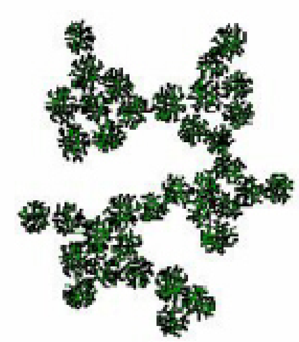
Sol-gel polymerization: three stages

1. Polymerization of monomers to form particles
2. Growth of particles
3. Linking of particles into chains, then networks

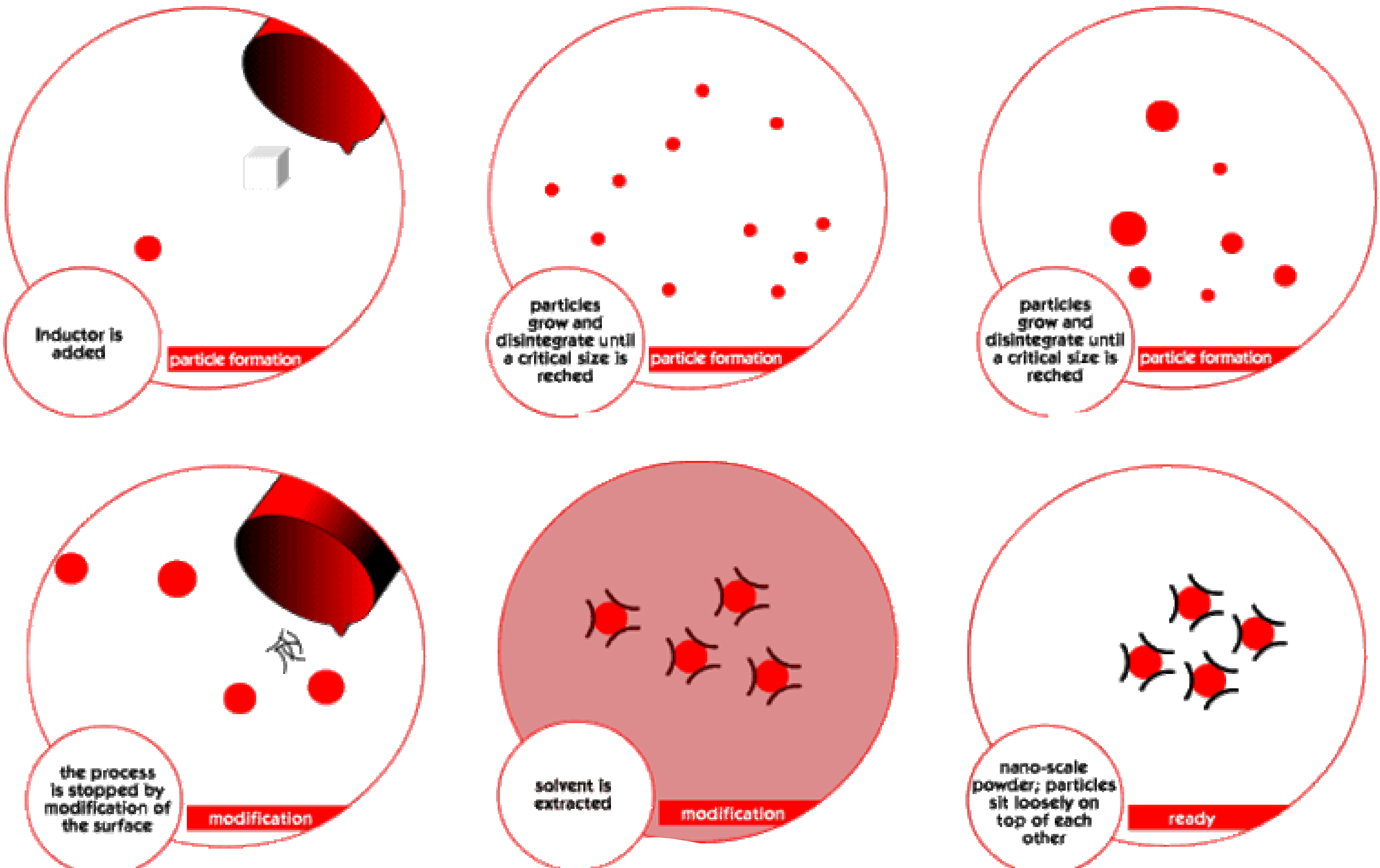
- many factors affect the resulting silica network:
  - pH
  - temperature
  - time of reaction
  - reagent concentrations
  - catalyst nature and concentration
  - H_2O/Si molar ratio
  - aging temperature and time

- Acid-catalyzed
  - yield primarily linear or randomly branched polymer

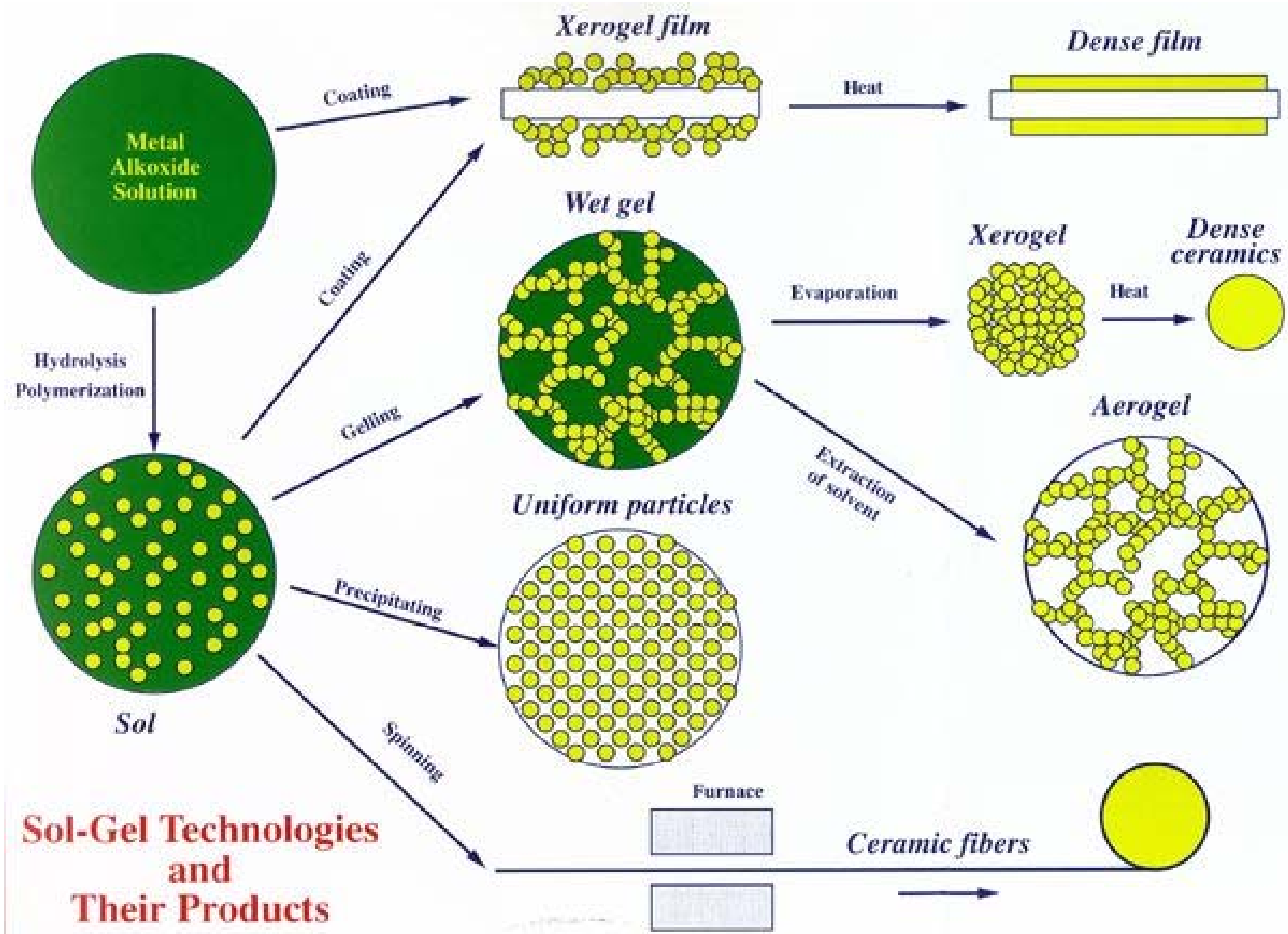
- Base-catalyzed
  - yield highly branched clusters



The sol-gel process



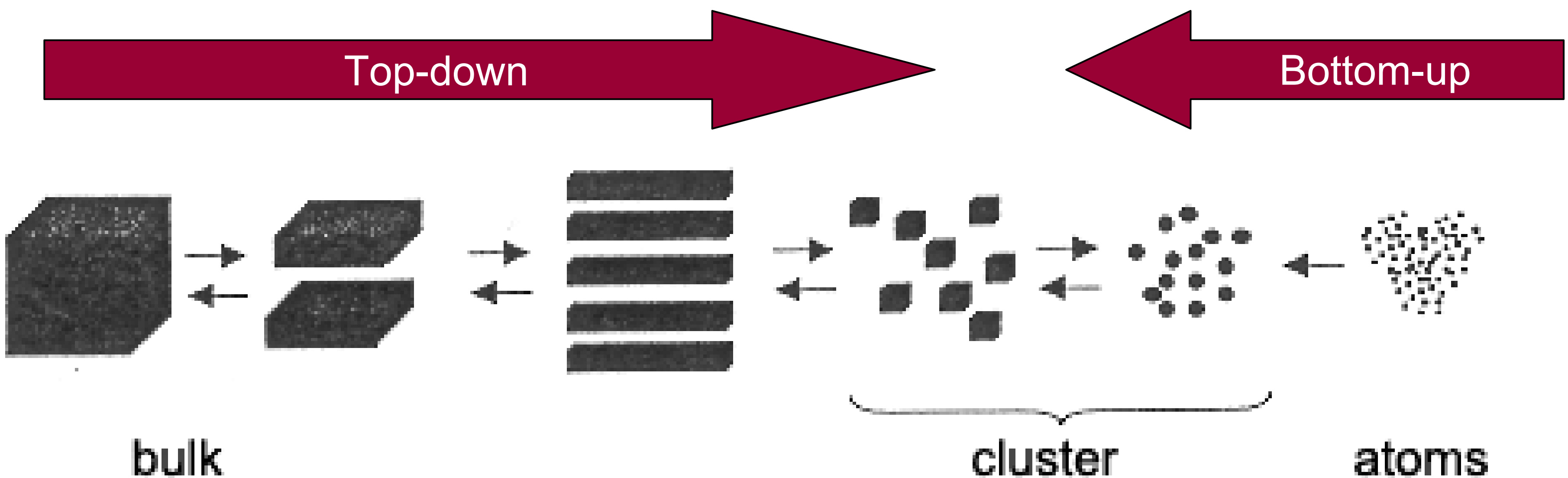
Sol-gel technologies



Chemical methods

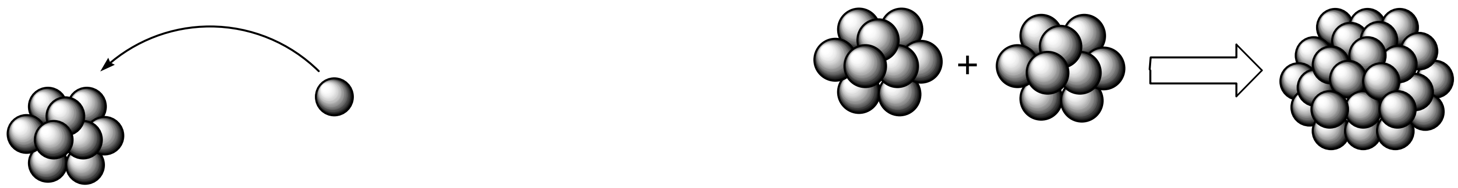
Top-down and bottom-up methods

- bulk material is reduced using physical tools.
- nanostructures from molecular structures via chemical reactions. The bottom-up method provides better results for the synthesis of nanomaterials with good reproducibility and yields

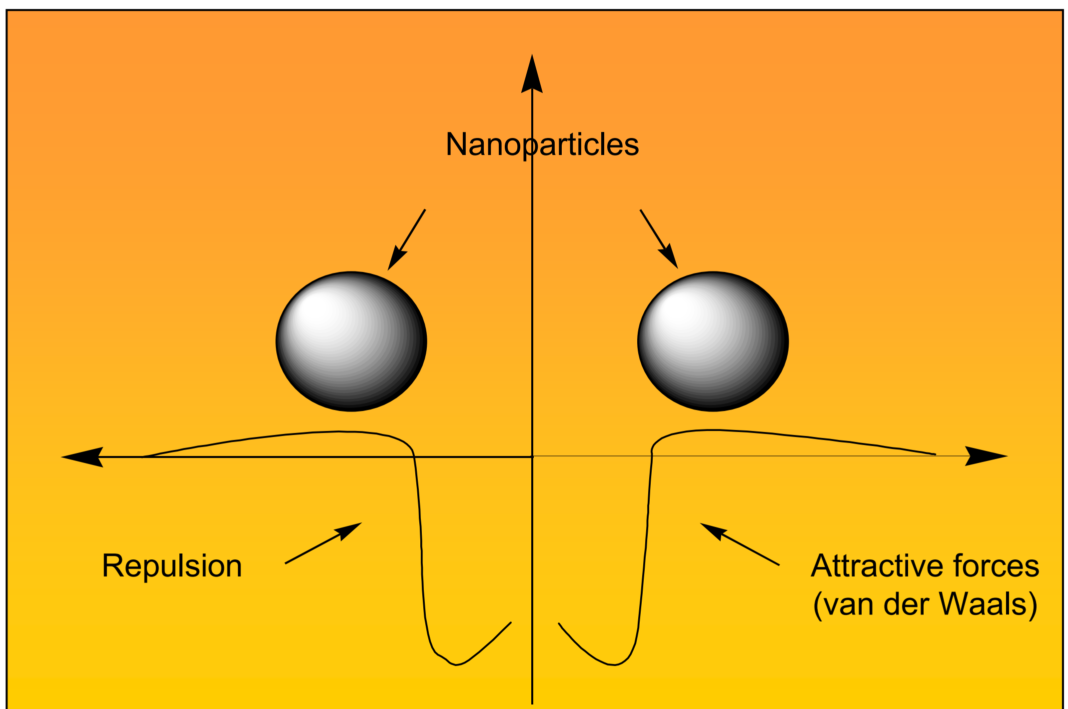


Growth and Electrostatic stabilization of nanoparticles

- Homogeneous and heterogeneous nucleation



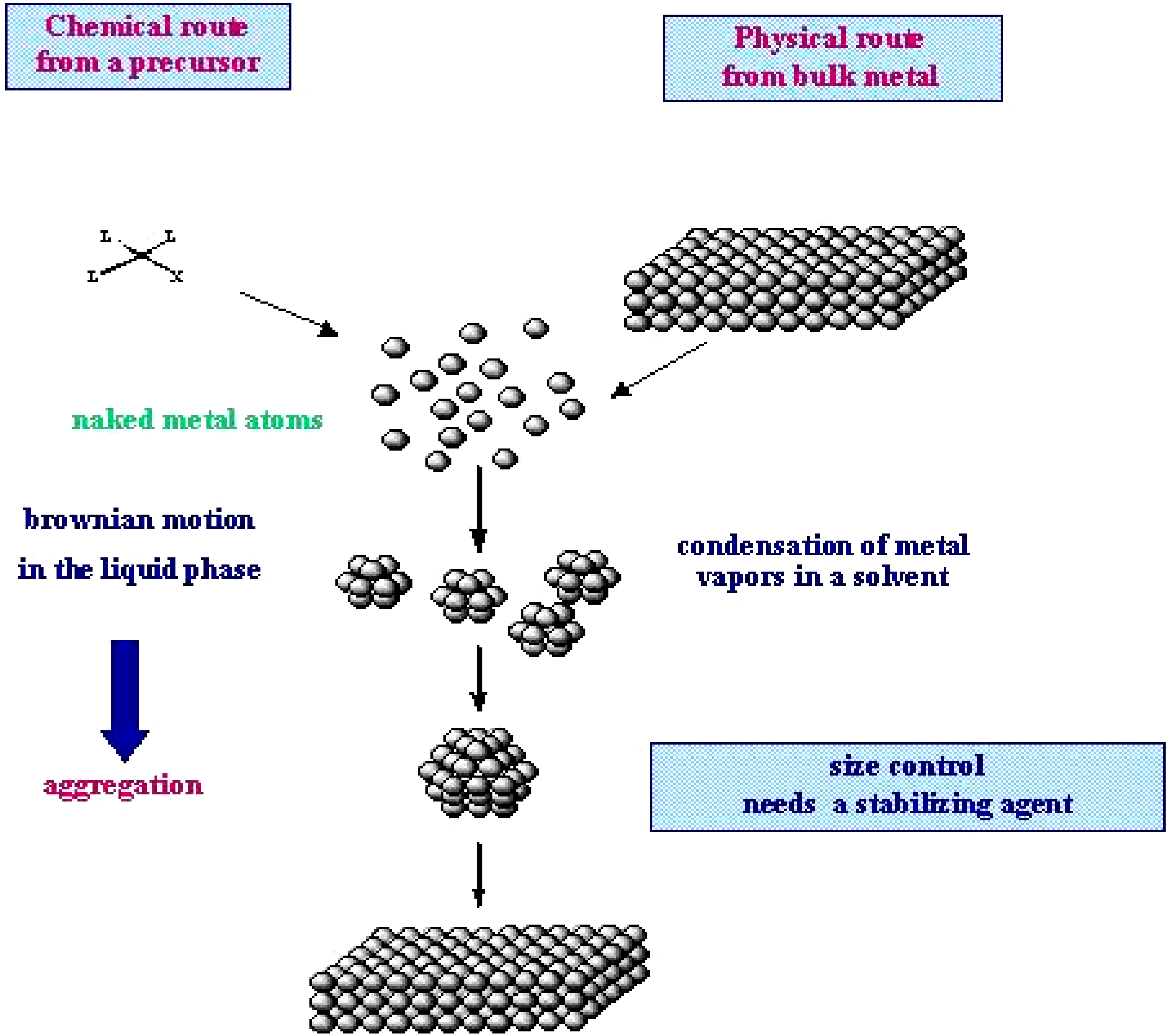
- Control of the dispersion



Synthesis of colloids

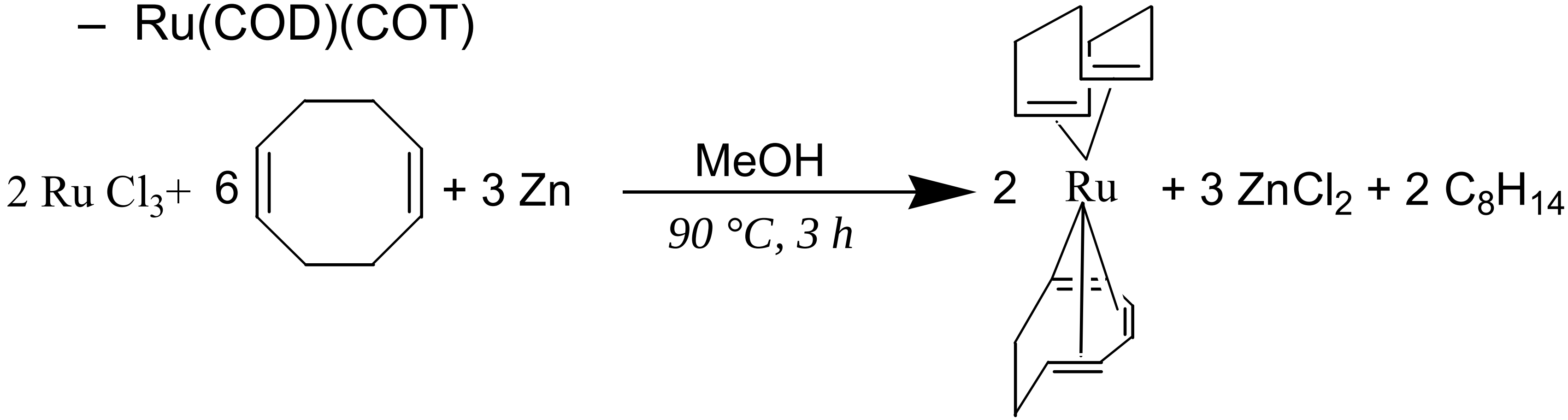
- Radiation induced synthesis of colloids
- Electrochemical synthesis of colloids
- Ultrasound-assisted electrochemical synthesis
- Salt reduction
- Organo-metallic synthesis
  (thermal decomposition, ligand reduction or ligand displacement)

Synthesis of colloidal solutions of metal nanoparticles

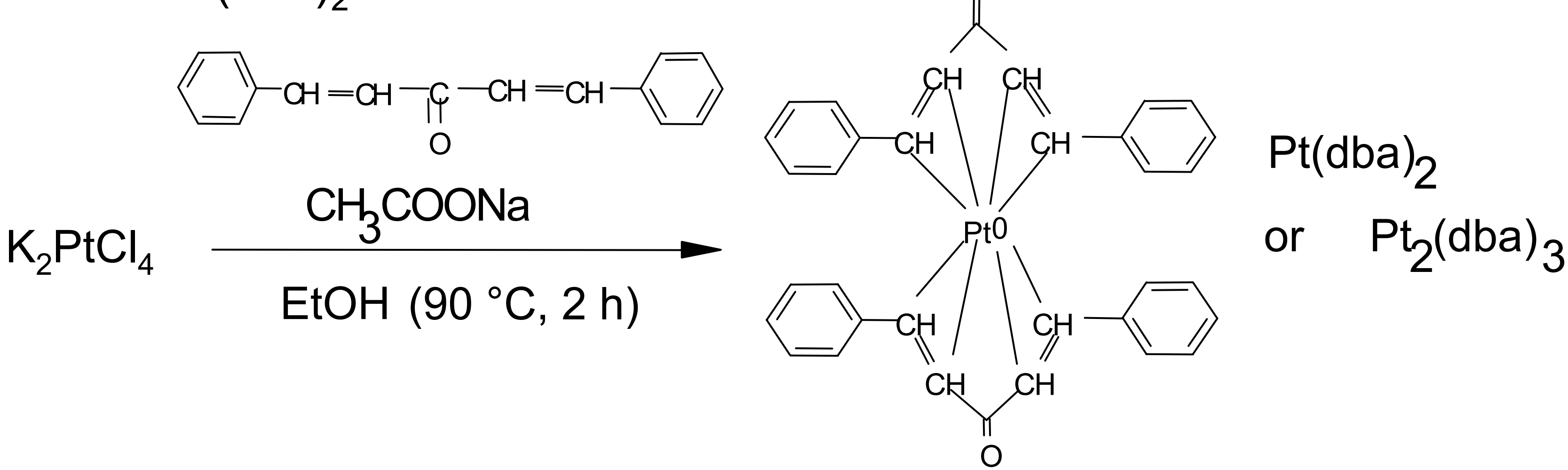


Organometallic Precursors

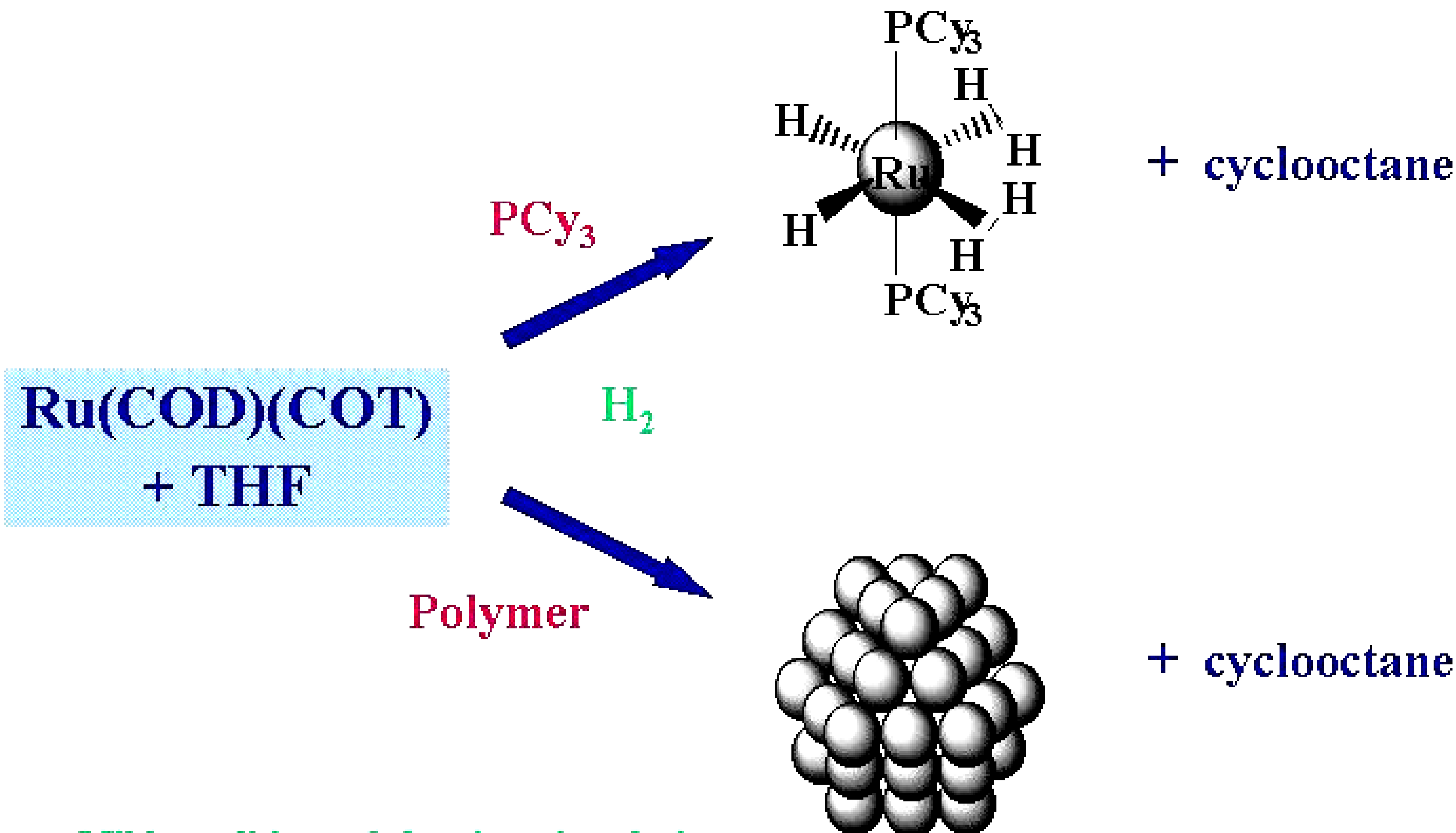
- Ruthenium-1,5-cyclooctadiene-1,3,5-cyclooctatriene
  - Ru(COD)(COT)



- Bis(dibenzylideneacetone)platinum(0)
  - $Pt(dba)_2$



Preparation by organo-metallic chemistry



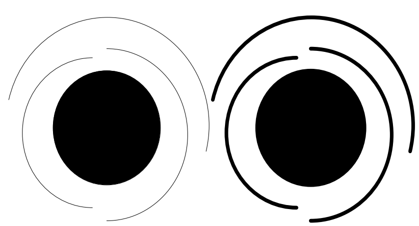
Mild conditions of chemistry in solution

Precipitation

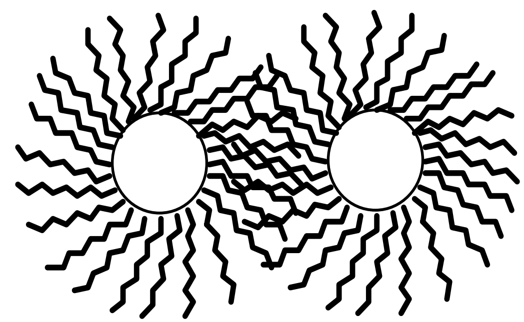
- Decomposition of organometallic precursors
- Precipitation
  - Control of the process
  - Monodisperse nanoparticles

Stabilization

- Stabilisation by amplification of the repulsive forces
- Sterical stabilisation by ligands or polymers



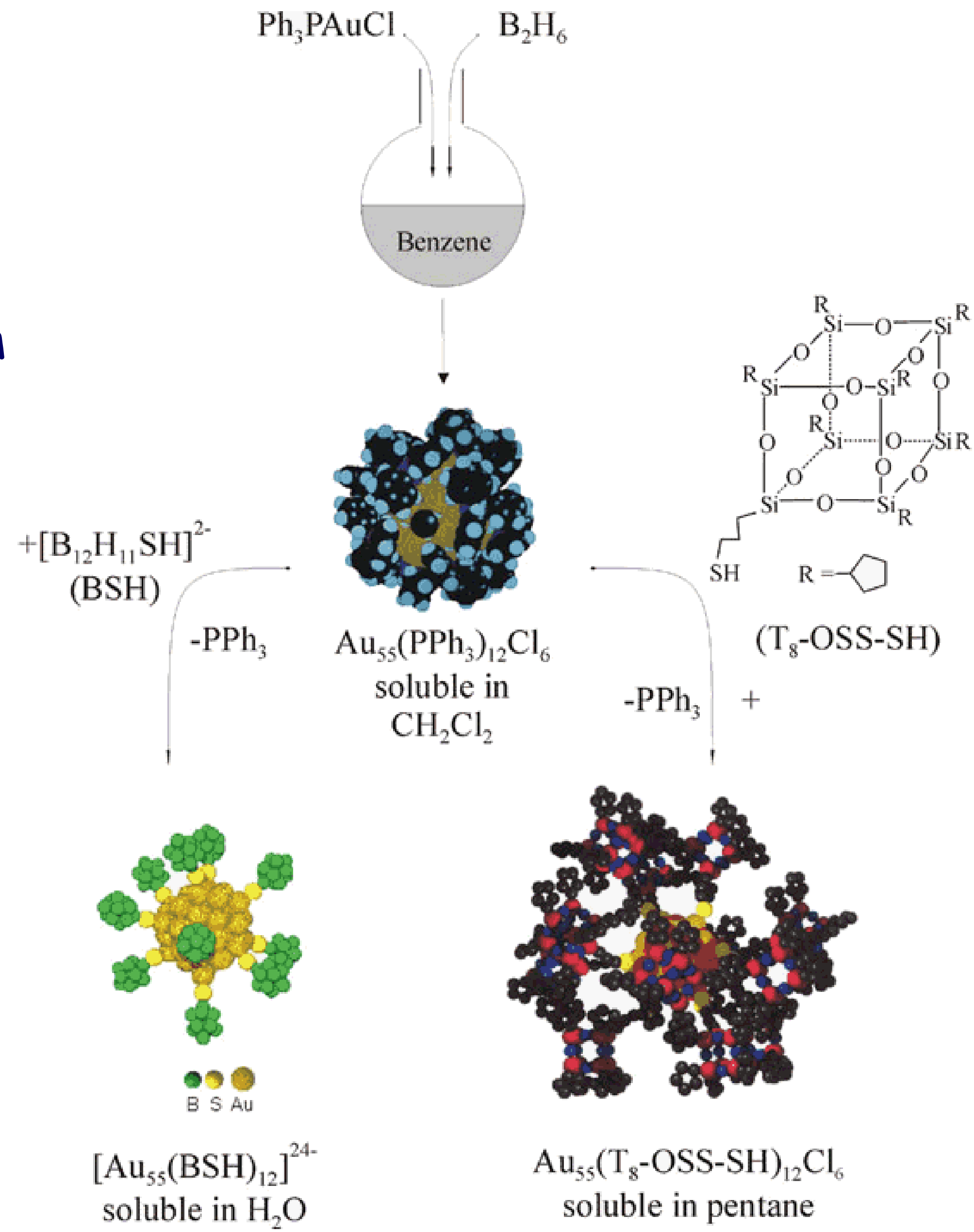
a)



b)

Ligand-Stabilized Cluster

- *Controlled chemical synthesis of well-defined Gold-, Palladium-, Platinum-, Ruthenium or Rhodium cluster*
- *Bimetallic cluster:*
  - Gold and Rhodium
  - Palladium and Gold
- *A ligand layer is indispensable for their stabilization and application*



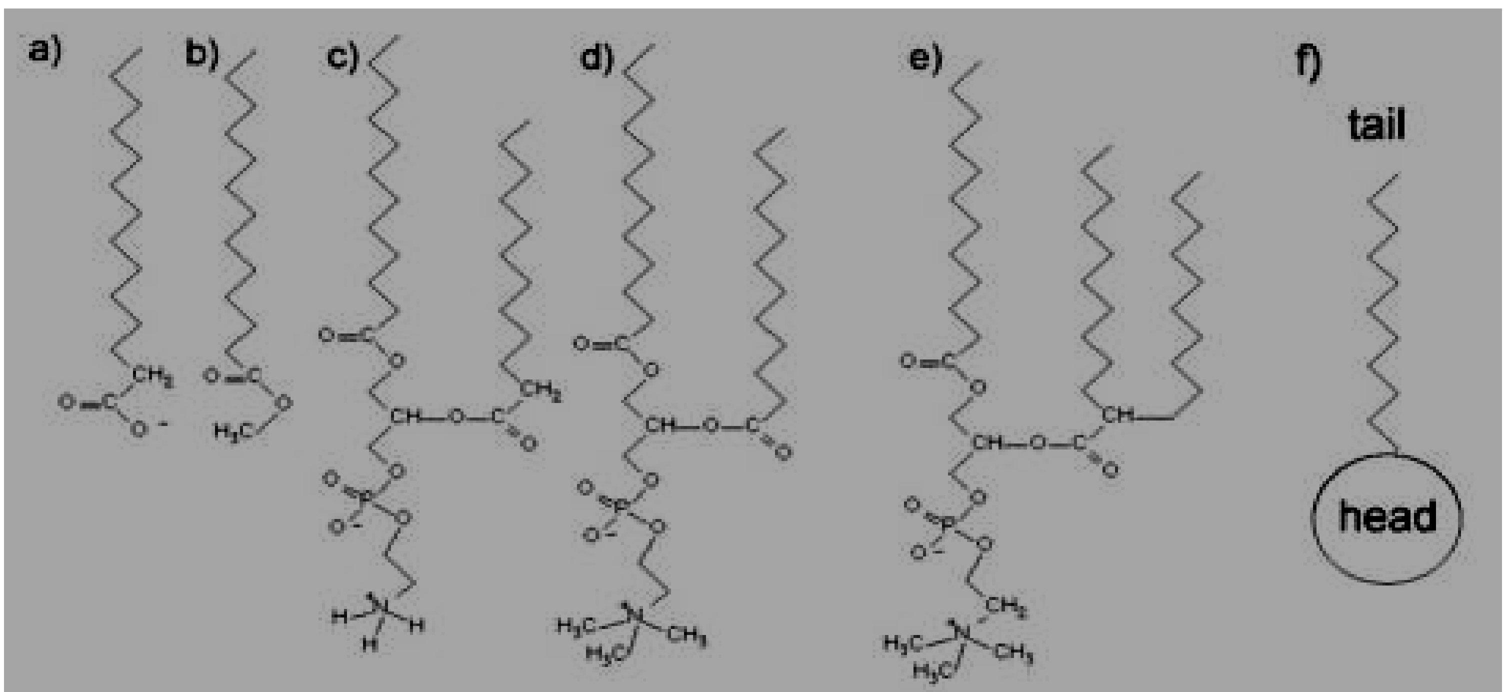
G. Schmid et al.

Monolayers

- single, closely packed layer of atoms or molecules
- **Langmuir monolayer** one-molecule thick insoluble layer of an organic material spread onto an aqueous subphase
- compounds used to prepare are amphiphilic materials that possess a hydrophilic headgroup and a hydrophobic tail

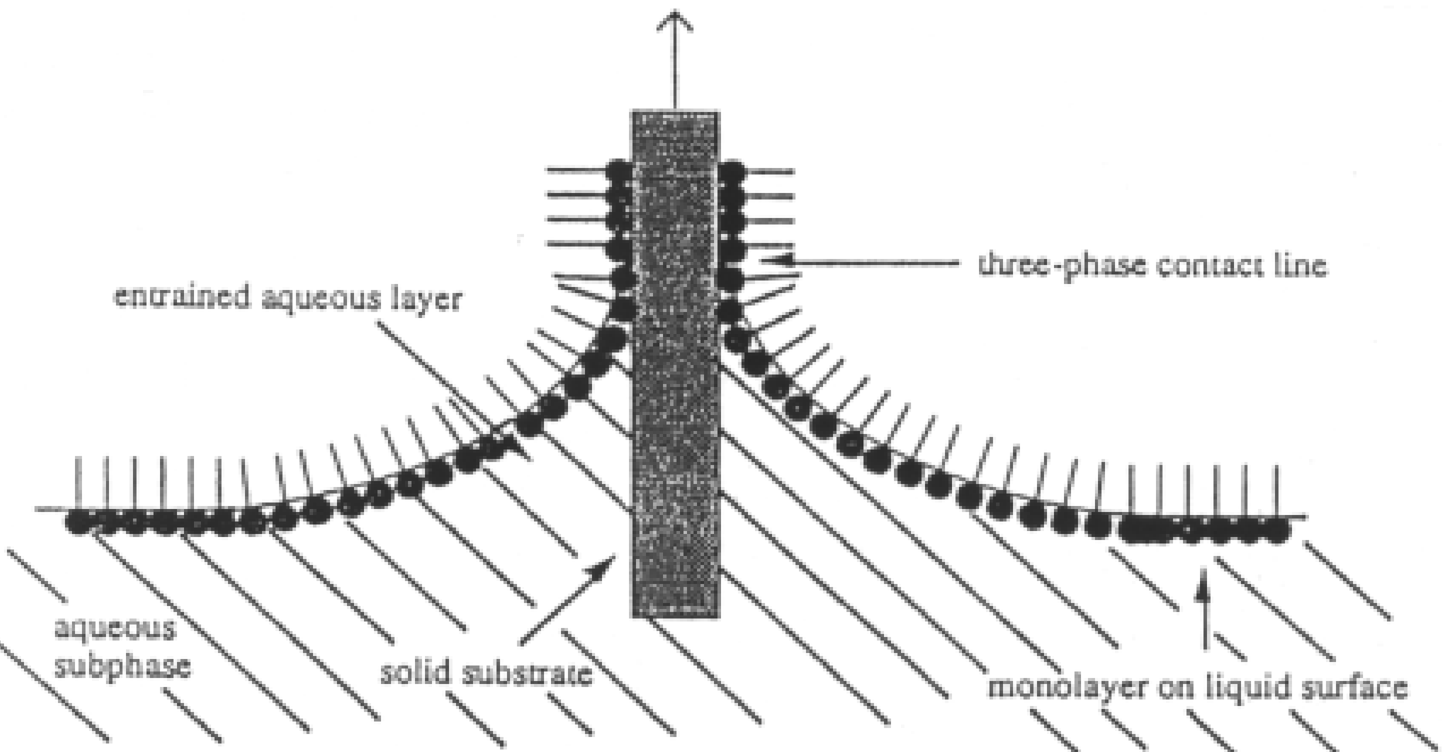
a) fatty acid — b) methyl ester

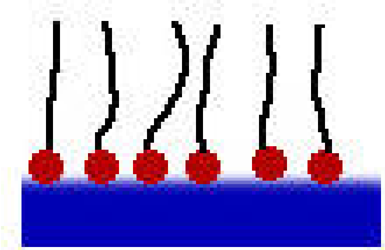
c)-e) phospholipids — f) schematic sketch



Langmuir-Blodgett film

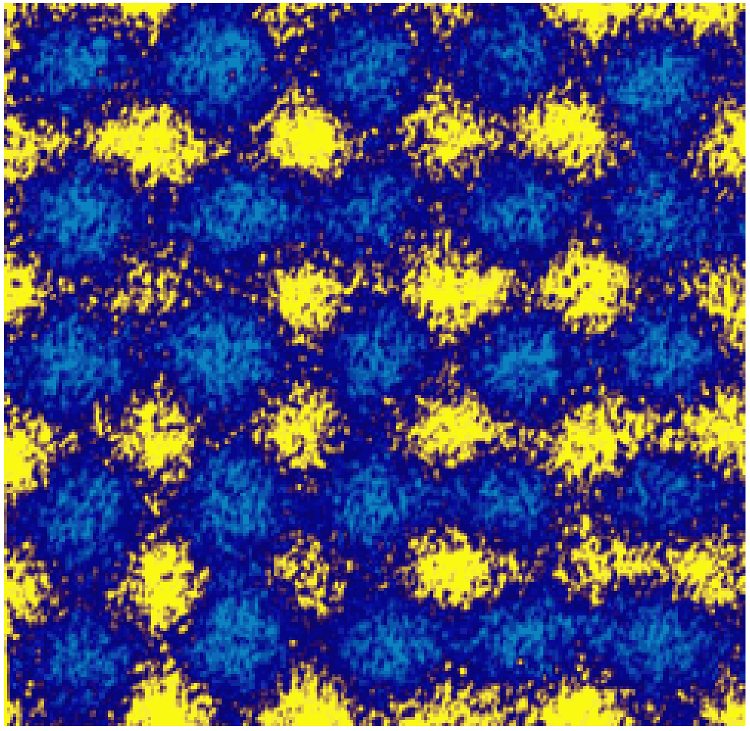
- Irving Langmuir and Katherine Blodgett (1900)
- transfer of monolayers from liquid to solid substrates
- deposition of multi-layer films on solid substrates
- structure of the film can be controlled at the molecular level
- films exhibit various electrochemical and photochemical properties
- LB-film memory chip: data bit is represented by a single molecule
- complex switching networks





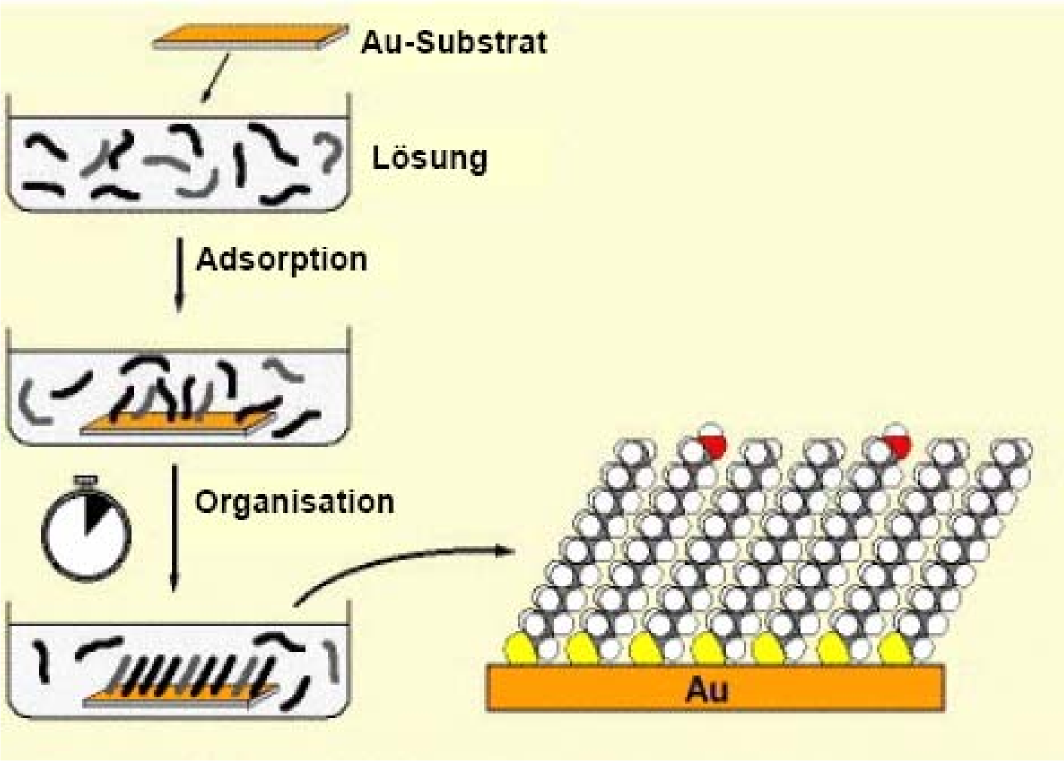
Self-organization

- generates structural organization on all scales from molecules to galaxies
- reversible processes: disordered components form structures of patterns
- static self-assembly: system is in equilibrium and does not dissipate energy
- dynamic self-assembly is when the ordered state requires dissipation of energy.
- Examples:
  - weather patterns
  - solar systems
  - self-assembled monolayers



Self-assembled monolayers

- surfaces consisting of a single layer of molecules on a substrate
- monolayers can be prepared simply by adding a solution of the desired molecule onto the substrate surface and washing off the excess

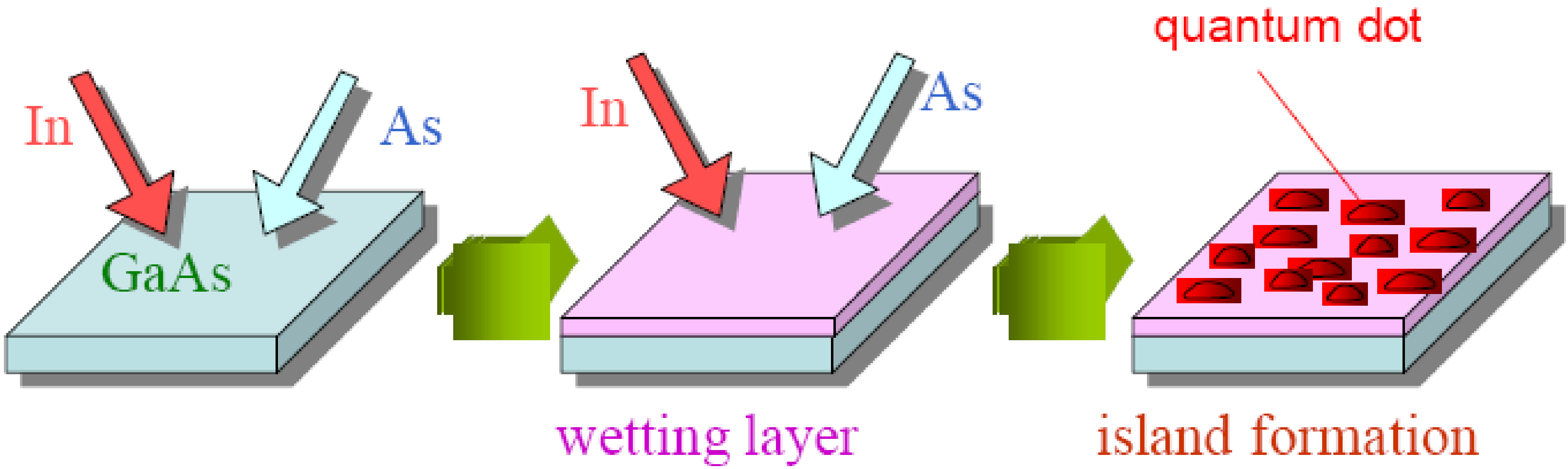


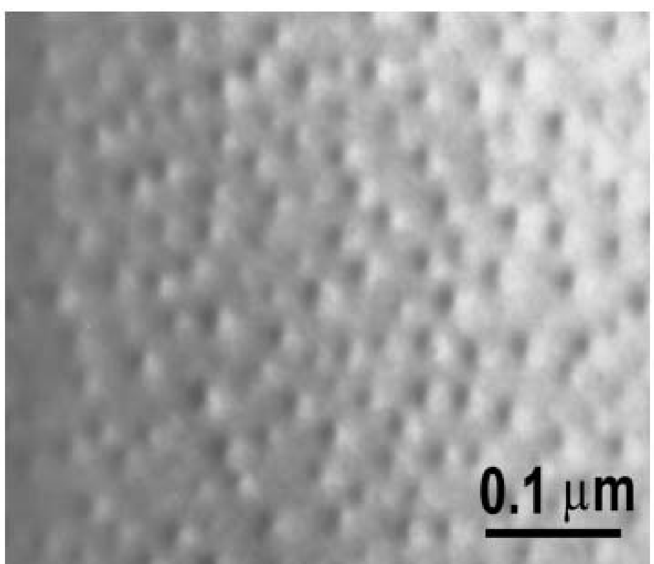
- Example: alkane thiol on gold
  - Sulfur has particular affinity for gold and an alkane with a thiol head group will stick to the gold surface with the alkane tail pointing away from the substrate.

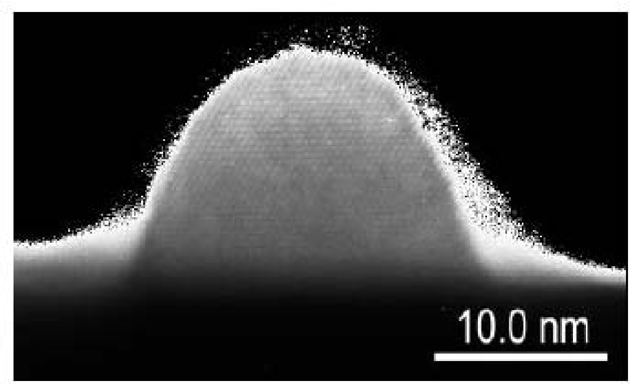
G. Schmid, M. Bäumle, N. Beyer, Angew. Chem., 2000, 112, 187-189; Angew. Chem. Inter. Ed. Engl., 2000, 39, 181."Geordnete zweidimensionel Monolagen von Au55-Clustern"

Self organized Growth of Quantum Dots

- Self organization occurs during the layer growth



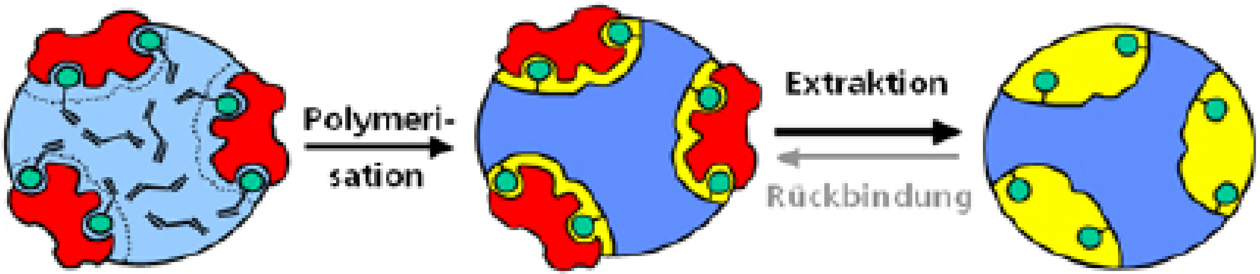




scanning electron microscope

transmission electron microscope

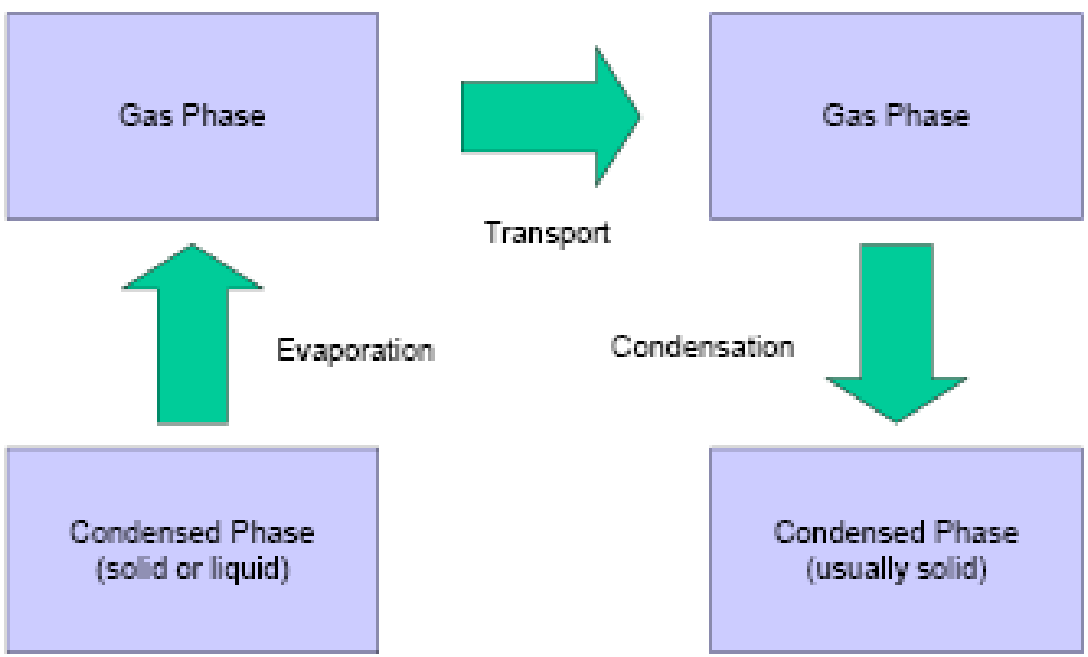
Molecular Printing

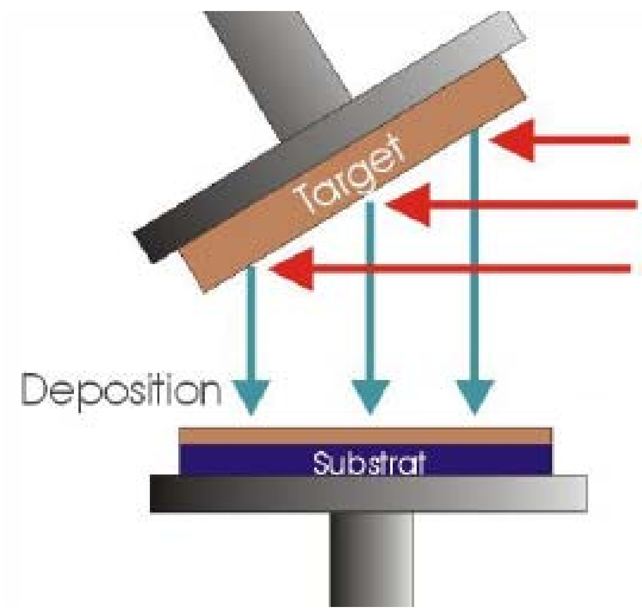


- Synthesis of a networked polymer in presence of a template molecule
- Template molecule controls by its defined geometry the growth, structure and arrangement of the system
- Functional groups of the monomer are fixed on the template and copy the form of the template
- Extraction of the template
- Defined cavities with layout
- Selection of the host molecule works by molecular identification and can be fixed

Physical Vapor Deposition (PVD)

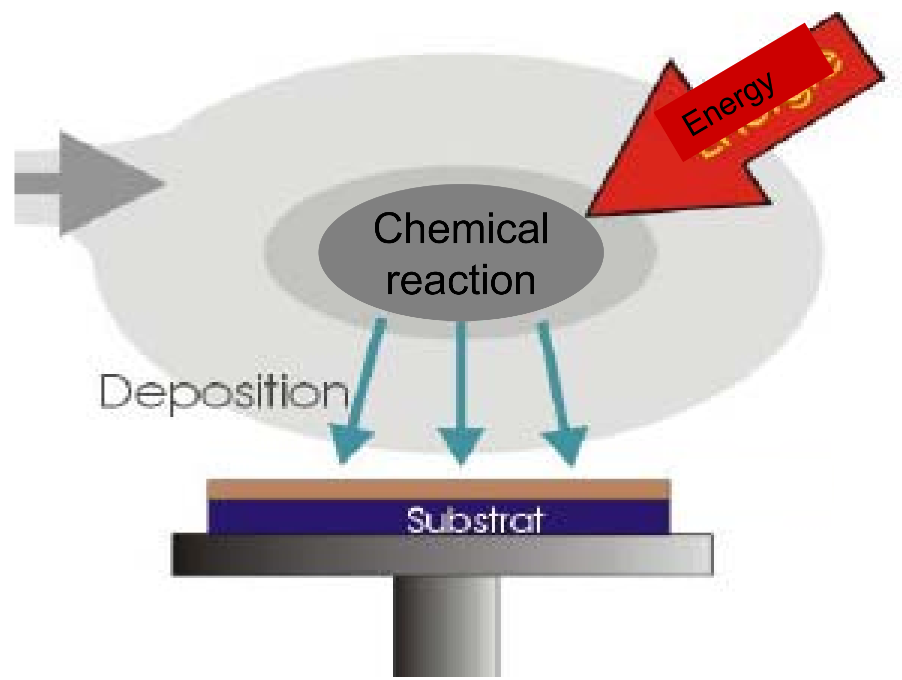
- Deposition of thin films of various materials onto various surfaces (e.g. semiconductor wafers) by physical means
- Application:
  - semiconductor devices,
  - aluminized mylar for balloons and snack bags
  - coated cutting tools for metalworking.
- Variants of PVD include:
  - Evaporative deposition
  - Sputtering
  - Pulsed laser deposition





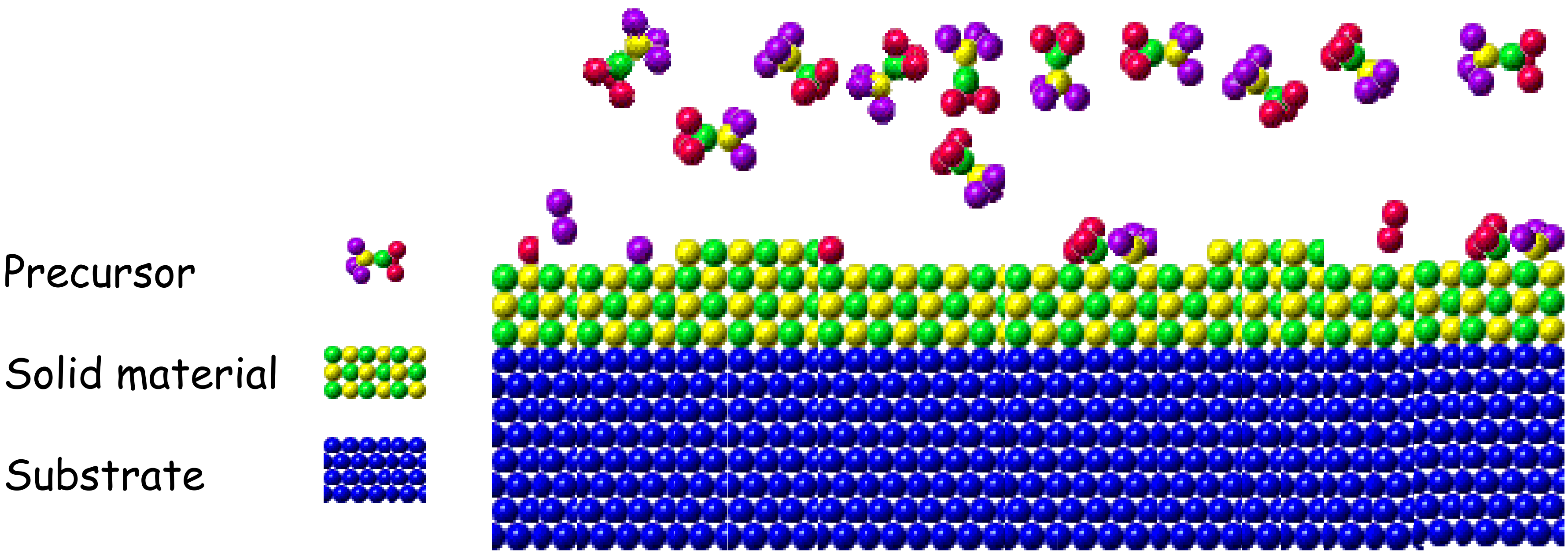
Chemical Vapor Deposition (CVD)

- Chemical process for depositing thin films of various materials
- The substrate is exposed to one or more volatile precursors, which react and/or decompose on the surface to produce the desired deposit
- Volatile byproducts are removed by gas flow through the reaction chamber
- The CVD process is also used to produce synthetic diamonds
- Application in semiconductor industry to deposit various films including:
  - Polycrystalline and amorphous silicon,
  - SiO_2,
  - silicon germanium,
  - tungsten, silicon nitride,
  - silicon oxynitride,
  - titanium nitride



CVD-Fundamental reaction steps

- Vaporization and Transport of Precursor Molecules into Reactor
- Diffusion of Precursor Molecules to Surface
- Adsorption of Precursor Molecules to Surface
- Decomposition of Precursor Molecules on Surface and Incorporation into Solid Films
- Recombination of Molecular Byproducts and Desorption into Gas Phase

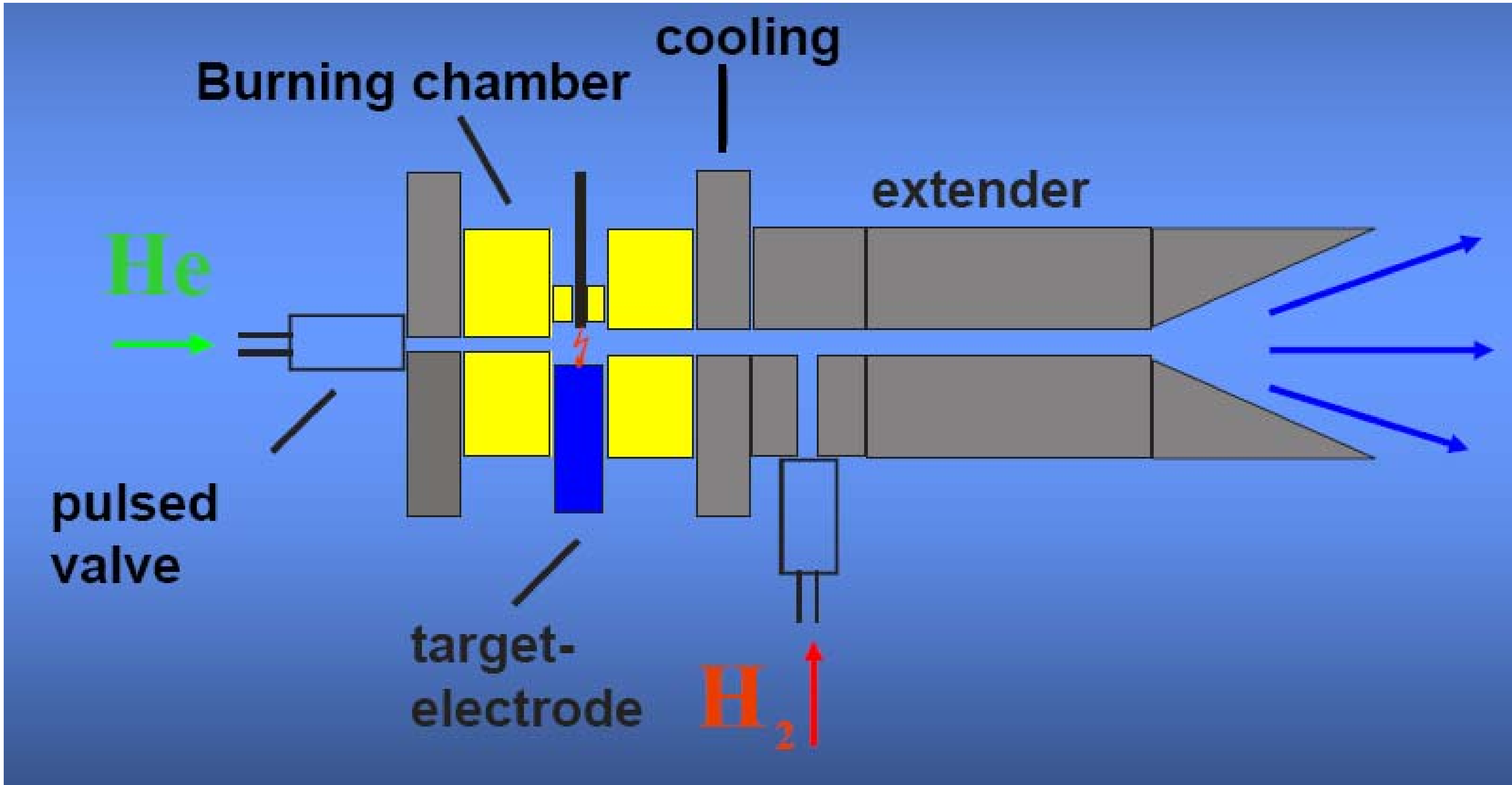


(Disadvantage: often with poor control over the thickness of the molecular layer)

Pulsed Arc Cluster Ion Source

Generation of cluster:

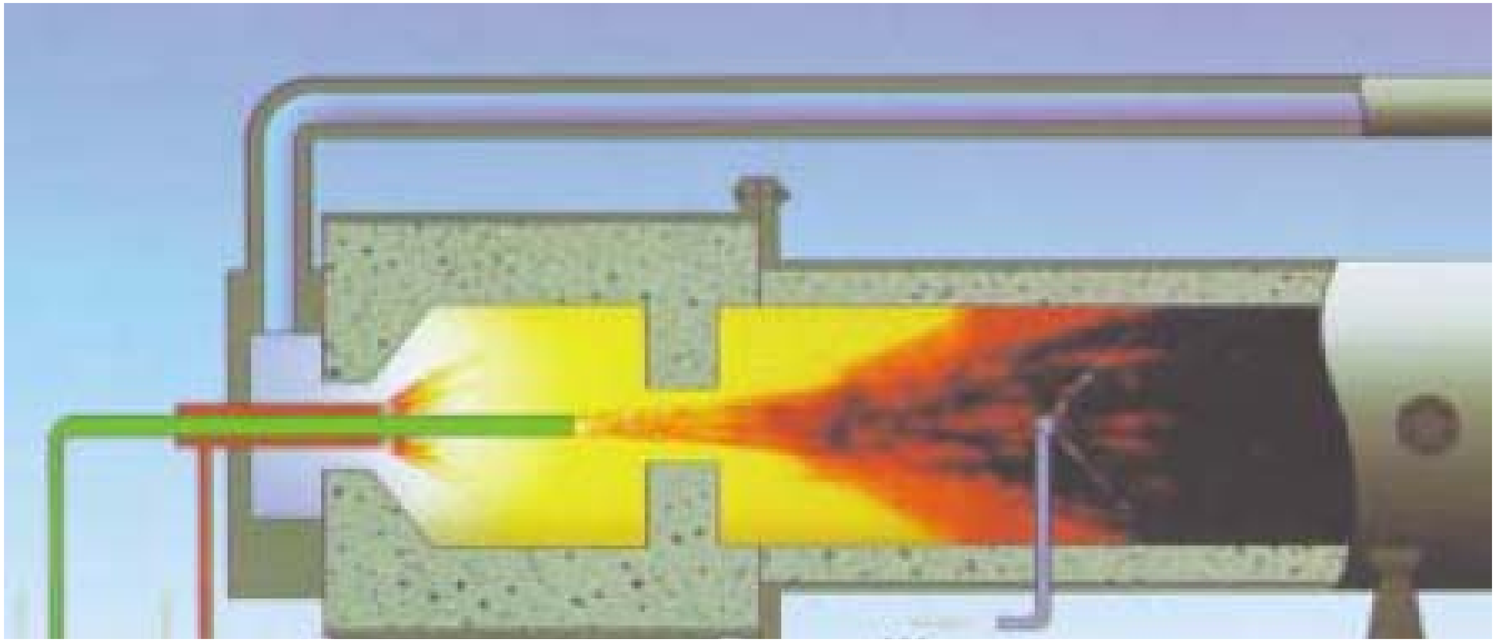
- Vaporization of the bulk material
- Condensation in carrier gas
- Mass separation



G.Ganteför, H.R.Siekmann, H.O.Lutz, and K.H.Meiwes-Broer, Chem.Phys.Lett. **165**, 293 (1990).

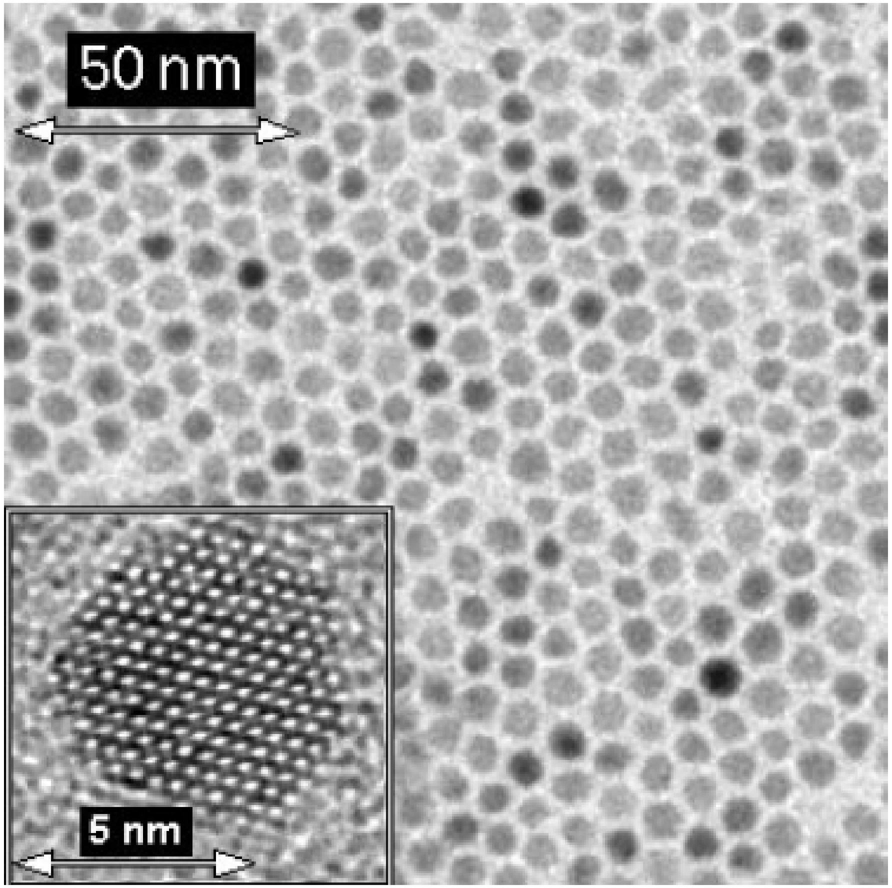
Flame assisted deposition

- Decomposition of precursors in a flame (1200 - 2200 °C)
- Ar/H_2
- Particle size depending on
  - Temperature
  - Precursor
  - Reaction time



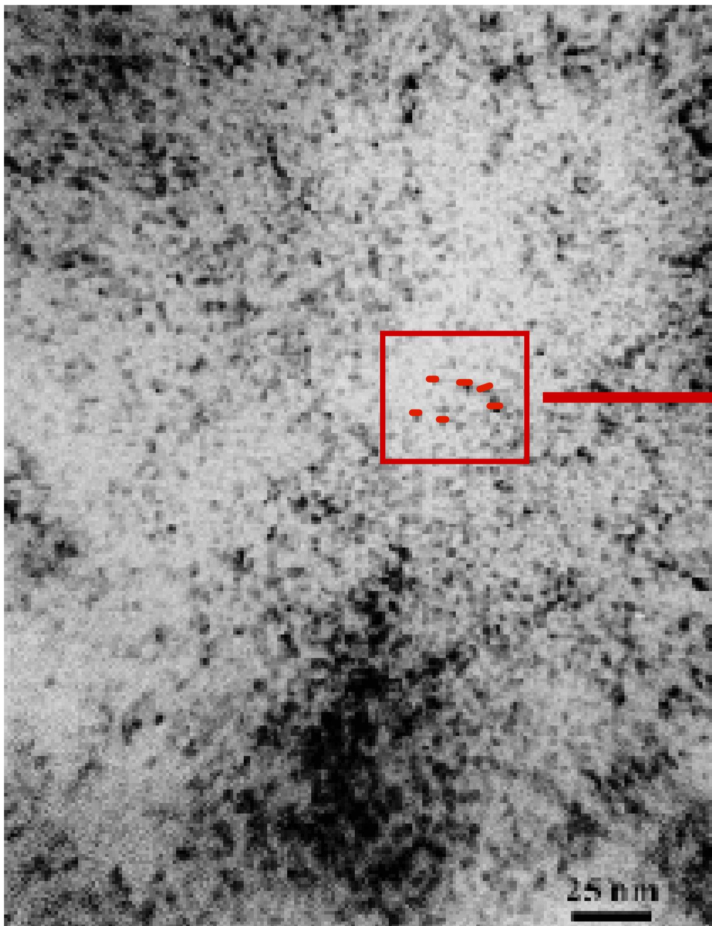
Transmission Electron Microscopy

- Cd/Se nanoparticles
- Organic ligand shell shows low contrast
- Structure
- Morphology
- Size

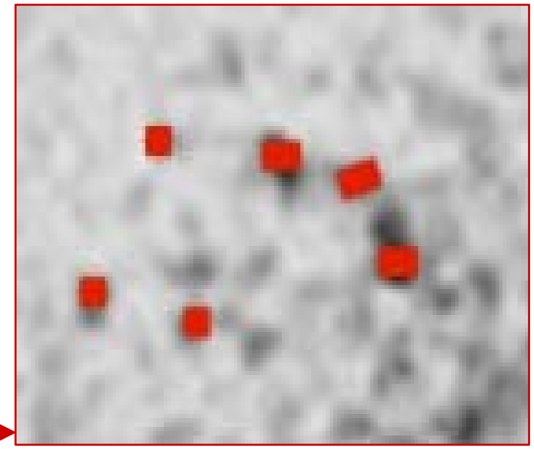


TEM Analysis

The size of the particles were determined by observation of more than 200 particles from a TEM picture.



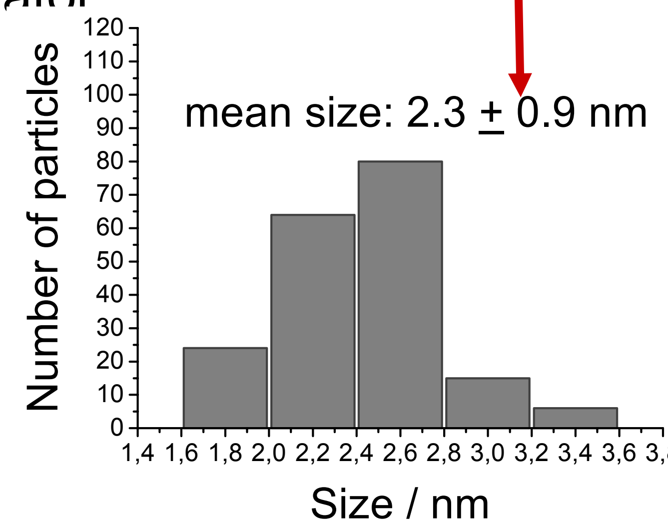
TEM



Adobe Illustrator

mm	nm
x	y

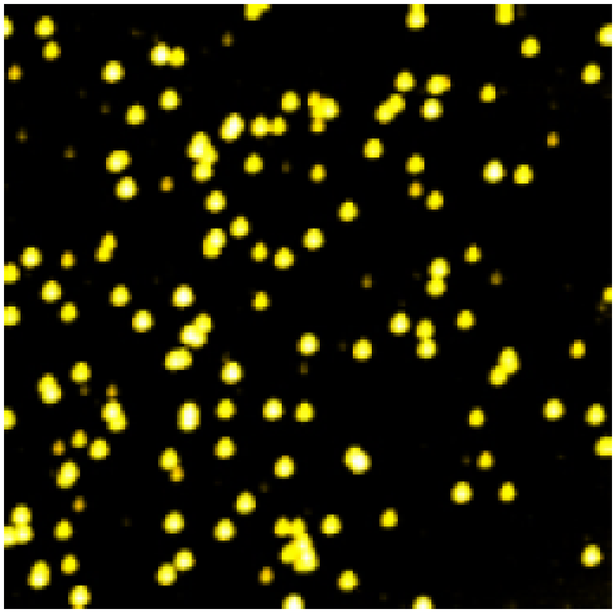
Origin



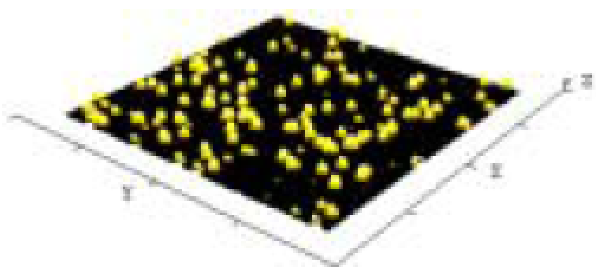
AFM Analysis

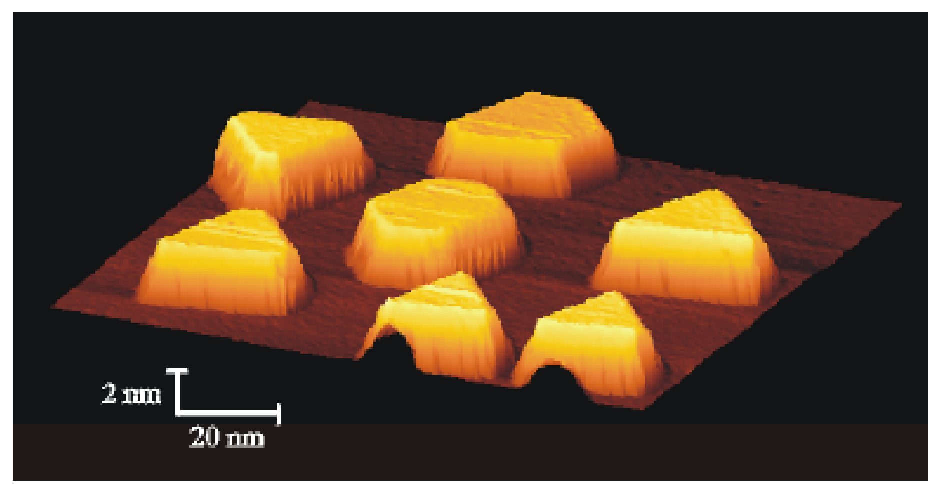
- Individual particles can be visualized:
  - length
  - Width
  - Height
  - Morphology
  - Surface texture
- Can distinguish between different materials
- Provide spatial distribution on material topographies

(a) 2D topography image



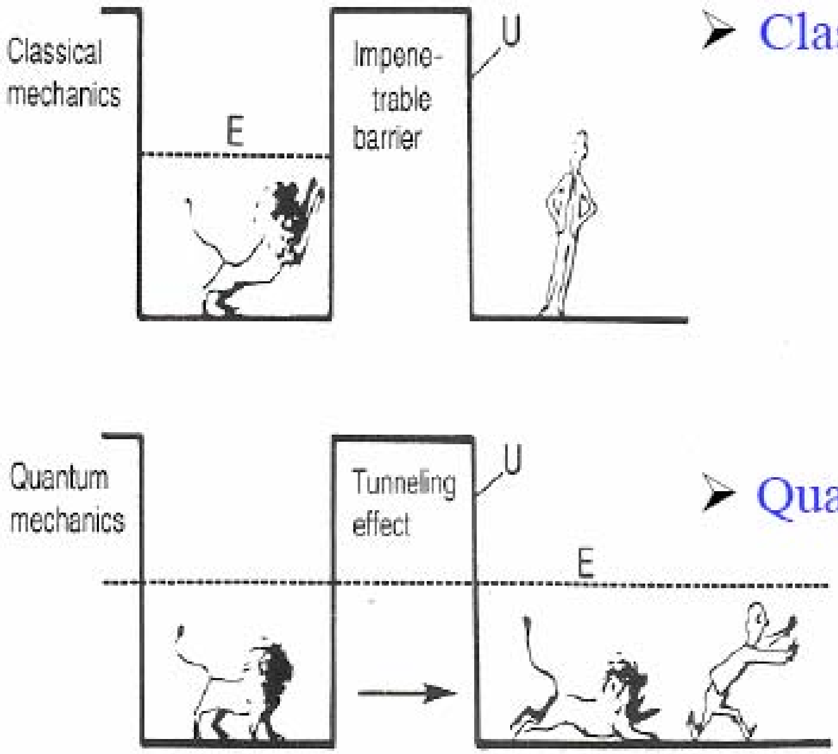
(b) 3D topography image



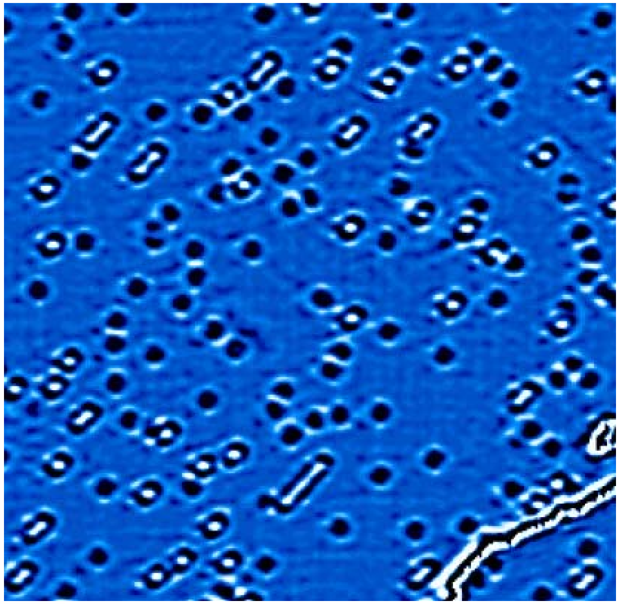


Scanning Tunneling Microscopy

- Tunneling of electrons



- Classical mechanics
- Quantum mechanics



Oxygen on Ru

Future

1st generation:

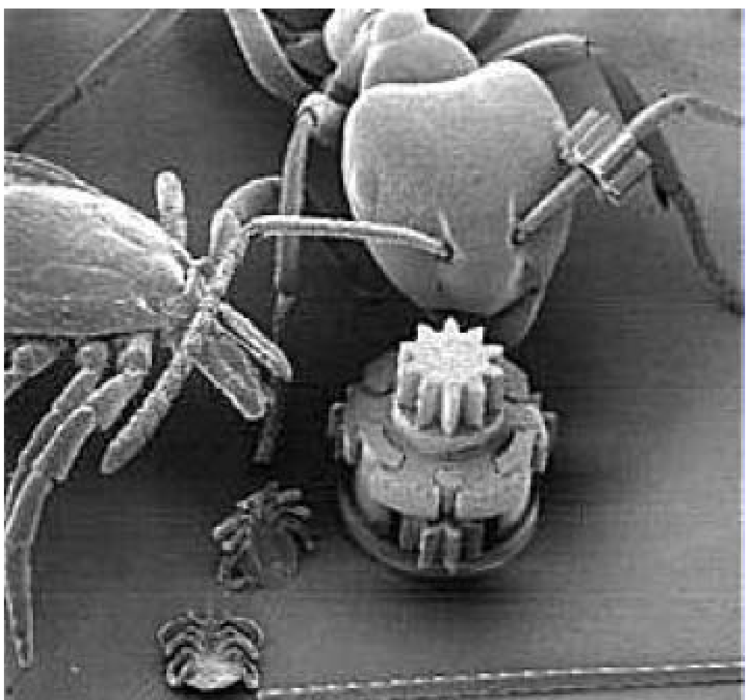
passive nanostructures: coatings, nanoparticles, nanostructured, materials, ceramics

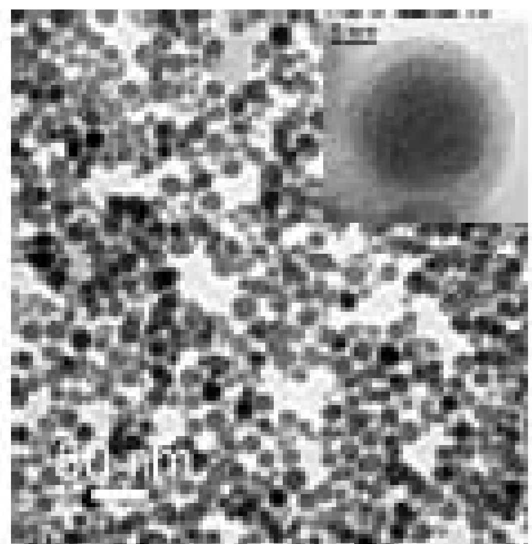
2nd generation:

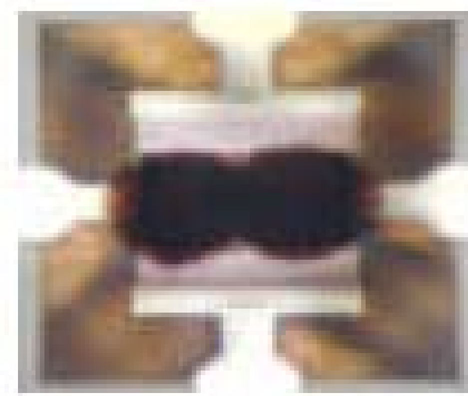
active nanostructures: gas sensors, medicine,

3rd generation:

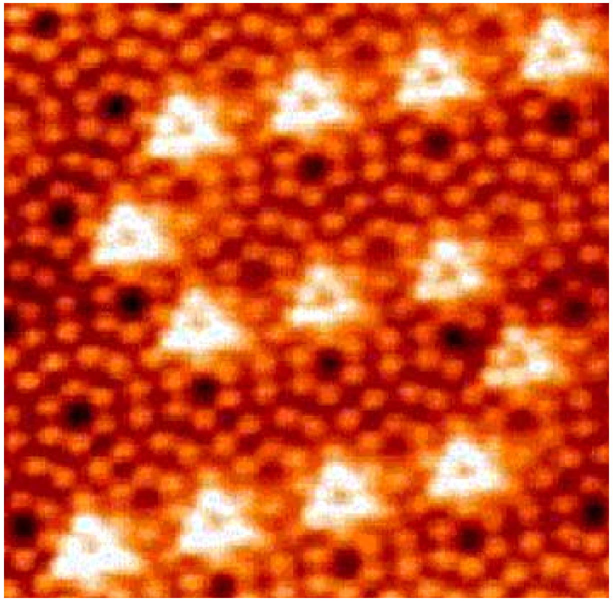
3D-nanosystems with assembling techniques (2010)







Thank you for your attention

Question  ?