Nanoparticle Technology
focus on gas phase processing

J. Ruud van Ommen
Product & Process Engineering (**cheme.nl/ppe**)
Dept. of Chemical Engineering
Delft University of Technology, the Netherlands
j.r.vanommen@tudelft.nl

JMBC course Particle Technology 2019

With input from: A. Schmidt-Ott, N. de Jaeger, and several others

Basic properties of nanoparticles

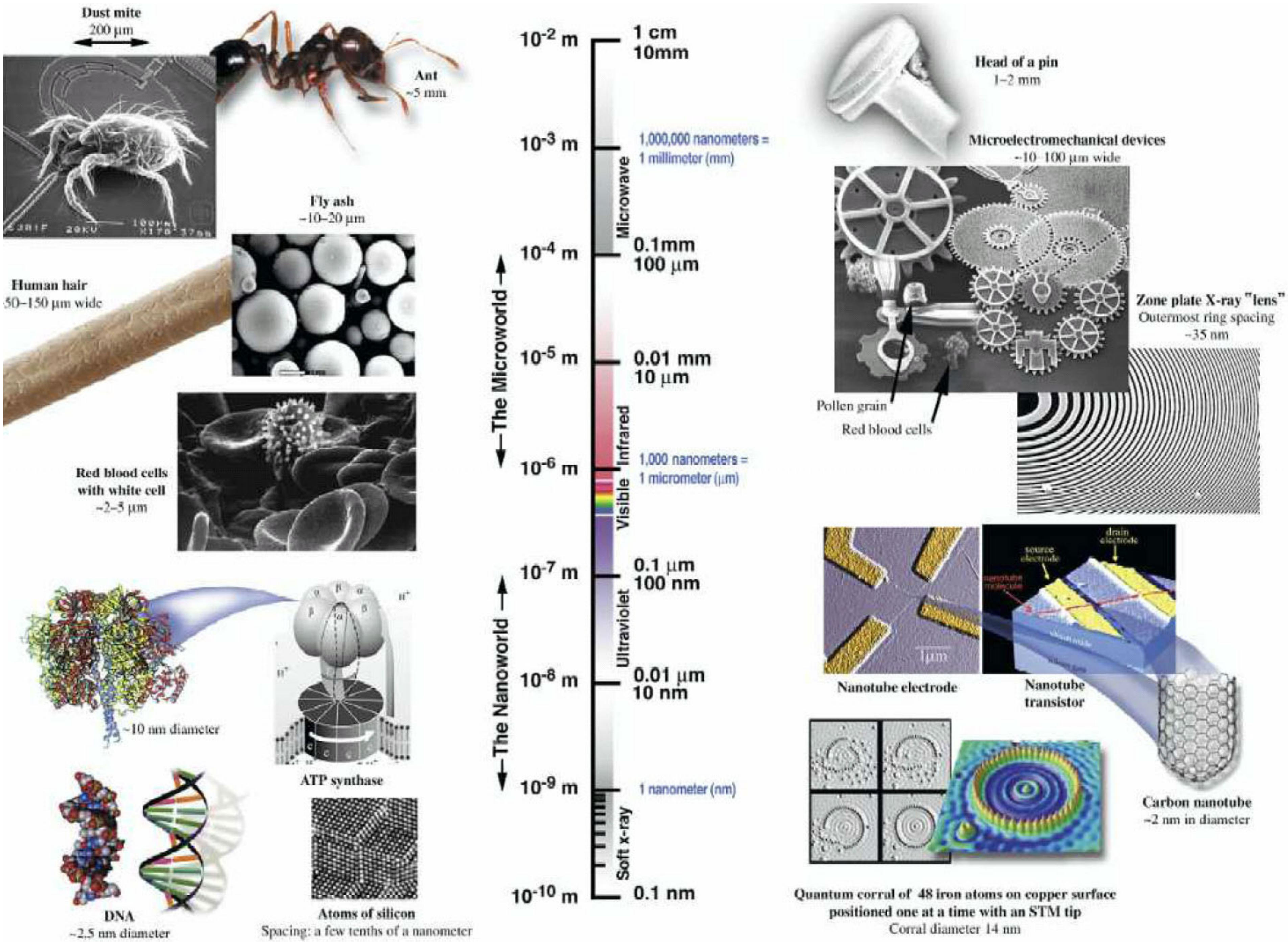
Gas phase production of nanoparticles

Sizing & forces on single particles

Particle-particle forces

Particle coating

Applications


Dust mite
200 µm
Ant
~5 mm
Fly ash
~10–20 µm
Human hair
50–150 µm wide
Red blood cells
with white cell
~2–5 µm
~10 nm diameter
ATP synthase
DNA
~2,5 nm diameter
Atoms of silicon
Spacing: a few tenths of a nanometer
10-2 m
1 cm
10mm
10-3 m
1,000,000 nanometers =
1 millimeter (mm)
Microwave
10-4 m
0.1mm
100 µm
10-5 m
0.01 mm
10 µm
Infrared
10-6 m
1,000 nanometers =
1 micrometer (µm)
Visible
10-7 m
0.1 µm
100 nm
Ultraviolet
10-8 m
0.01 µm
10 nm
10-9 m
1 nanometer (nm)
Soft x-ray
10-10 m
0.1 nm
The Microworld
The Nanoworld
Head of a pin
1–2 mm
Microelectromechanical devices
~10–100 µm wide
Pollen grain
Red blood cells
Zone plate X-ray "lens"
Outermost ring spacing
~35 nm
Nanotube electrode
Nanotube
transistor
Carbon nanotube
~2 nm in diameter
Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Corral diameter 14 nm

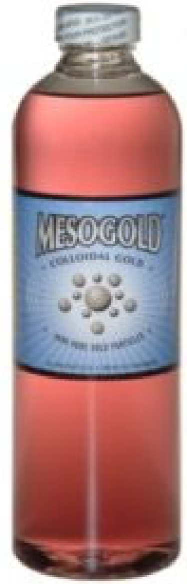
Present and future applications of nanoparticles

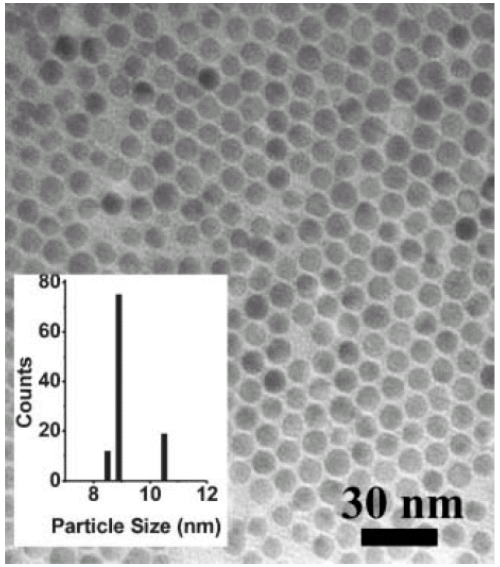
Medical diagnostics
Drugs targeted to specific cells
DNA analysis
Information storage
Refrigeration
Optical computers
Improved ceramics and insulators
Harder metals
Batteries
Hydrogen storage
Solar cells
Fuel cells
Catalysts
Chemical sensors
Paints
Sunscreen creams

What determines the properties of solid matter?

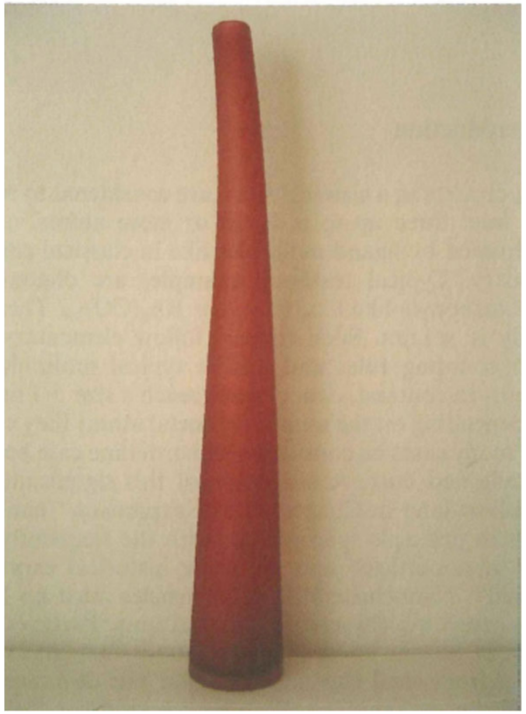
Size also determines properties!

Convert to small particles →

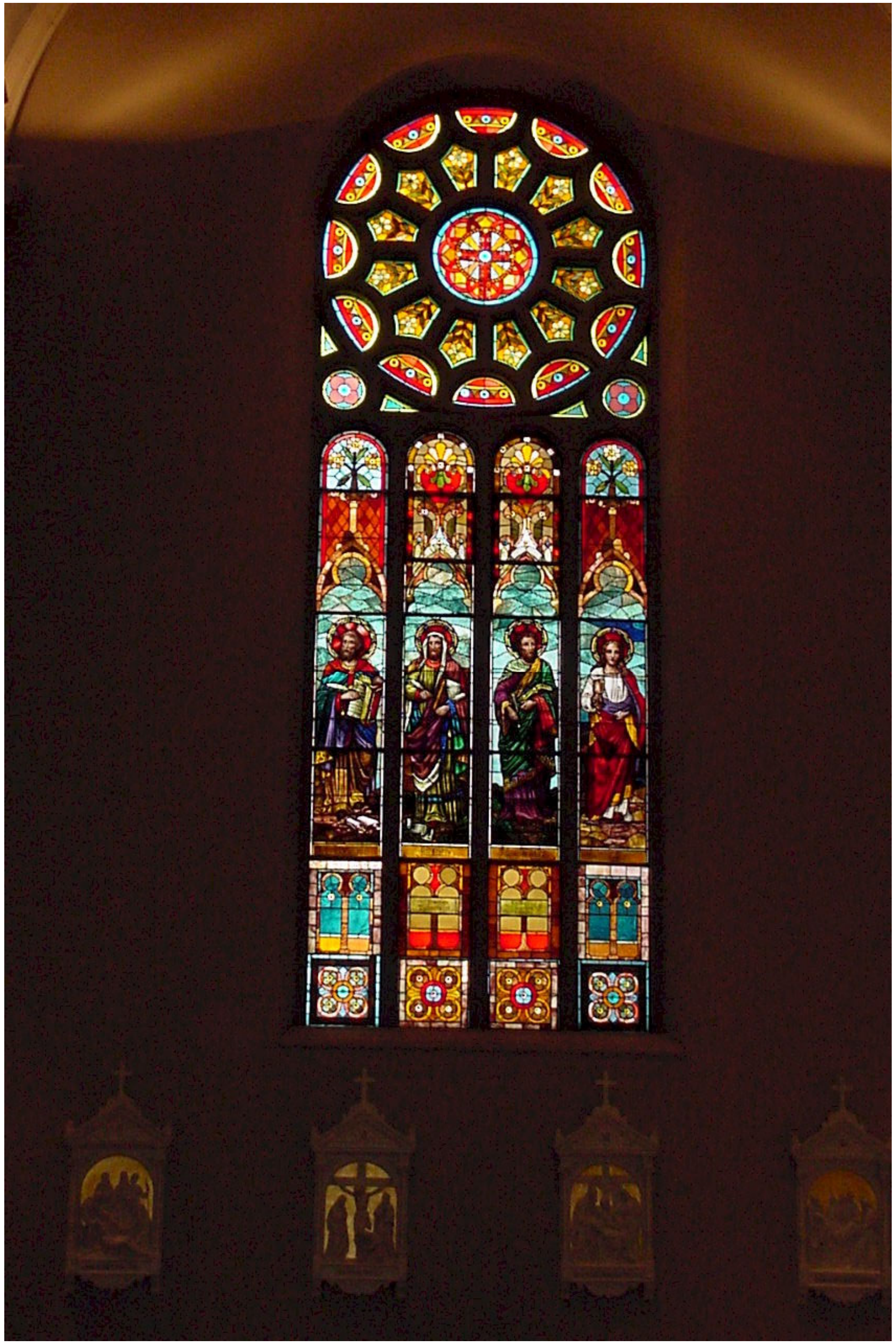




The color of gold depends on size!



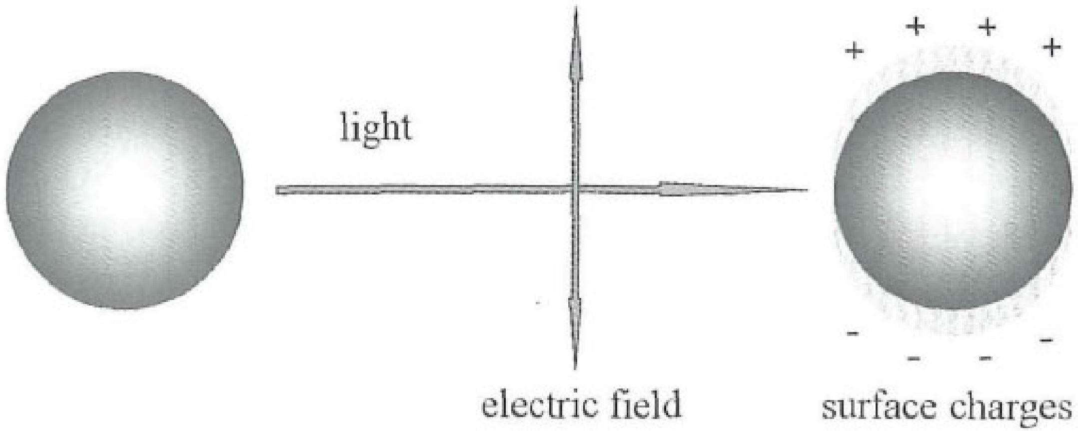
From Metal Clusters in Catalysis and Material Science, ed. By B. Corain, G. Schmid and N. Toshima, Elsevier, Amsterdam 2008



Reason for size dependence of light absorption in metal nanoparticles:

Surface plasmon resonance

Frequency of photons matches the natural frequency of oscillating surface electrons



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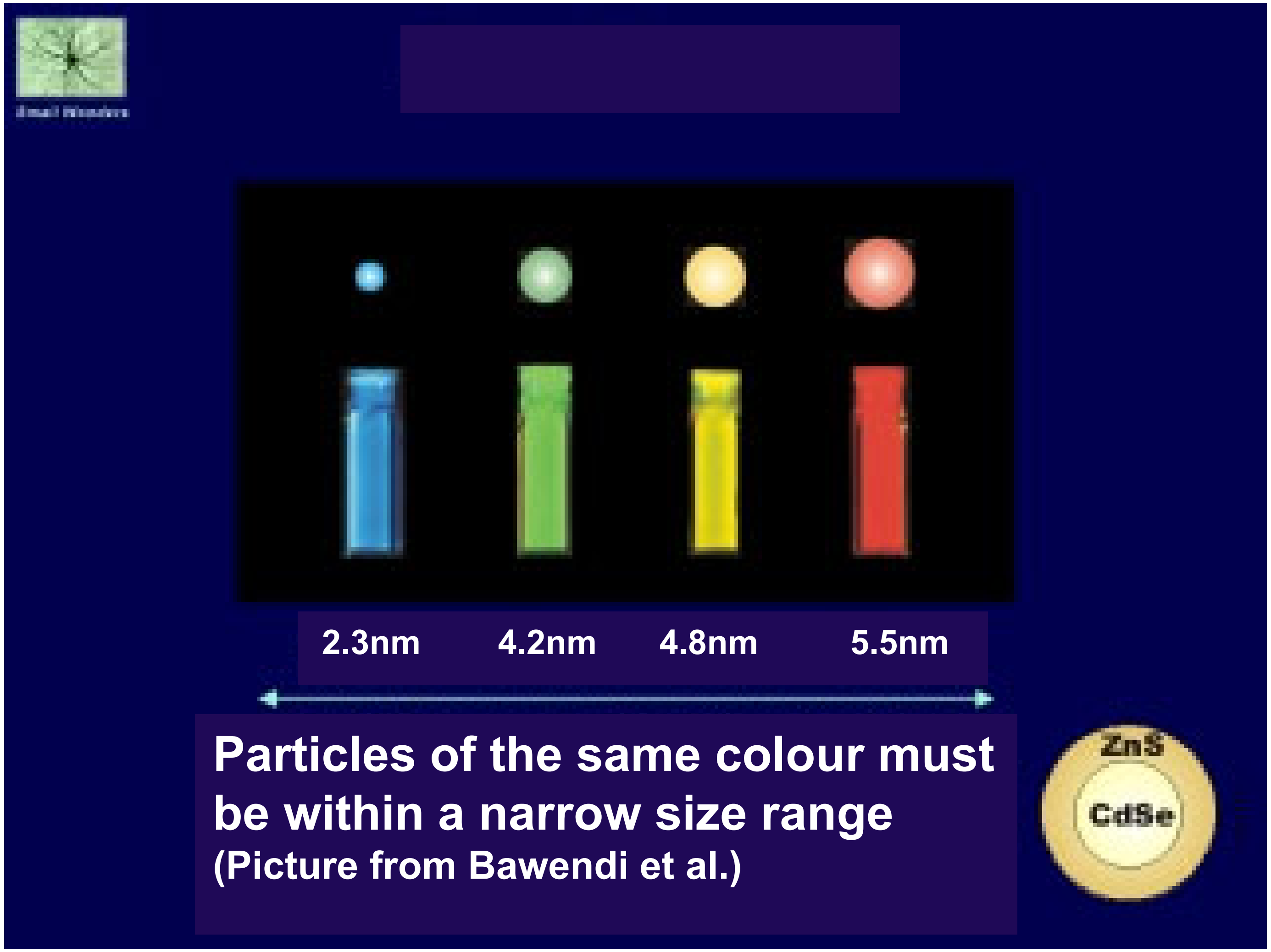
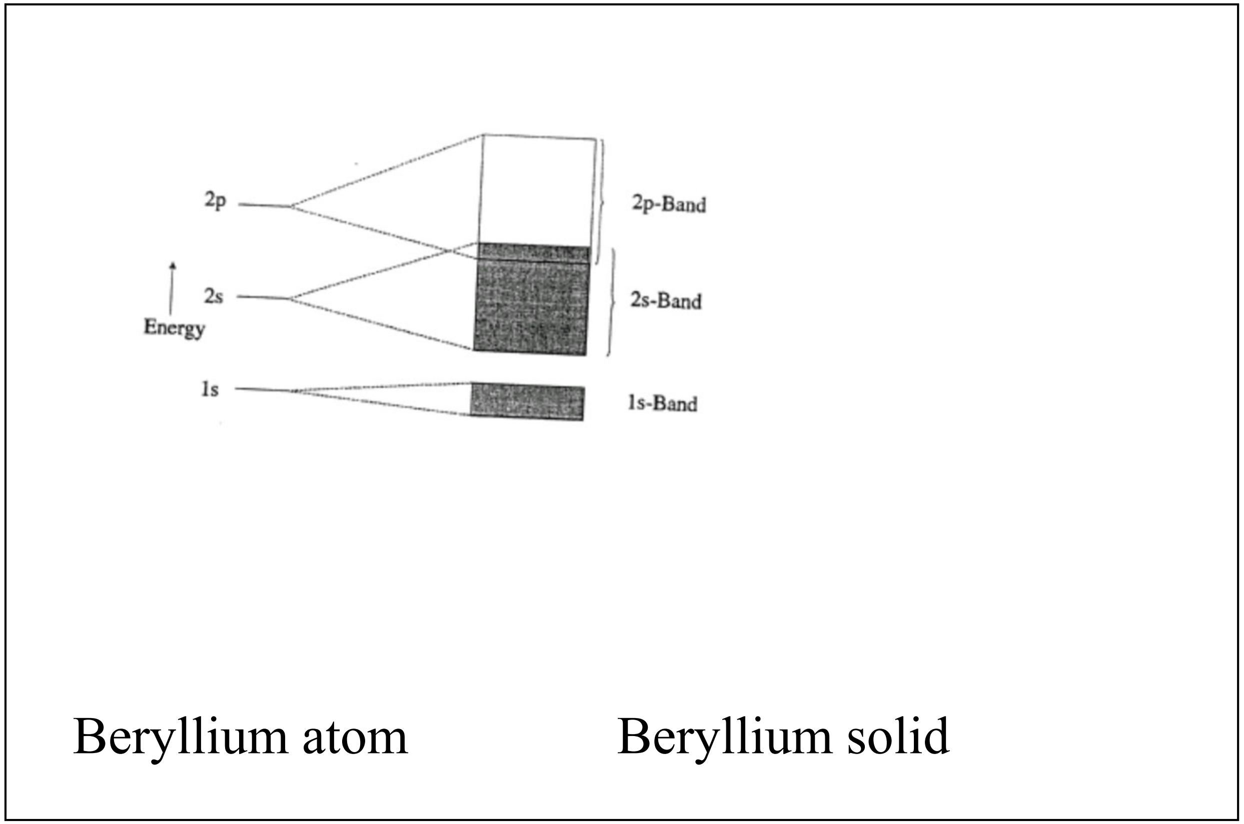
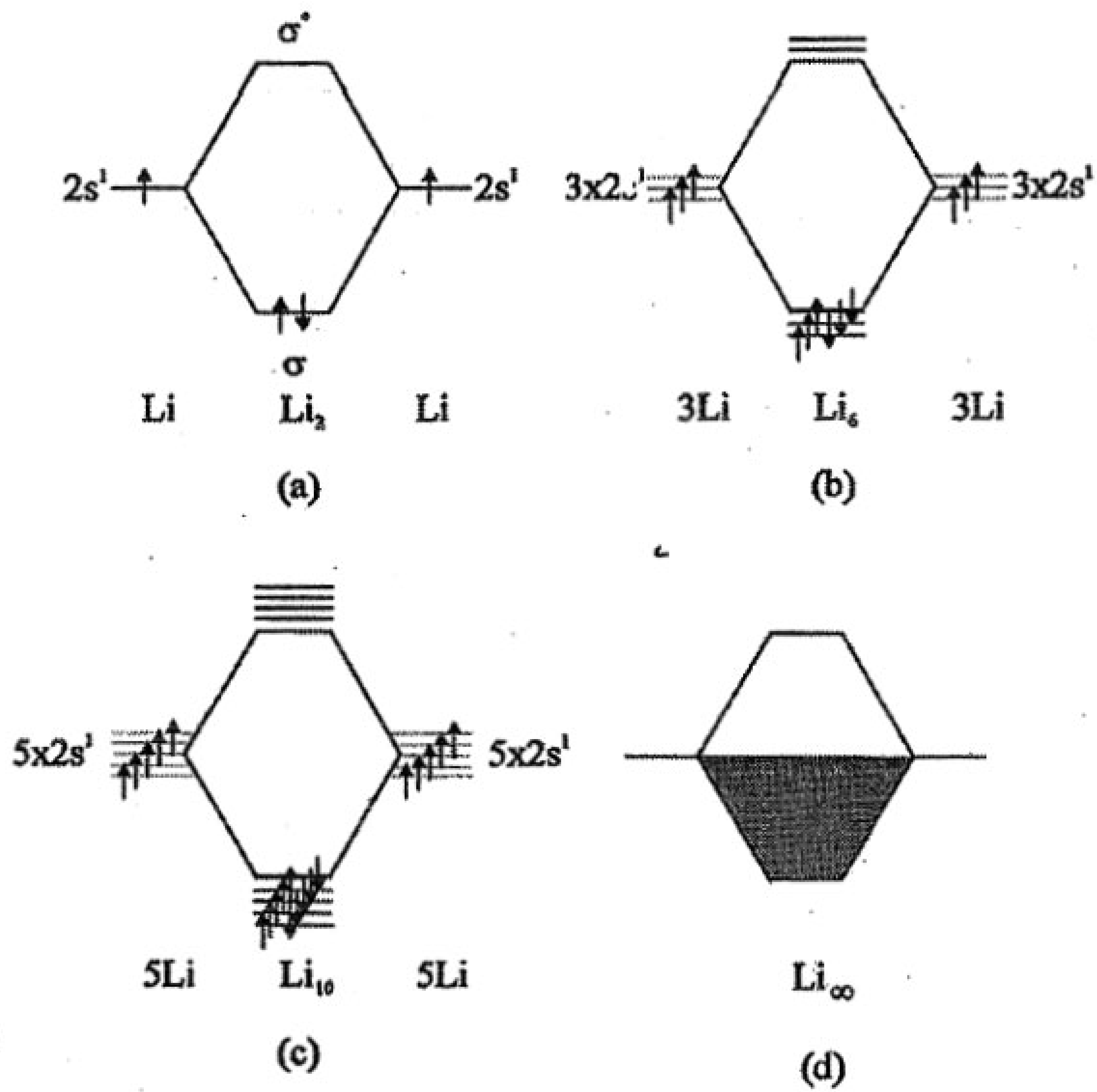
Quantum dots



Semiconductors: the band gap mainly determines optical properties, and is particle size dependent:



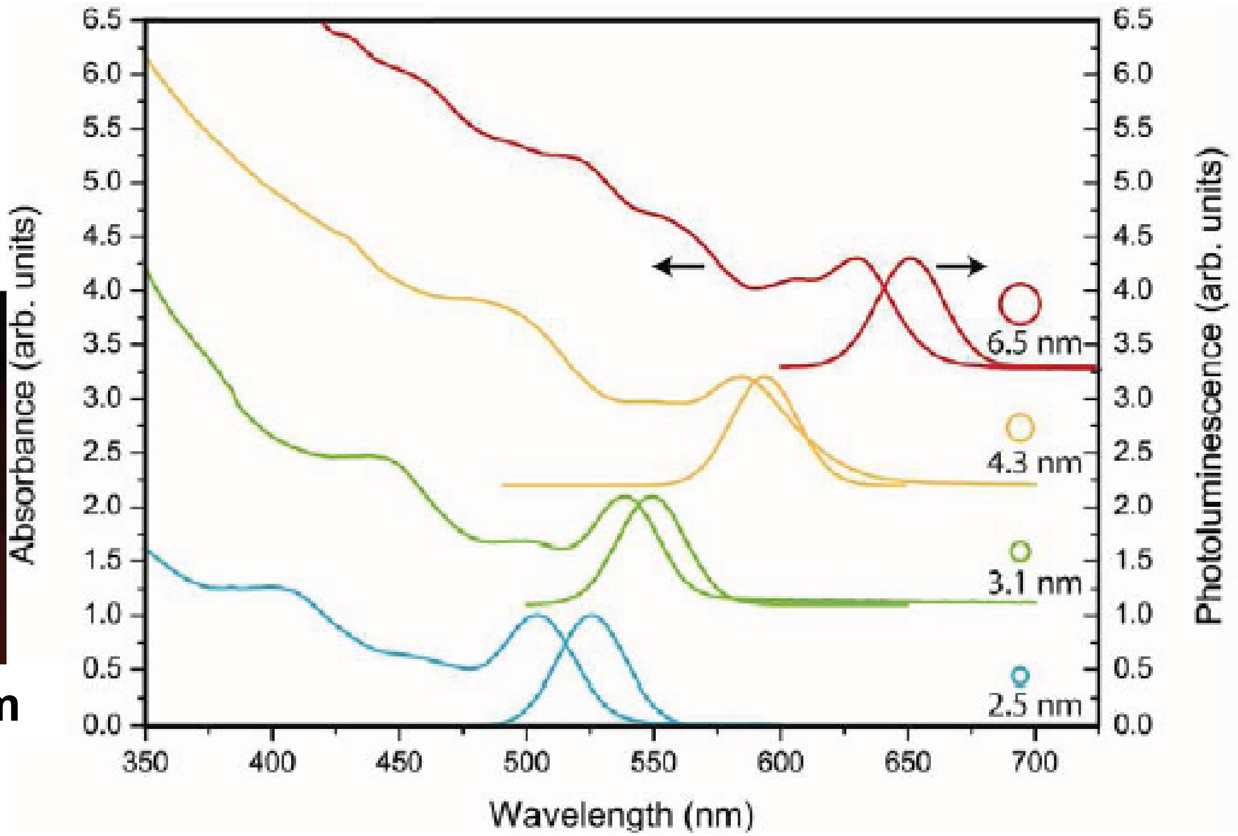
→ Very small metal particles are semiconductors!



Formation of a metallic state, exemplified by lithium.

Quantum dots

6 nm 2.5 nm

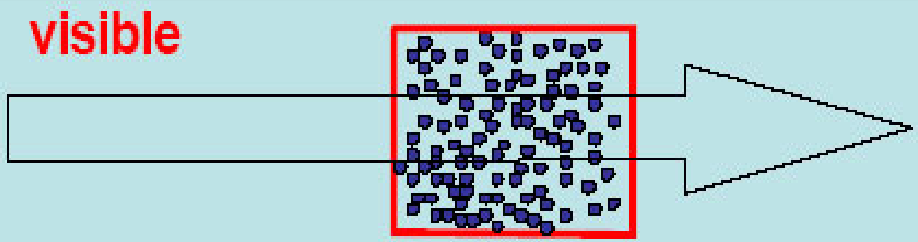


Sunscreen

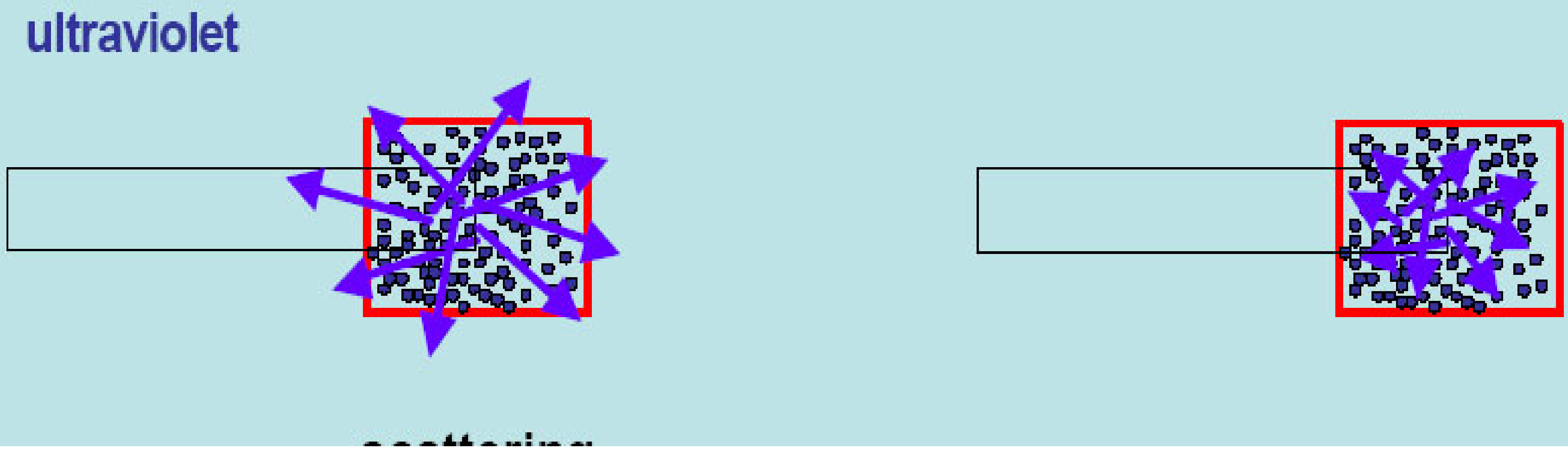
TiO_2 or ZnO nanoparticles block ultraviolet radiation but do not scatter visible light

Rayleigh scattering intensity I_{total} *:*

$$d << \lambda \quad (d : Diameter, \ \lambda : Wavelength)$$



$$I_{total} \propto d^6 / \lambda^4$$



3 reasons to "go nano":

Curiosity!

Structuring in the nano regime leads to more possible properties of matter, and these are continuously tunable!

The smaller the faster!

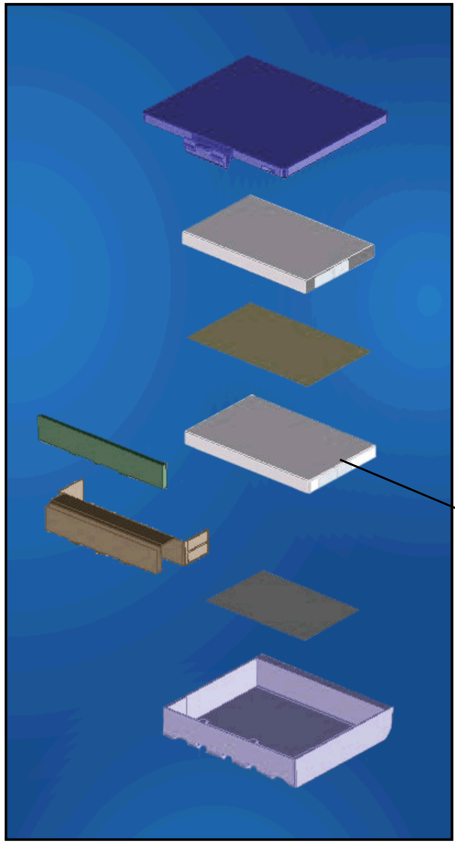
As the particle size becomes smaller: Diffusion becomes faster!

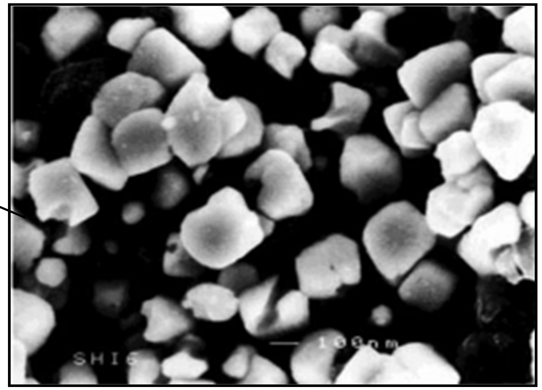
Mean square diffusion length over time t: $\overline{x^2} = 4Dt$

Diffusion length ≈ particle radius → $t \propto R^2$

$$\frac{t(10nm)}{t(10\mu m)} = 10^6$$

Nanoparticulate Electrode of Lithium-Ion Battery: Charging in 1 Minute!





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Nanoparticle Based Chemical Sensor

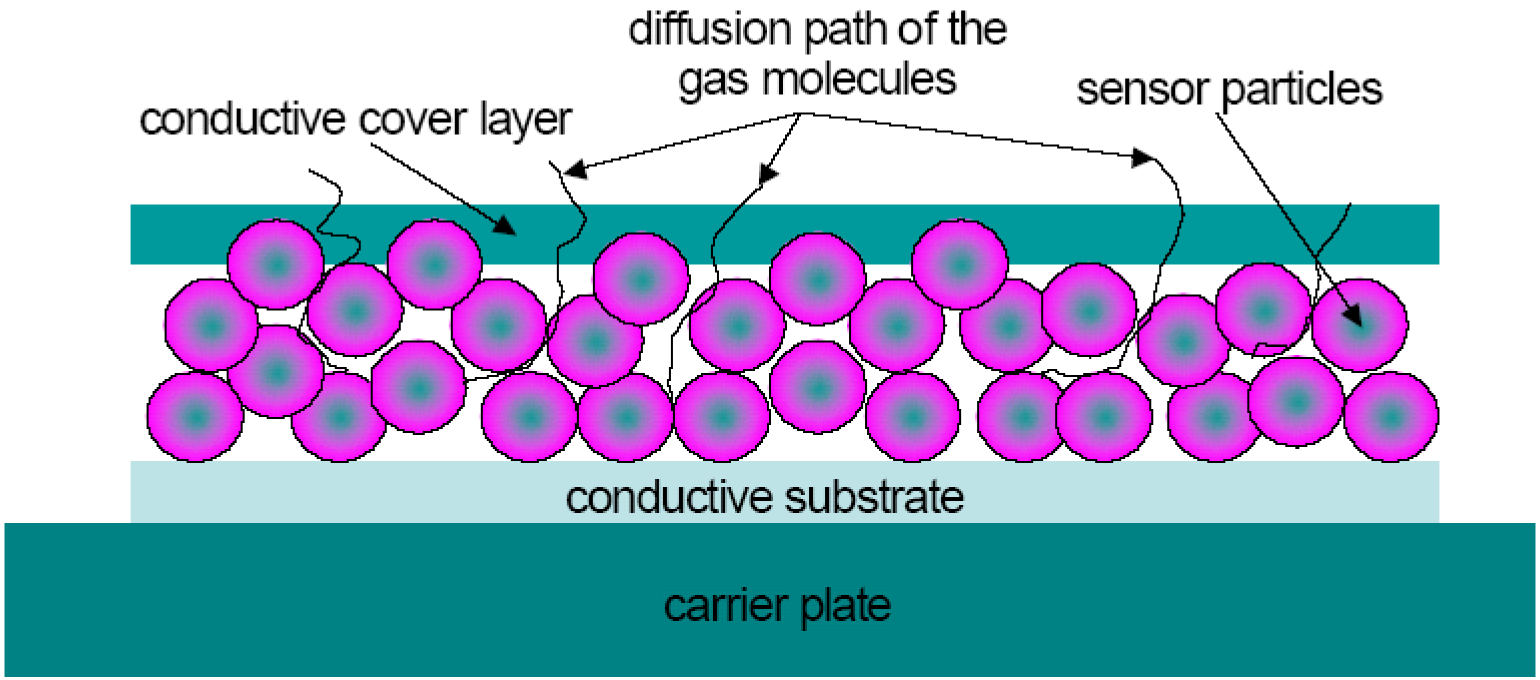
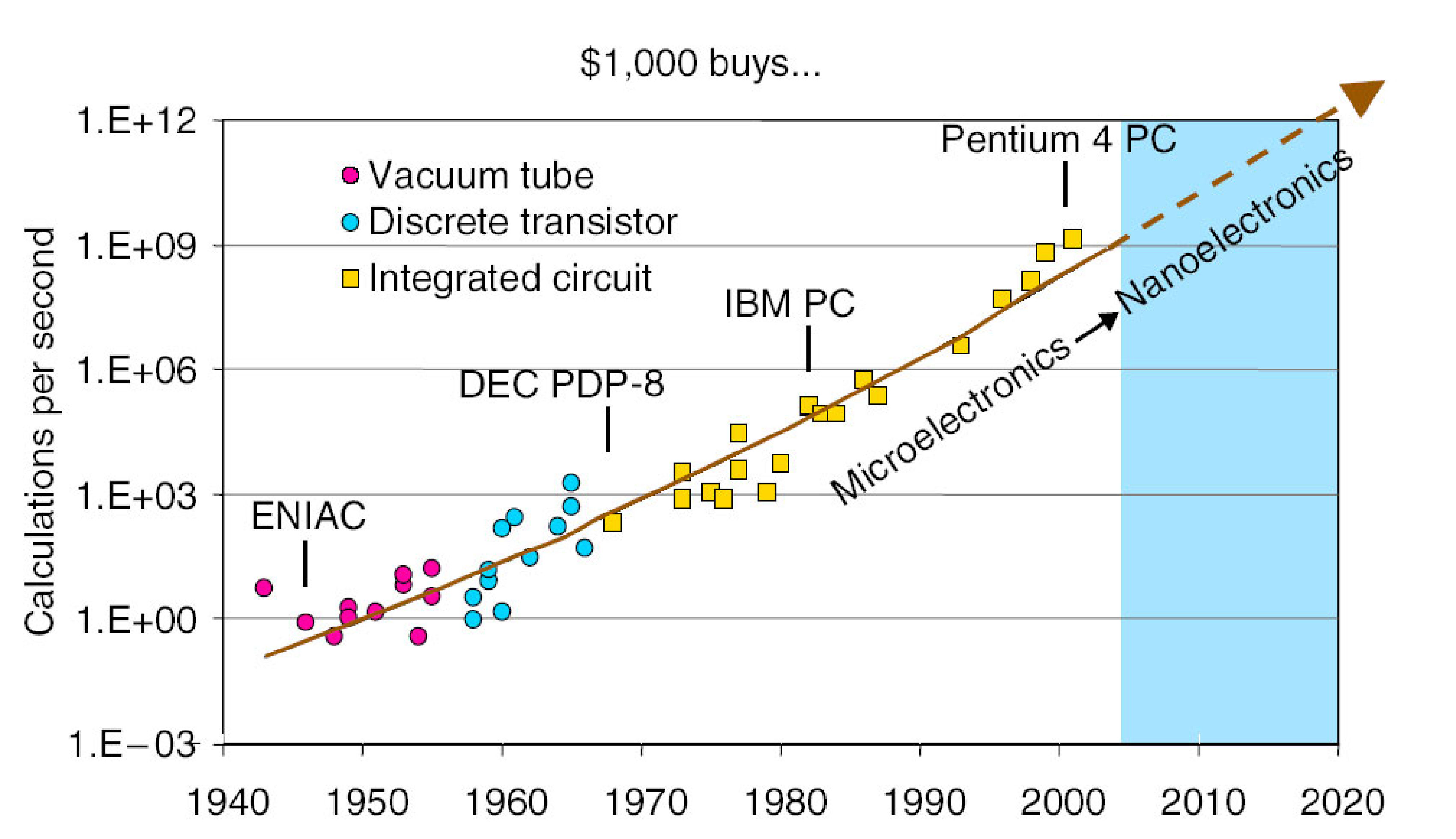


FIGURE 1.1.1 The increasing miniaturization of components in computing and information technology. Adapted from R. Kurzweil, *The Age of Spiritual Machines*, Penguin Books, 1999.



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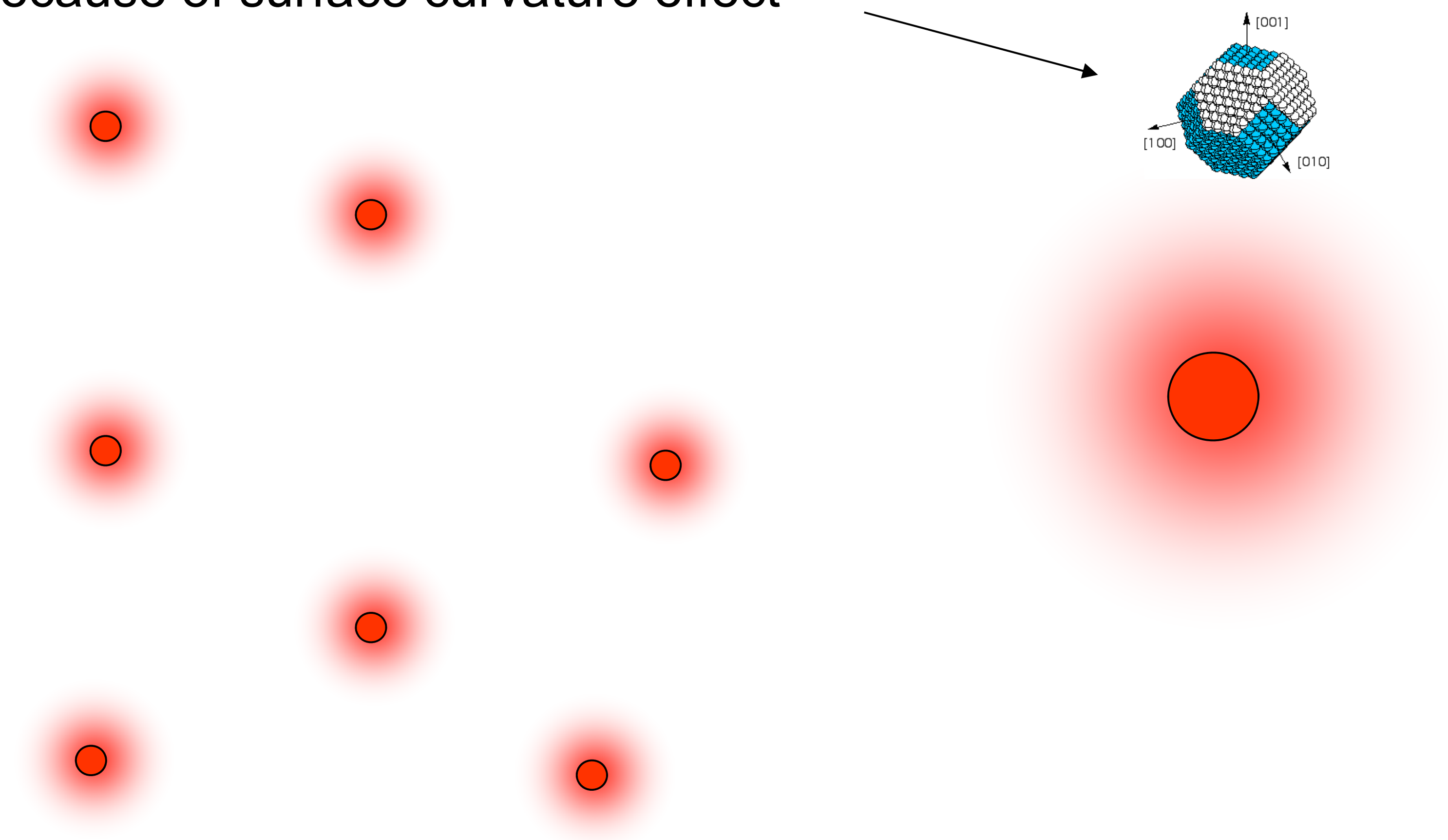
Many small particles dissolve faster than few large ones of the same volume

a) because of larger joint surface area

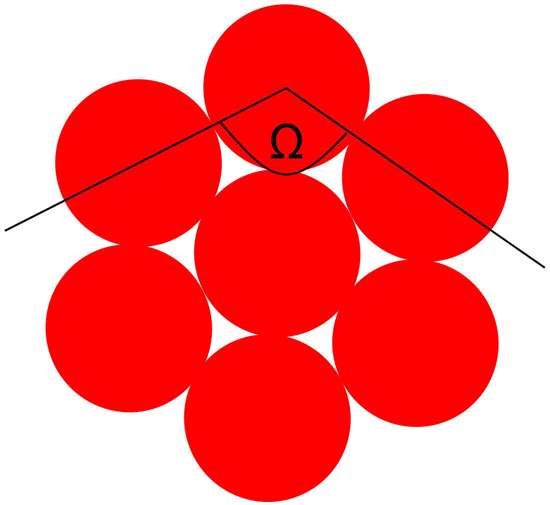
a) because of surface curvature effect

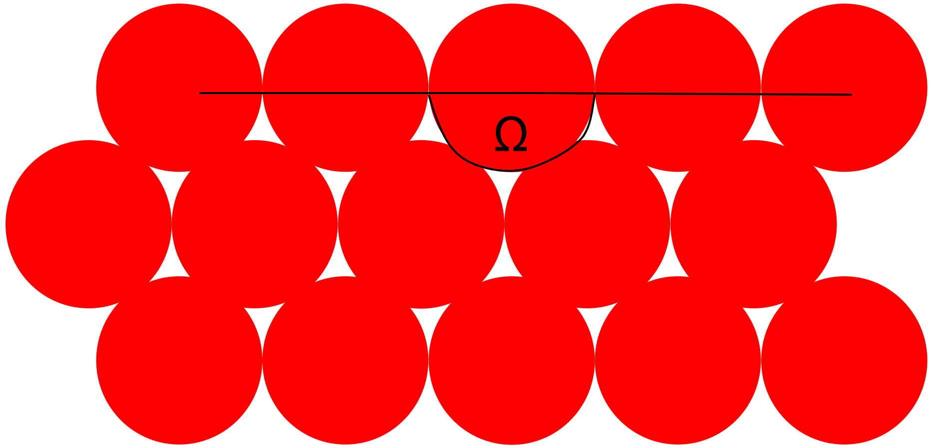


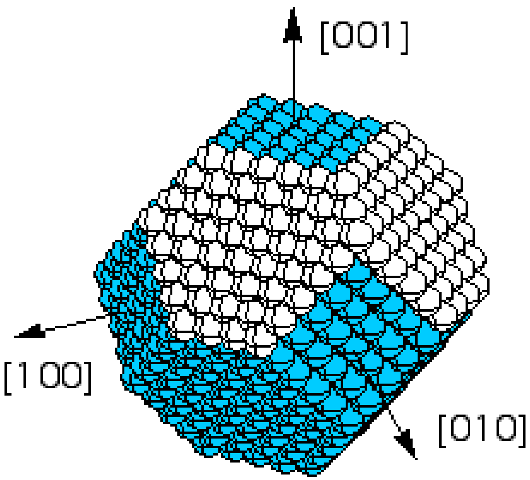
Particle smaller → coordination number smaller → binding energy smaller →

vapor pressure larger

melting point smaller







Co particle (M. Jamet et al. 2000)

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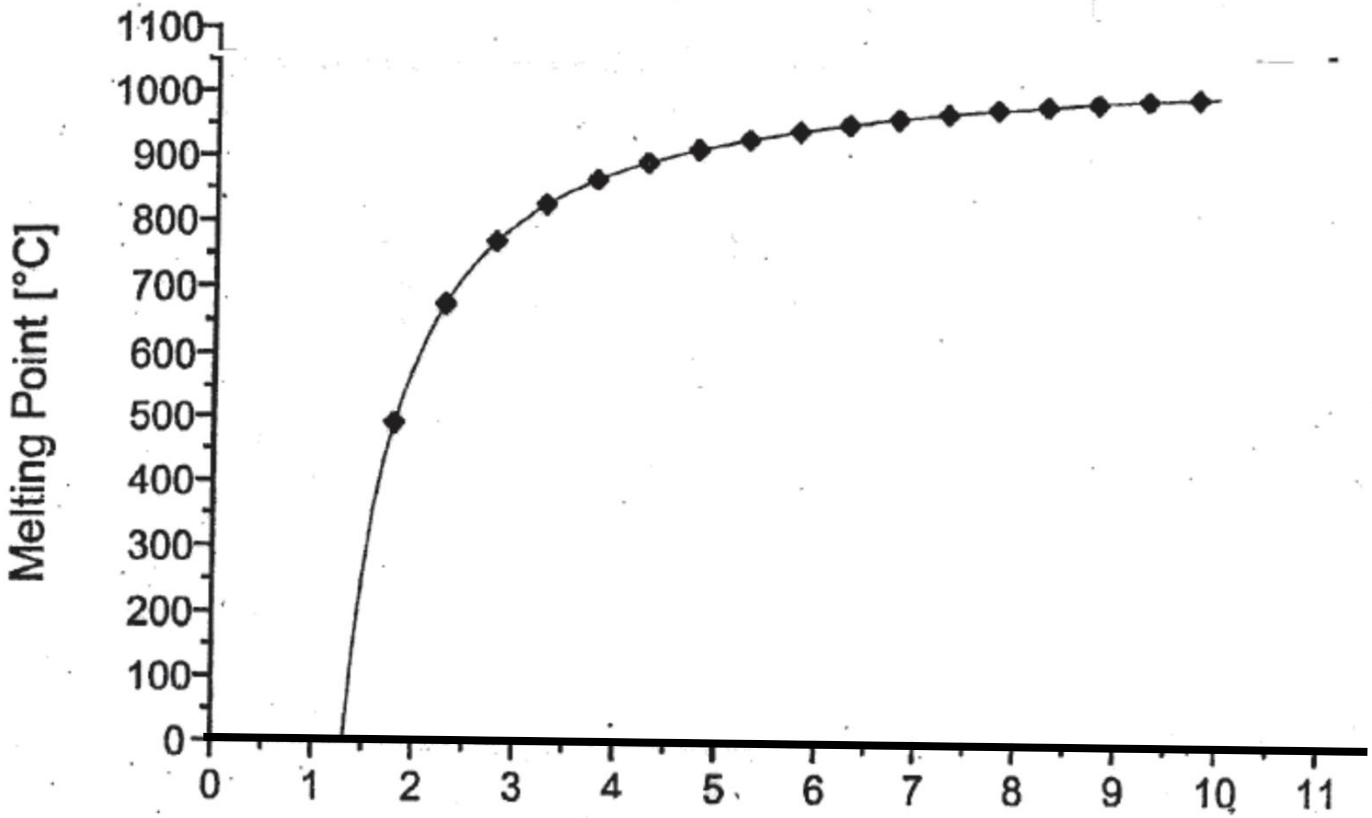
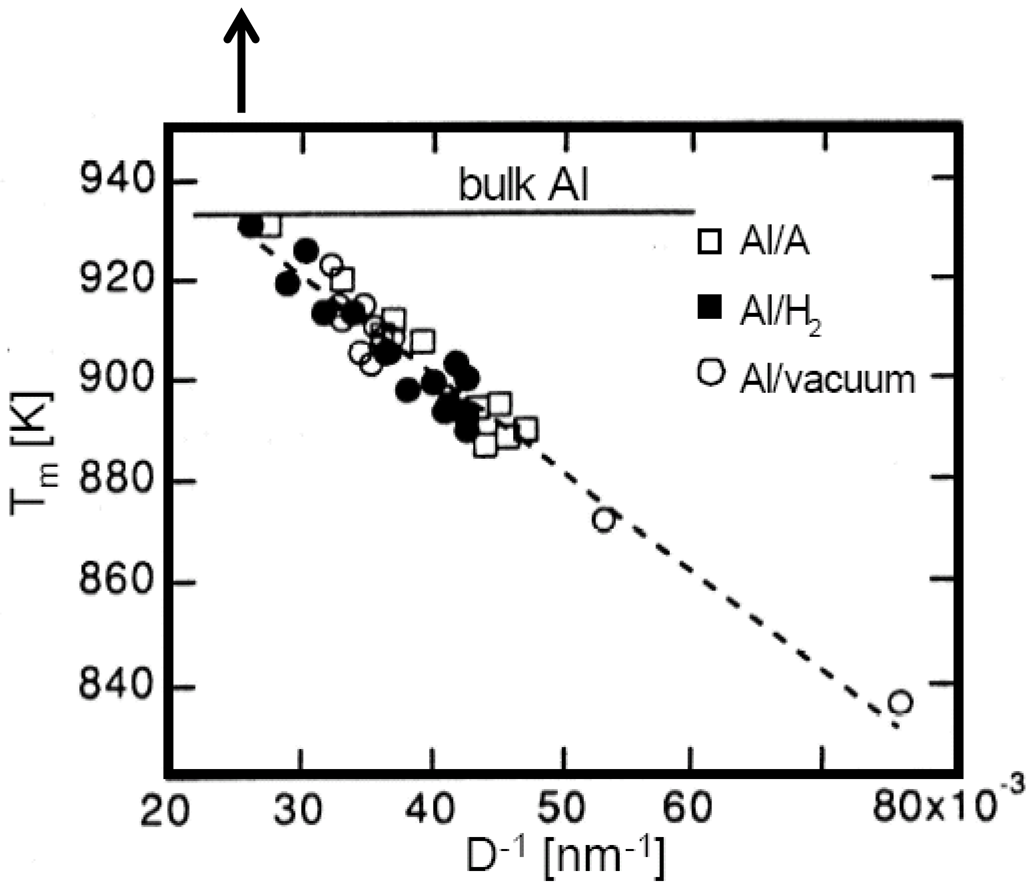
The relation between the melting point of Au particles and their size (Buffat et al.)



Particle Radius [nm]

~40 nm



R. Eckert, Caltech, 1993

Melting point of Al vs. particle size

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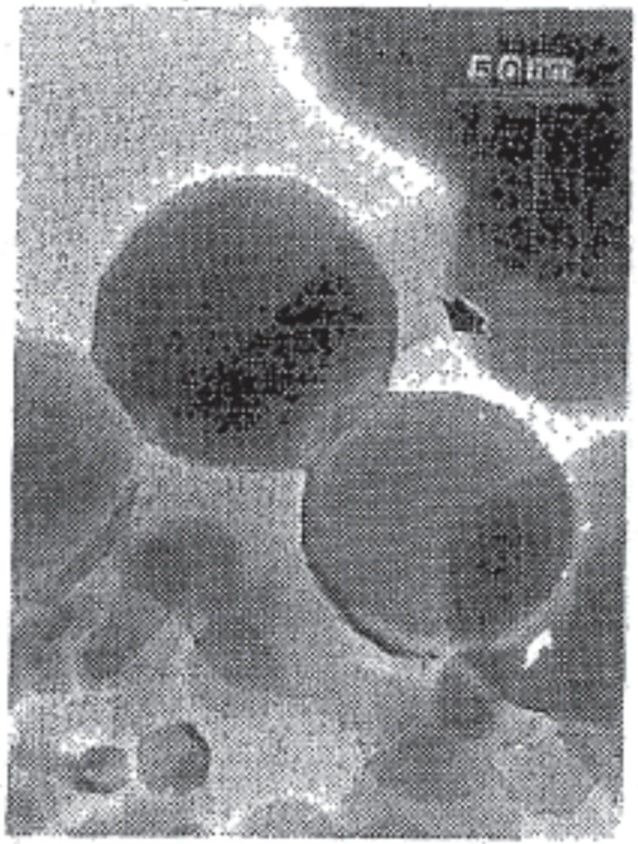


Two alumina nano particles heated at 1350 °C for 2 h coalesced partially to form a neck (Fusing point of Al_2O_3 > 2000 ° C)

Vapor pressure p of a small droplet (particle) in terms of saturation ratio:

$$\frac{p}{p_s} = \exp \frac{4\gamma M}{\rho R T D_p}$$

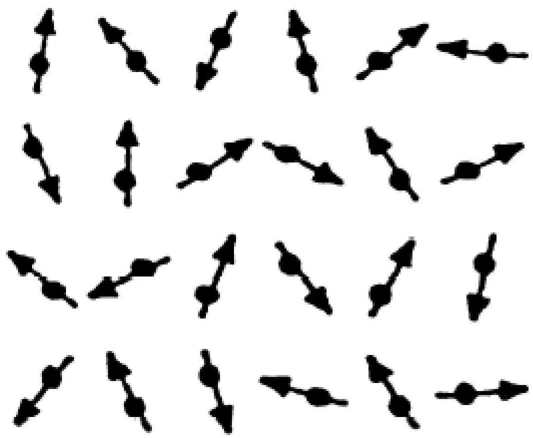
γ: Surface tension
M: Molar weight
ρ: Density
R: Gas constant
T: Temperature
Dp : Particle diameter
V_m : Molar volume

$$\frac{M}{\rho} = V_m \quad \longrightarrow$$

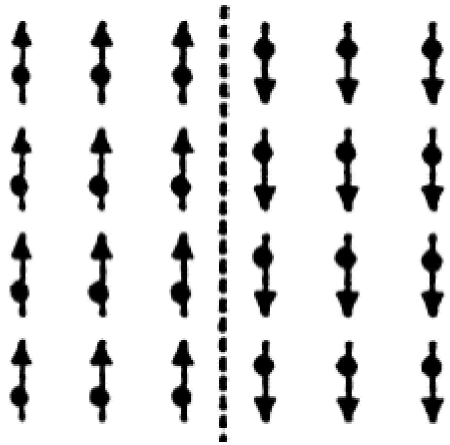
$$\frac{p}{p_s} = \exp \frac{\frac{4\gamma}{D_p} V_m}{RT}$$

$$\frac{4\gamma}{D_p} = \Delta p$$! (pressure difference inside/outside particle)

Forms of magnetism



paramagnetic



ferromagnetic

superparamagnetic

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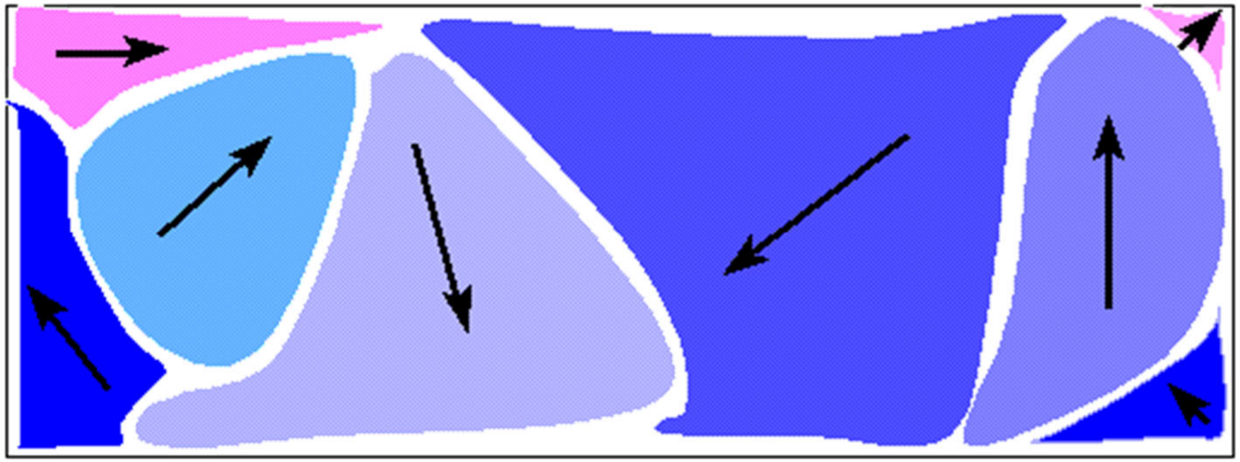
Ferromagnetism



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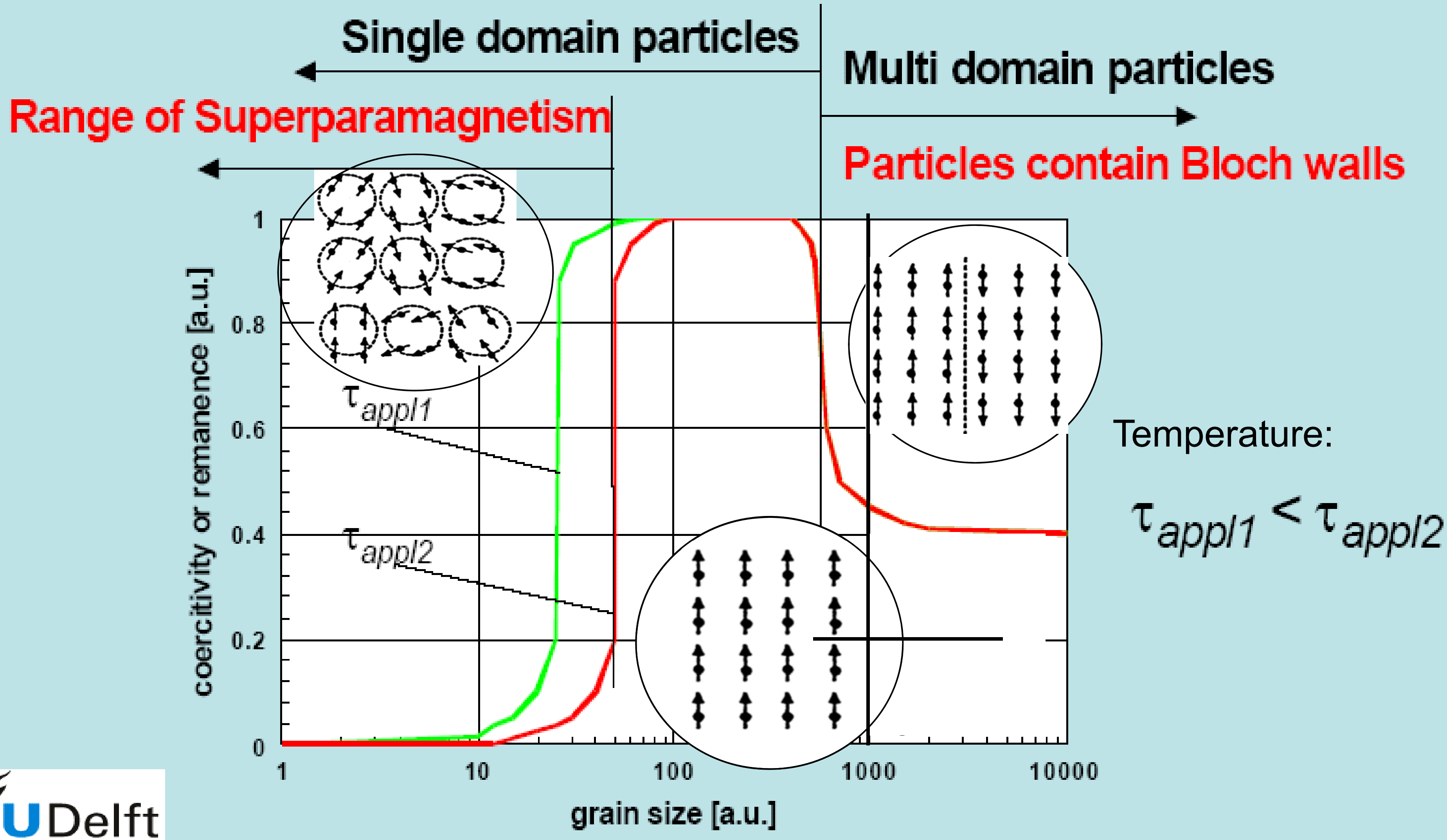
Remanence and Coercitivity of Ferrites as Function of the Particle Size

(from D. Vollath)



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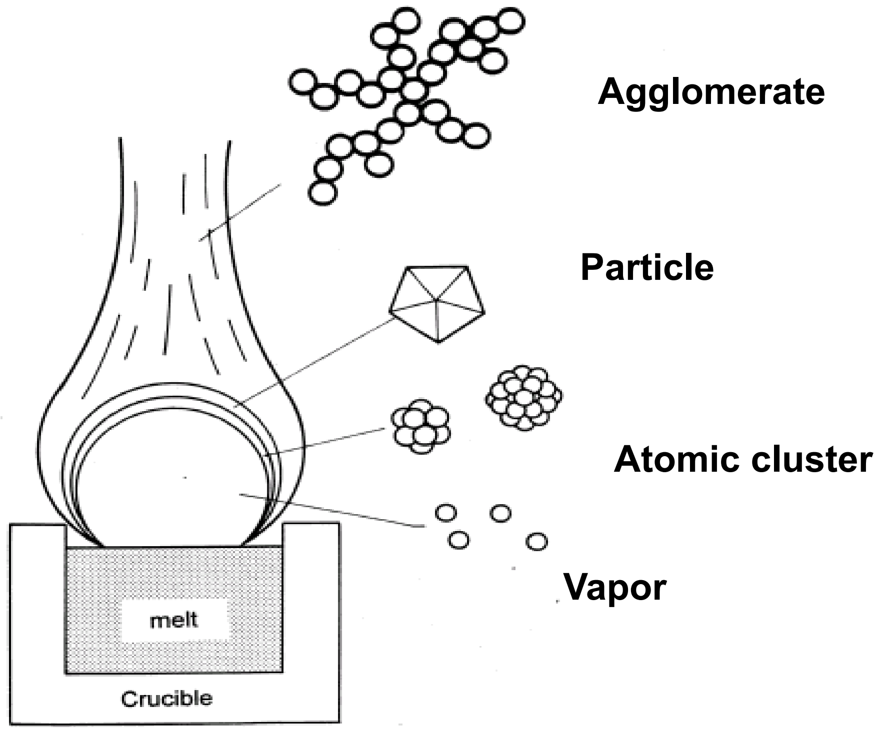
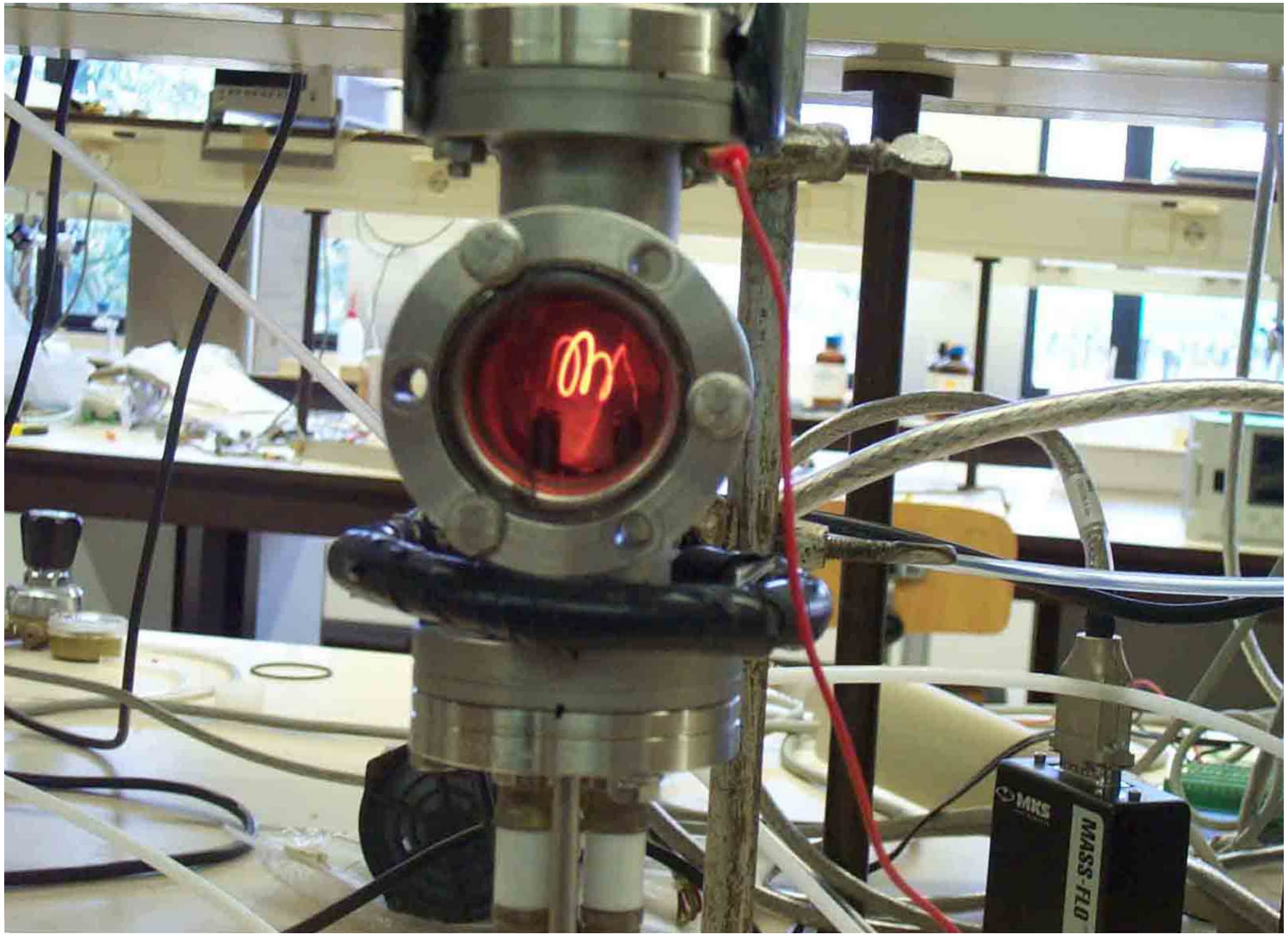
Particle Production by Homogeneous Nucleation of Vapor



Glowing Wire Generator



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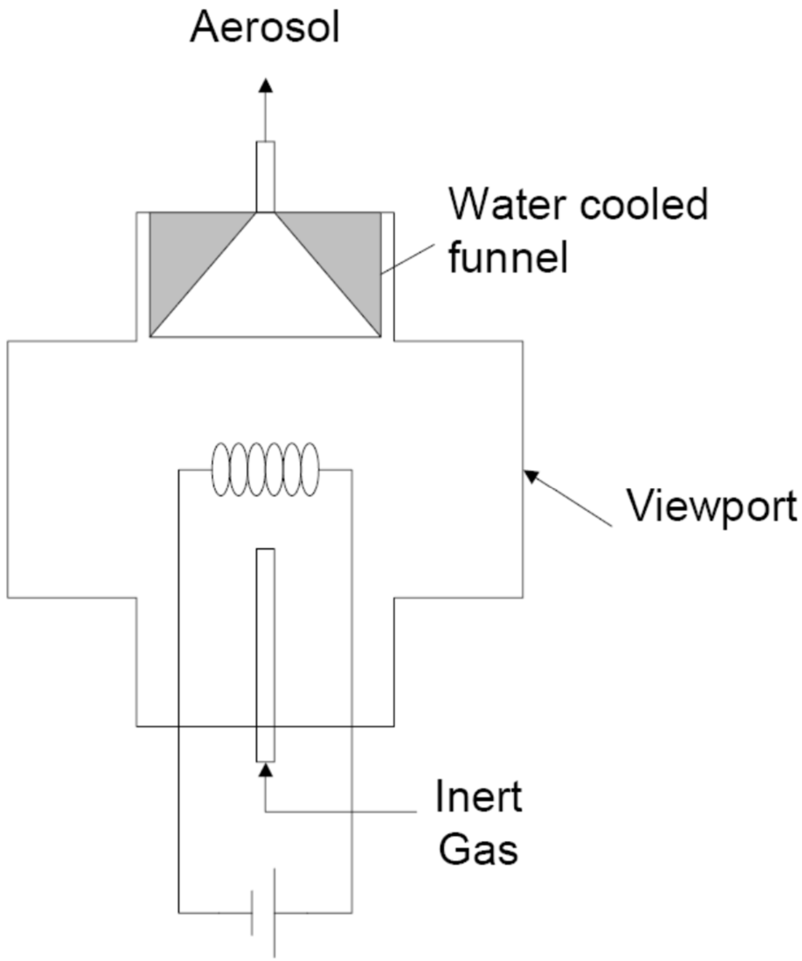
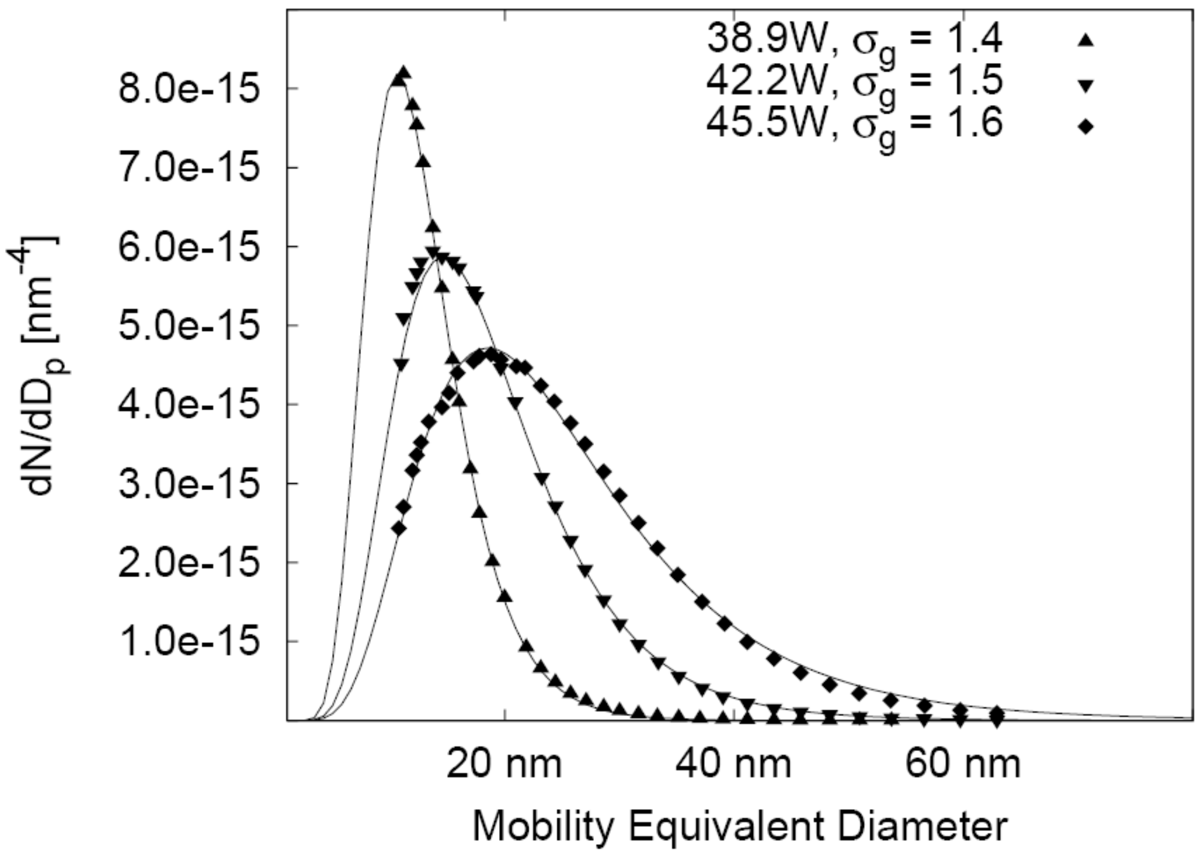
Hot Wire Particle Generator



Material is evaporated from a resistively heated wire and subsequently quenched by a gas stream.

Peinike et al., J. Aerosol Science 37 (2006) 1651 – 1661

Size Distributions on Ag Nanoparticles from a Hot Wire: Variation of the Wire Temperature



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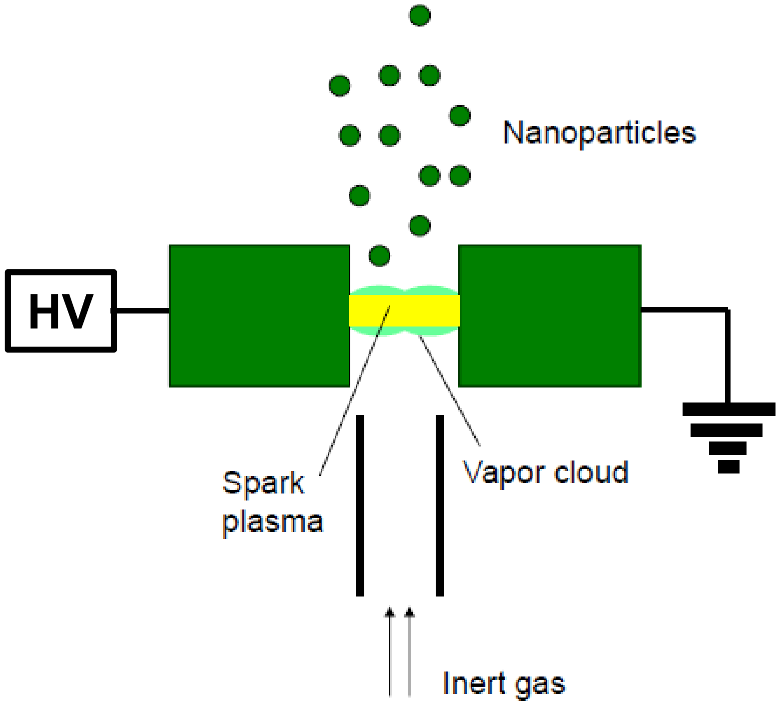
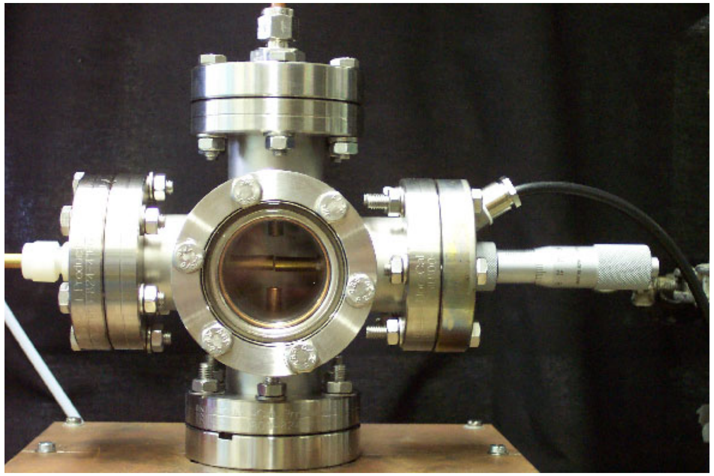
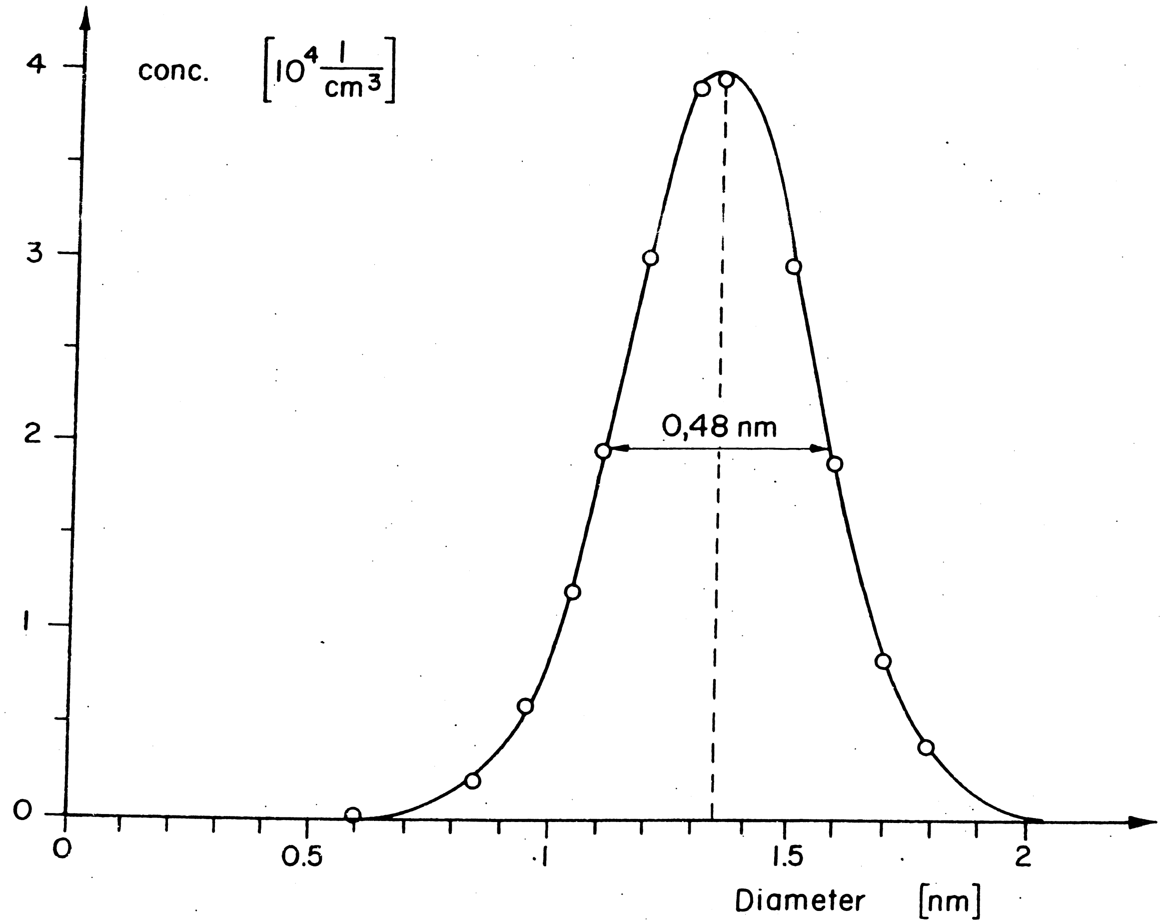
Particle Generation by Spark Discharge





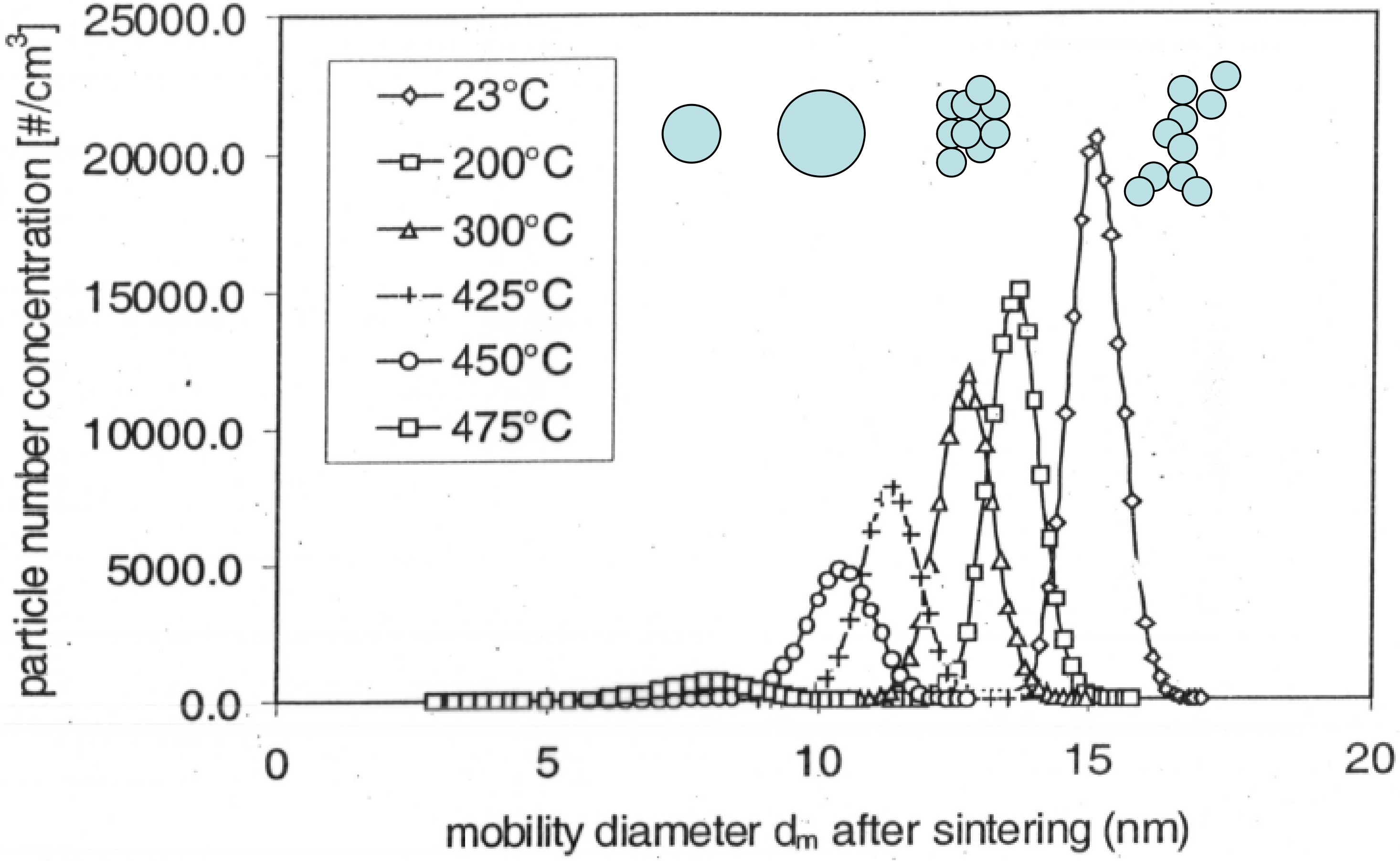
- Produces high-purity particles similar to laser ablation
- Works for any conducting and semiconducting material
- Production of mixed particles possible!
- A high fraction of the particles are charged

Size distribution of gold particles produced by spark discharge



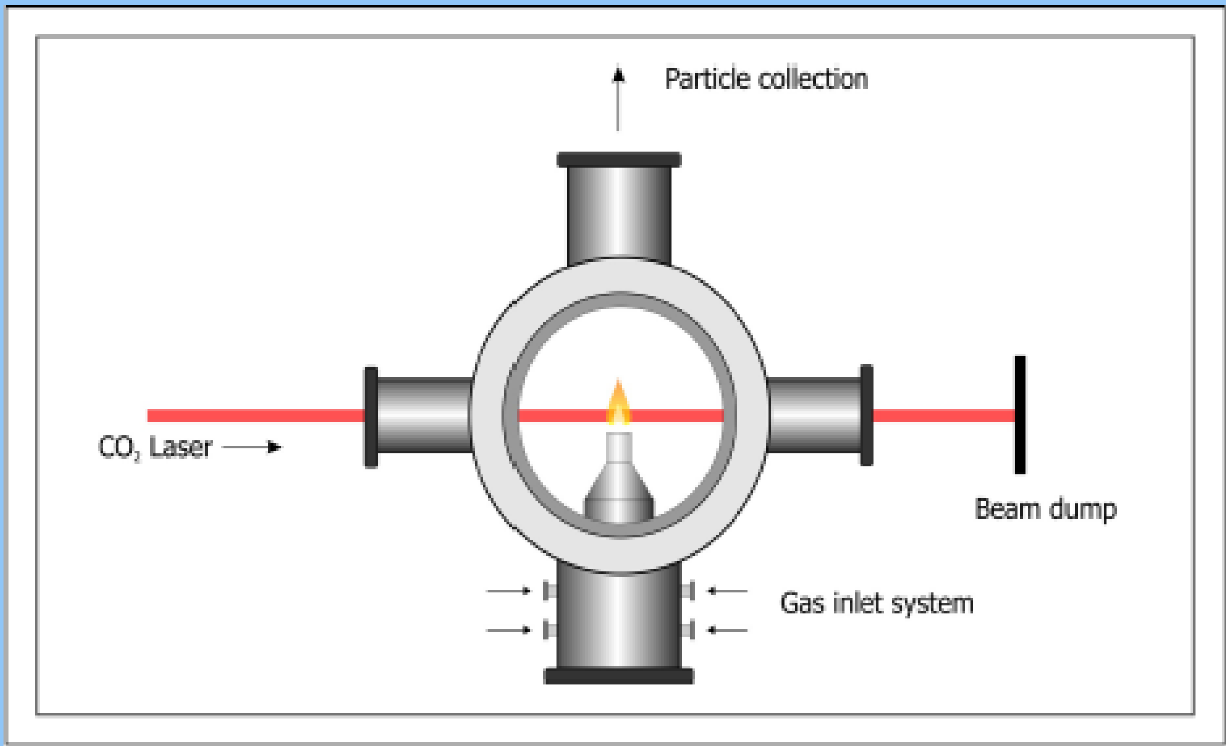
Producing monocrystalline particles by heating in gas suspension

(E. Kruis et al.)



E. Kruis et al., *Size distribution of size-selected PbS nanoparticles (d_m=15 nm) as a function of sintering temperature.*

Laser pyrolysis of a volatile precursor



Precursors: e.g. SiH_4 , Ferrocene, …

Advantage: Large particle production rate (kilograms/day) possible

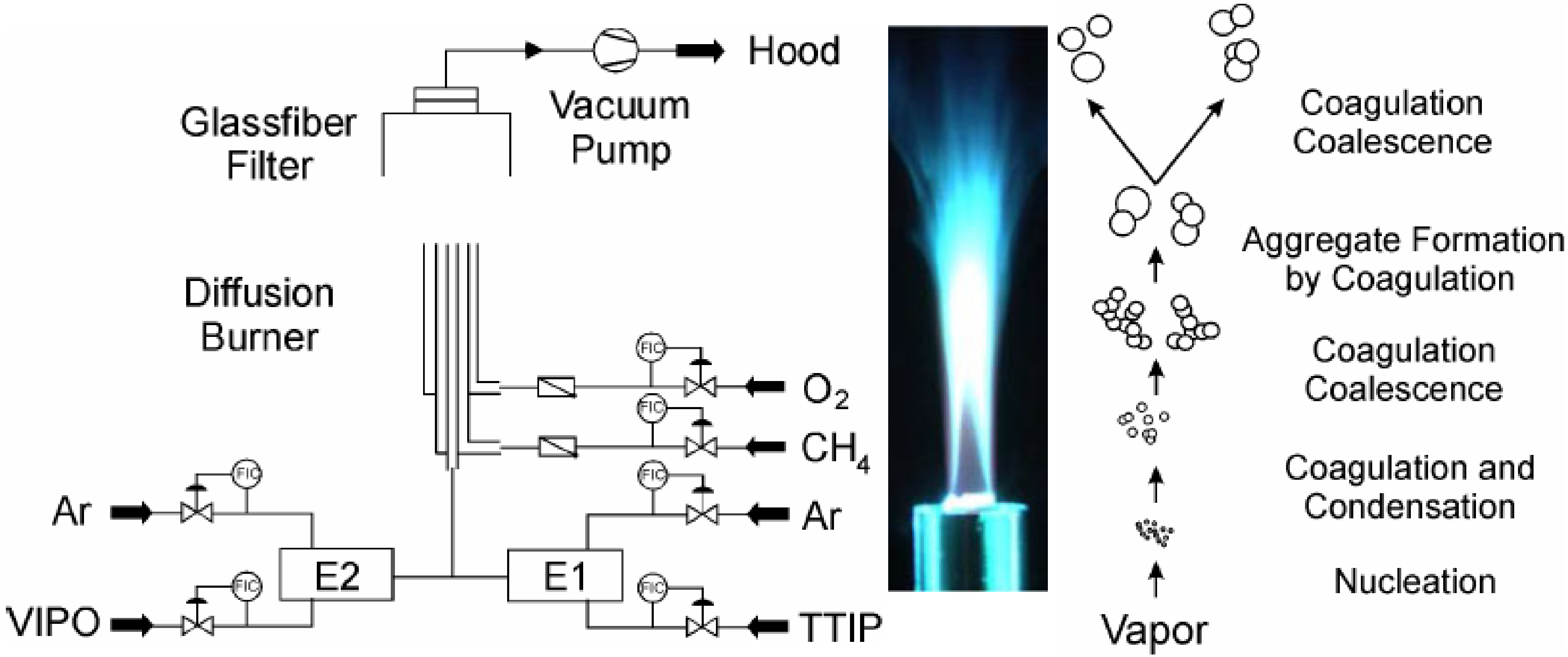
Disadvantage: For each particle material a (mixture of) precursor(s) has to be found.

Kelder et al., TU Delft

Flame synthesis

Good scale-up potential compared to earlier techniques

Vanadia / Titania nanoparticles



Stark et al., ETH: http://www.ptl.ethz.ch/posters/Stark_titania_vanadia.pdf

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Intermezzo: aerosols

A suspension of *liquid* or *solid* particles in a gaseous medium with some degree of stability.

Anthropogenic	Natural
Tobacco smoke	Clouds, fog
Fly ashes	Mineral particles
Soot	Resuspended soil
Medicine	Salt particles from the sea
Pesticides	Viruses and bacteria

Particle size ranges

Typical aerosol particle sizes are in the range of:

1 nm $<d_p<$100 μm

10^{-9} m$<d_p<10^{-4}$ m

Size range: 5 orders of magnitude!

Most aerosol sizing instruments effectively measure a size range no larger than 1.5 – 2 orders of magnitude

Transport losses

Six deposition mechanisms in a duct

1. Interception
2. Inertial impaction
3. Diffusion
4. Gravitational settling
5. Electrostatic attraction
6. Thermophoresis (hot gases through could pipe)

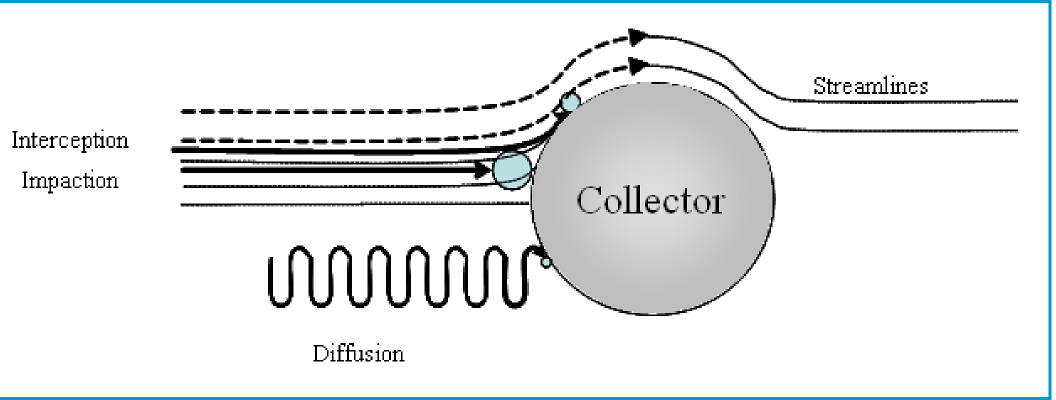

Figure from A. Ortiz-Arroyo, PhD thesis, Université Laval

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Interparticle forces

Particles in the gas phase

van der Waals Force

(London – van der Waals Force)

Van der Waals force between flat surfaces:

$$F_{\mathrm{vdw,f}} = \frac{H_v}{6\pi h^3} A$$

Van der Waals force between spheres:

$$F_{\mathrm{vdw,s}} = \frac{H_v d_{\mathrm{p}}}{12 h^2}$$

A	Contact area between flat plates	m^2
d_p	Particle diameter	m
h	Separation distance between surfaces / particles	m
H	Hamaker constant	J

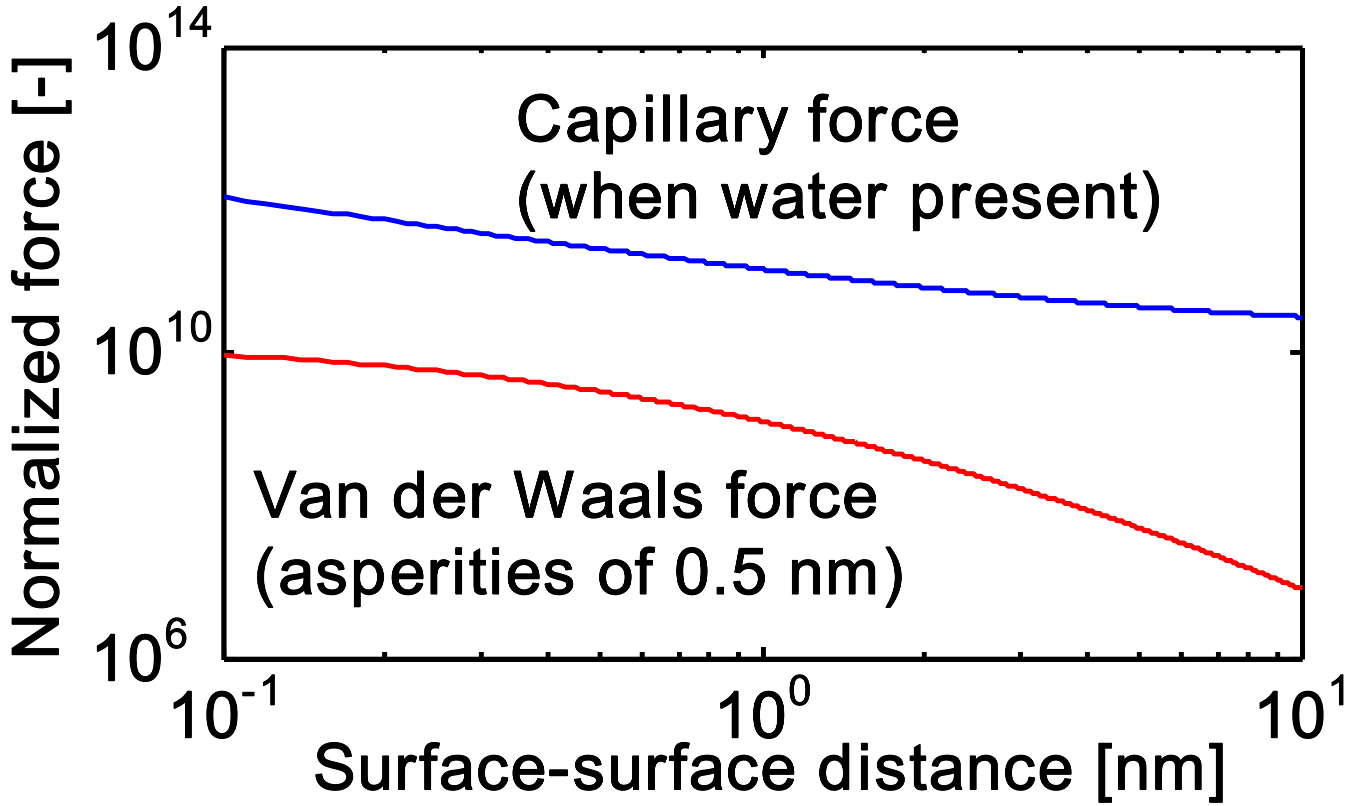
Typical range 10^{-21} – 10^{-19} J, depends on surface chemistry and separating medium

Question:

Compare vdW force and gravity for two 10 nm particles with 1 nm distance

Interparticle forces

The main forces between two silica particles of 10 nm as a function of the interparticle distance, normalized by gravity.



Hamaker constants

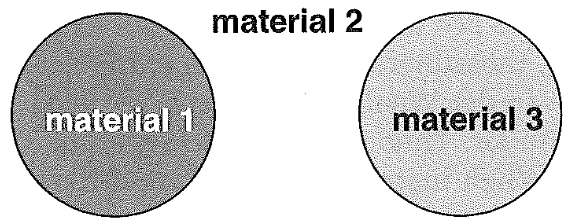
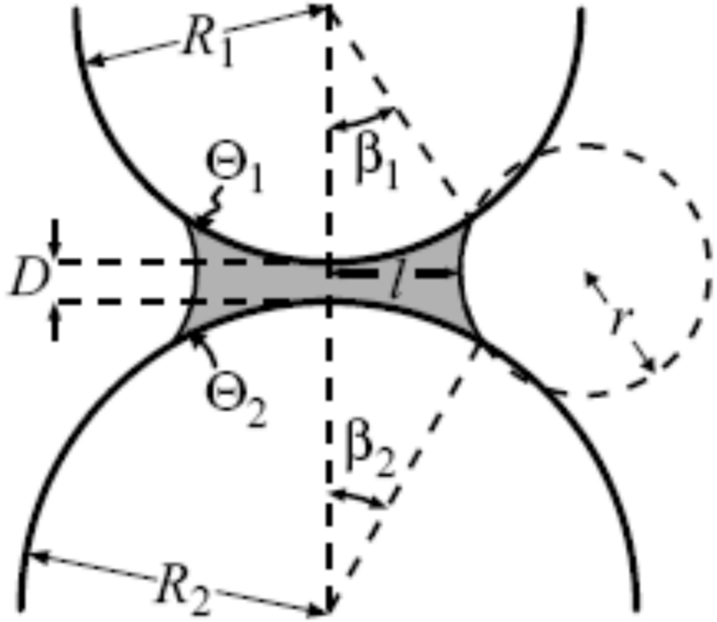


Table 5.1 Hamaker constants of some common material combinations

Material 1	Material 2	Material 3	Hamaker constant (approximate) (J)	Example
Alumina	Air	Alumina	15×10^{-20}	Oxide minerals in air are strongly attractive and cohesive
Silica	Air	Silica	6.5×10^{-20}	
Zirconia	Air	Zirconia	20×10^{-20}	
Titania	Air	Titania	15×10^{-20}	
Alumina	Water	Alumina	5.0×10^{-20}	Oxide minerals in water are attractive but less so than in air
Silica	Water	Silica	0.7×10^{-20}	
Zirconia	Water	Zirconia	8.0×10^{-20}	
Titania	Water	Titania	5.5×10^{-20}	
Metals	Water	Metals	40×10^{-20}	Conductivity of metals makes them strongly attractive
Air	Water	Air	3.7×10^{-20}	Foams
Octane	Water	Octane	0.4×10^{-20}	Oil in water emulsions
Water	Octane	Water	0.4×10^{-20}	Water in oil emulsions
Silica	Water	Air	-0.9×10^{-20}	Particle bubble attachment in mineral flotation, weak repulsion

Rhodes, Introduction to Particle Technology – 2nd ed., John Wiley Ltd, Hobroken, USA, 2008.

Capillary force



$$F = 2\pi\gamma_L R^* \left(\cos\Theta_1 + \cos\Theta_2 - \frac{D}{r} \right)$$

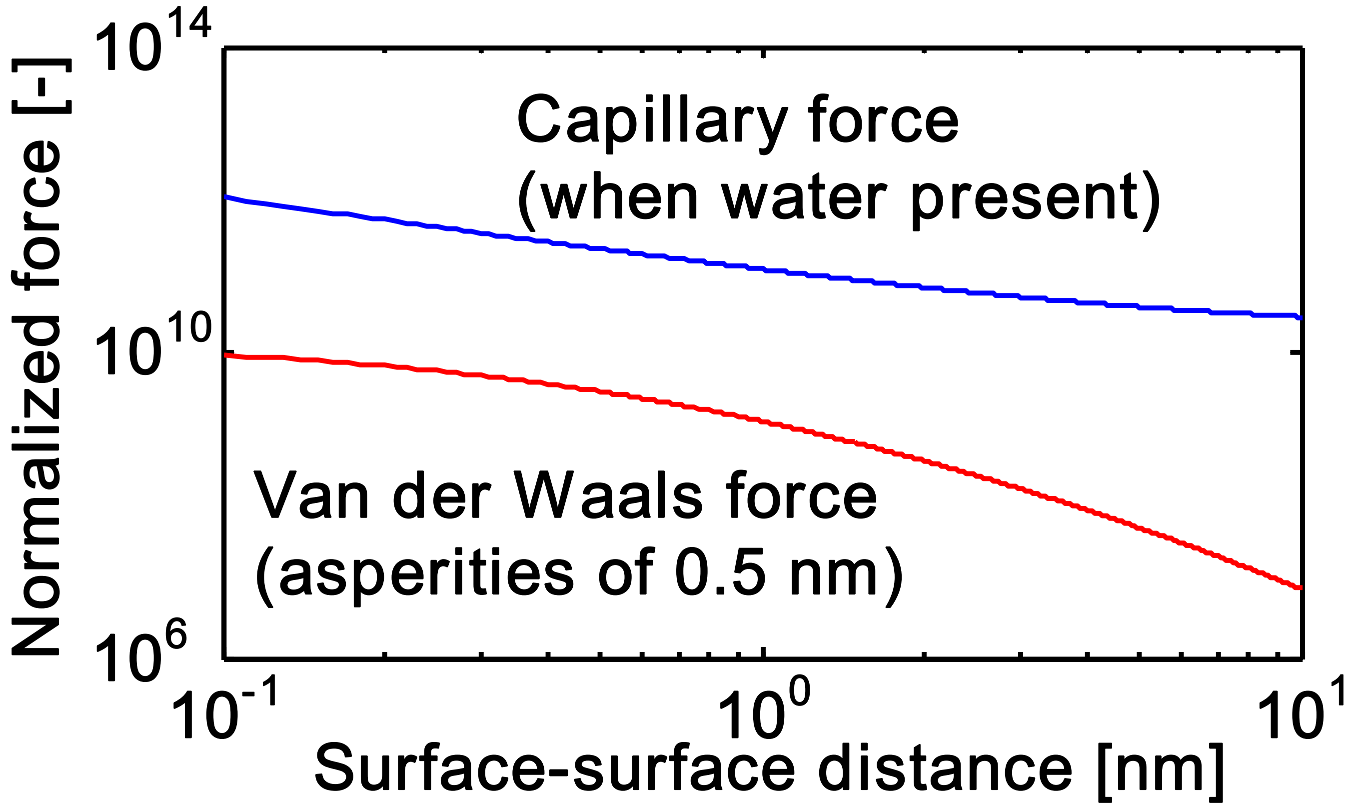
$$R^* = \frac{R_1 R_1}{R_1 + R_2}$$

γ_l = surface tension (N/m)

Butt, H.J., Kappl, M., 2010. Wiley VCH, Weinheim.

Interparticle forces

The main forces between two silica particles of 10 nm as a function of the interparticle distance, normalized by gravity.



Particles in the liquid phase

For a dispersion of powder in liquid, the interparticle forces are more complicated

Colloid: heterogeneous system consisting of a mixture of particles between 1 nm and 1000 nm dispersed in a continuous medium (typically a liquid).

The Basics of Colloid Science

- London-Van der Waals attraction
- Electrostatic repulsion
- Steric repulsion
- Electrosteric repulsion
- Ostwald ripening

Electrostatic Stability
DLVO

Two approaching particles undergo two forces:

1. London-Van der Waals attraction

2. Electrostatic repulsion

$$V_{tot} = V_{vdw} + V_{er}$$

The *total interaction energy* is the algebraic sum of these forces as a function of distance of approach of the particles

The DLVO theory is named after Derjaguin and Landau, Verwey and Overbeek.

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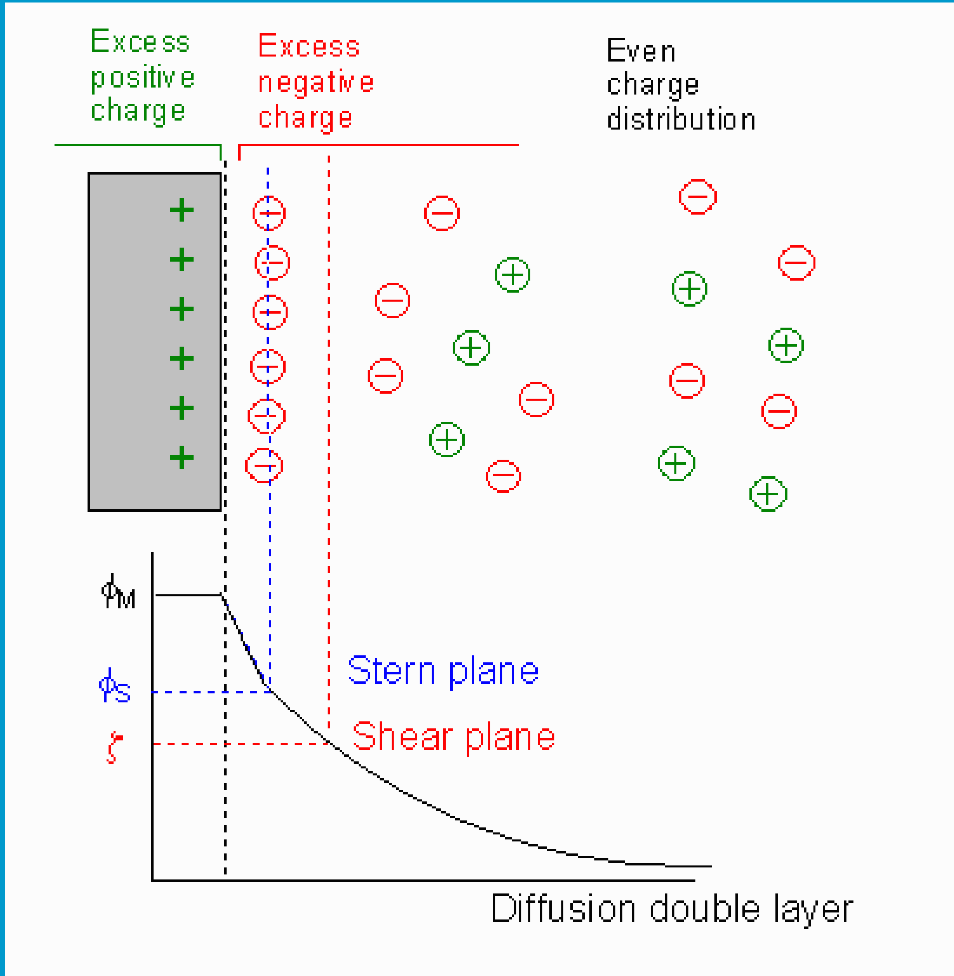
Electric Double Layer



www.chemistry.nmsu.edu/studntres/chem435/Lab14/double_layer.html

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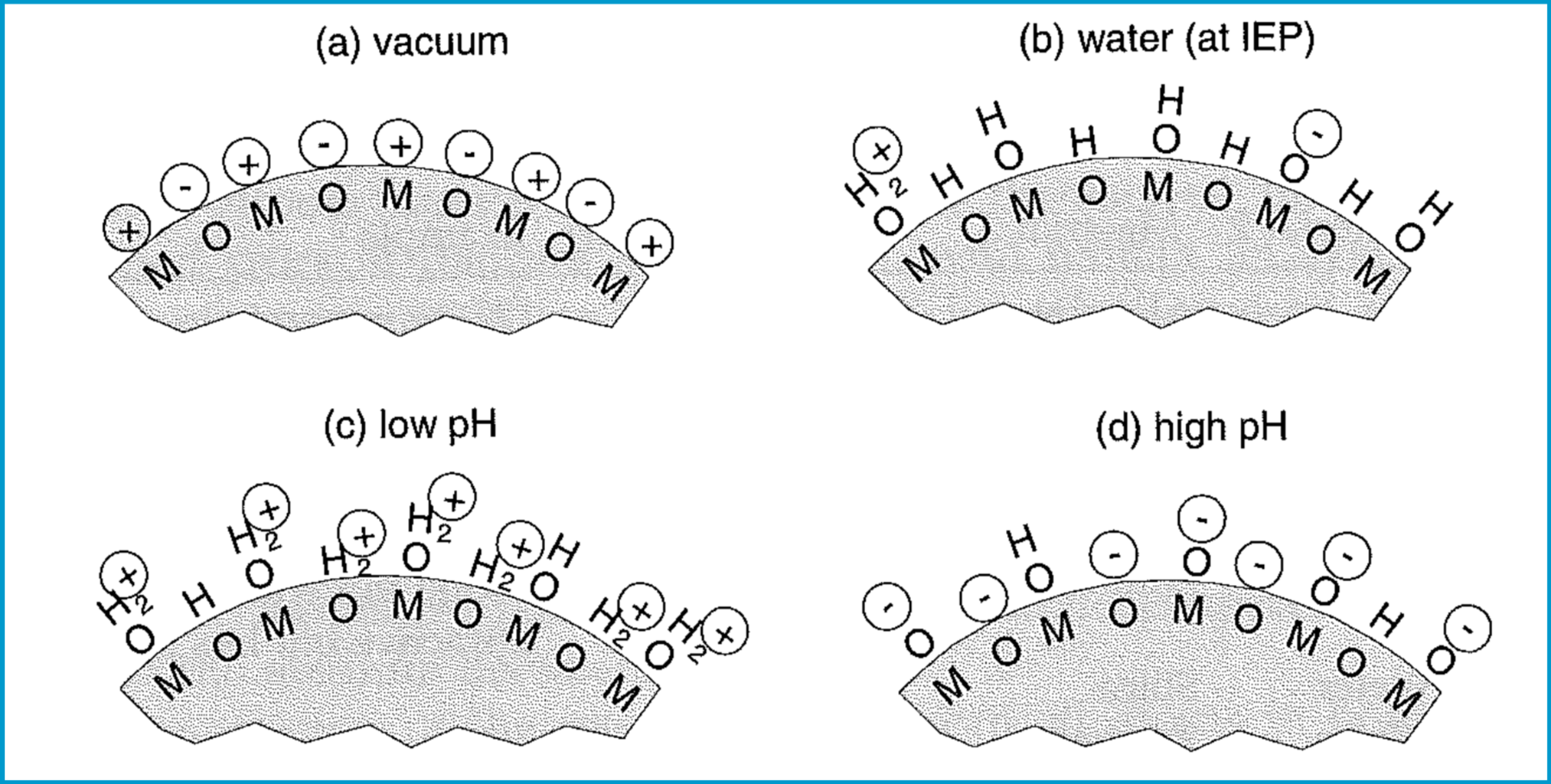
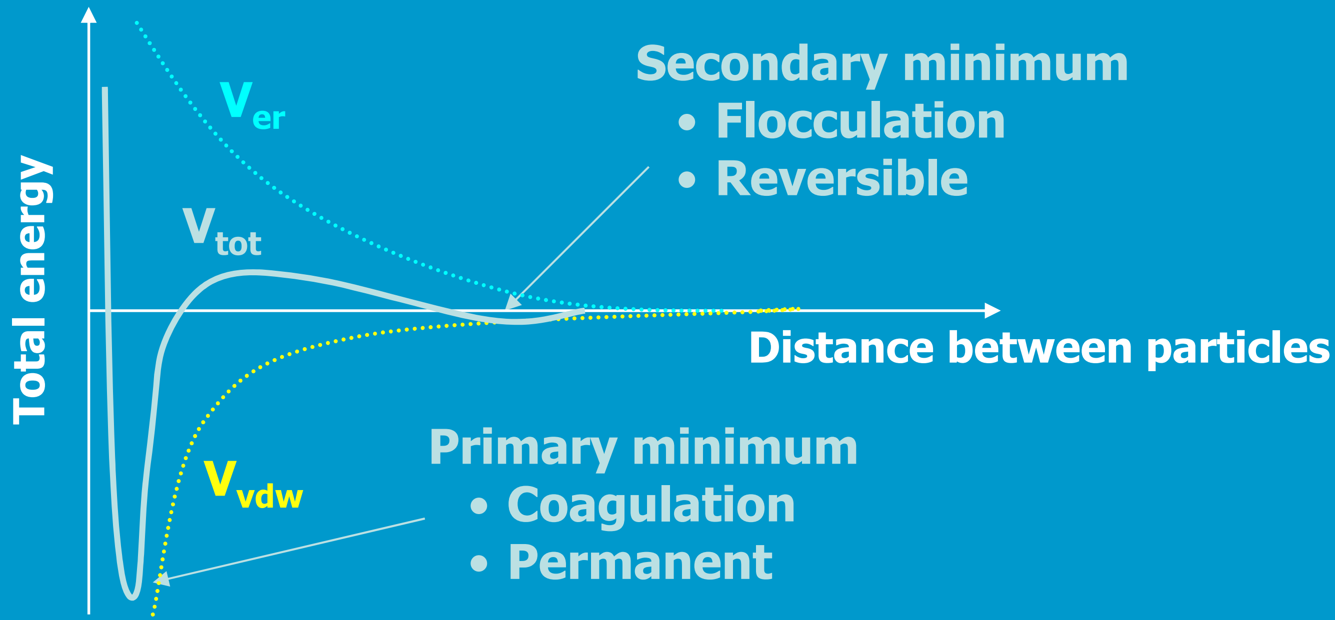
Surface charge depends on medium



The Total Interaction Energy Curve



Important parameters:

- 1/K Debye Length, double layer thickness: depends on conc.
- a particle size
- ζ surface charge
- A Hamaker constant, nature of particle & fluid

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Steric Stability

Two approaching particles undergo London-Van der Waals forces and forces arrising from the adsorption of polymeric or oligomeric molecules osmotic repulsion

$$V_{tot} = V_{vdw} + V_{ster}$$

Again the algebraic sum of these forces as a function of distance of approach of the particles gives the total interaction energy

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Electrosteric Stability

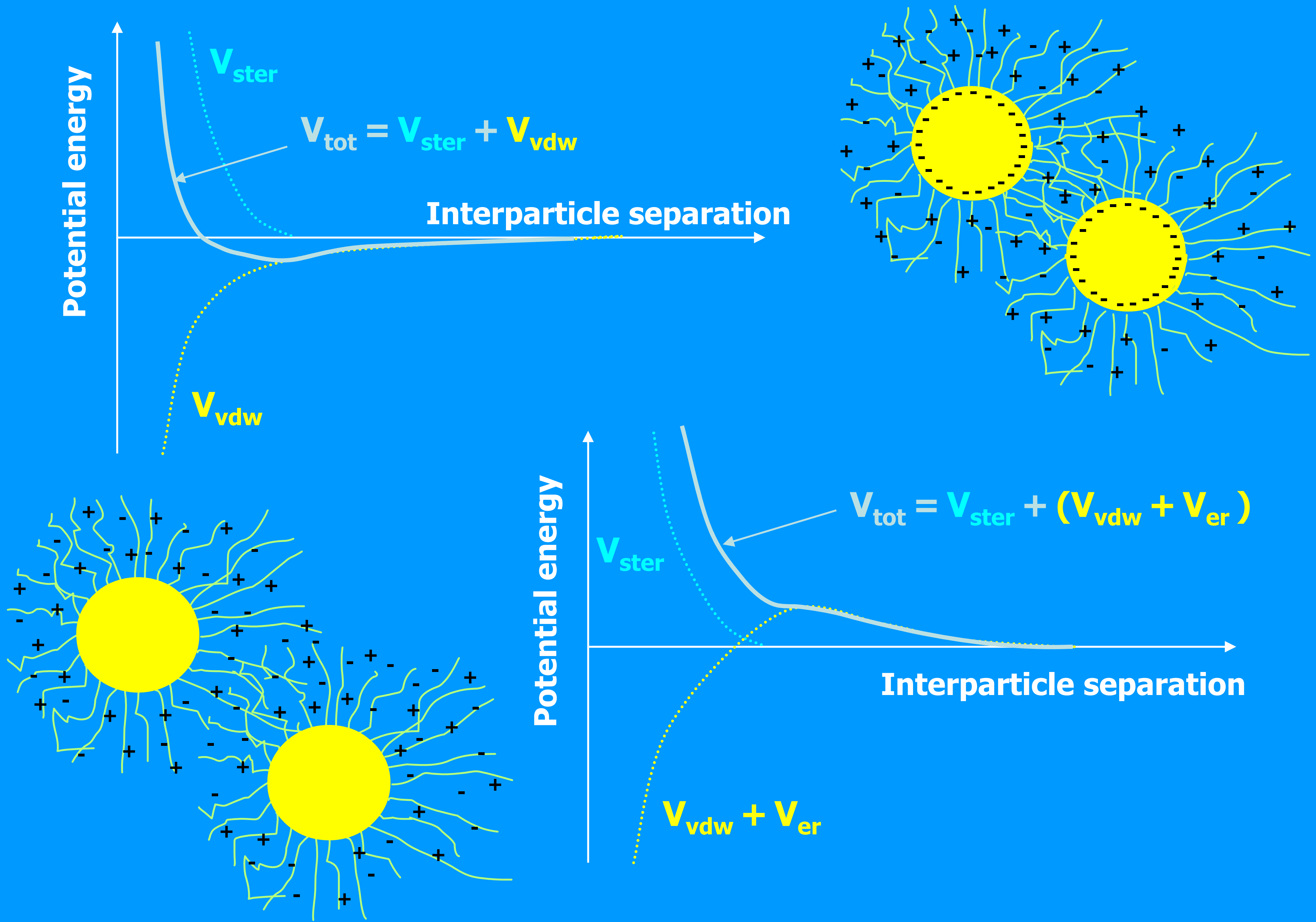
The combination of electrostatic and steric stability

Two situations can occur:

- **Depending on the length of stabilising functional group or molecular weight of a nonionic polymer, the steric barrier hides completely the electrostatic one**

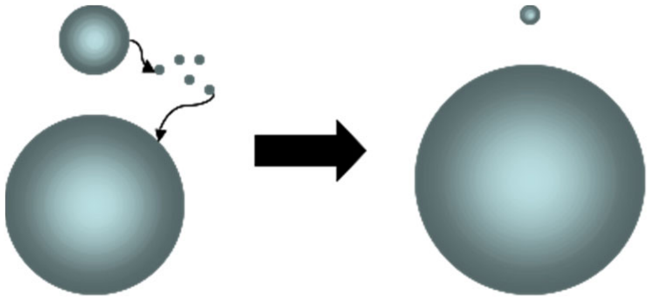
- **If the polymer is a polyelectrolyte, carrying charges itself, then the electrostatic barrier is visible in the curve**

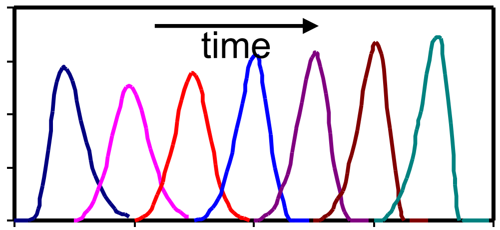
Electrosteric Stability



Ostwald Ripening

Ostwald ripening occurs as a consequence of the Kelvin equation, relating solubility of low soluble materials with particle size. The originally installed PSD drifts away as a function of time.





$$\frac{RT}{M}\ln\frac{S_2}{S_1}=\frac{2\sigma}{\rho}\left(\frac{1}{r_1}-\frac{1}{r_2}\right)$$

S_1 and S_2	solubilities of particles with radius r_1 and r_2
σ	specific surface energy
ρ	density
M	molecular weight
R	gasconstant
T	temperature

For an animation, see: http://www.roentzsch.org/OR/

Basic properties of nanoparticles

Gas phase production of nanoparticles

Sizing & forces on single particles

Particle-particle forces

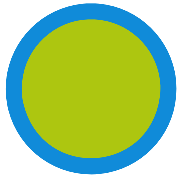
Particle coating

Applications

Two types of coating

- **Continuous coating**: A closed layer around a nanoparticle

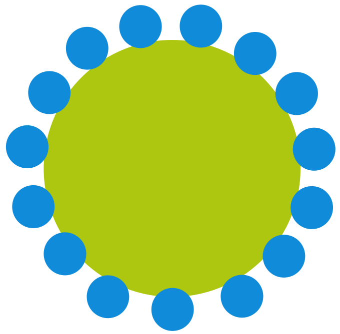
particle 10nm–10μm



coating 1 nm or larger

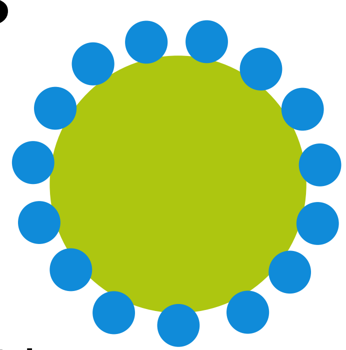
- **Discrete coating**: Deposition of nanoparticles on larger particles

host particle 1-100μm



guest particles 10nm–1μm

Discrete coating: applications



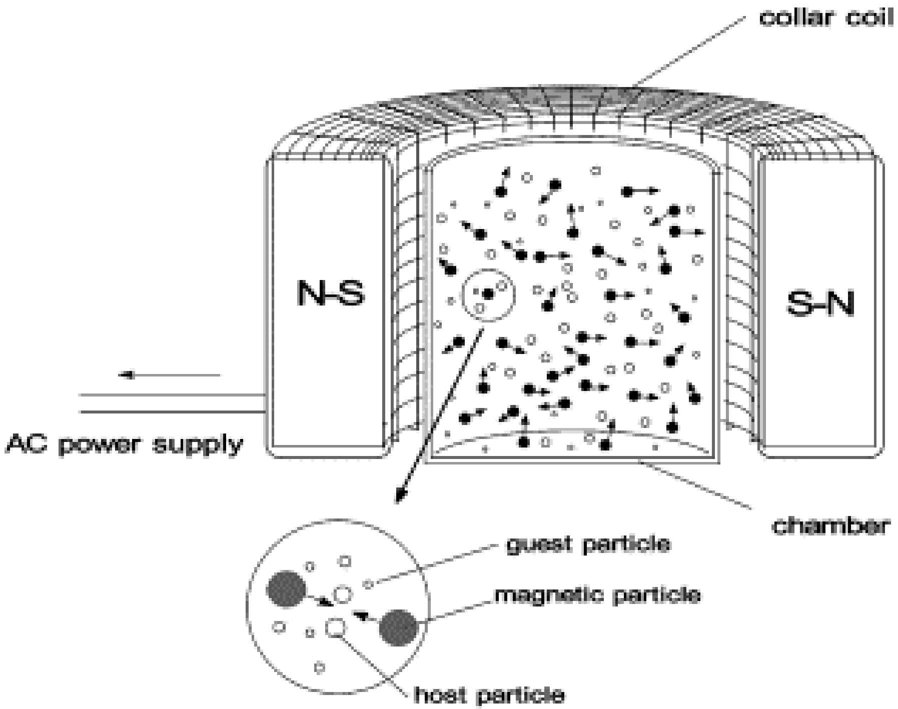
- Pharmaceutics with controlled-release properties
- Use for dry powder inhalers: carrier particles coated with active particles
- Coloring and UV protection in cosmetics
- Toner particles with different colors
- Improving liquid chromatography (HPLC) by using uniform polyethylene microspheres coated with silica
- Copper coated molybdenum particles: improved properties such as low porosity, high hardness, and a lower coefficient of thermal expansion

Pfeffer et al., Powder Technol 117 (2001) 40

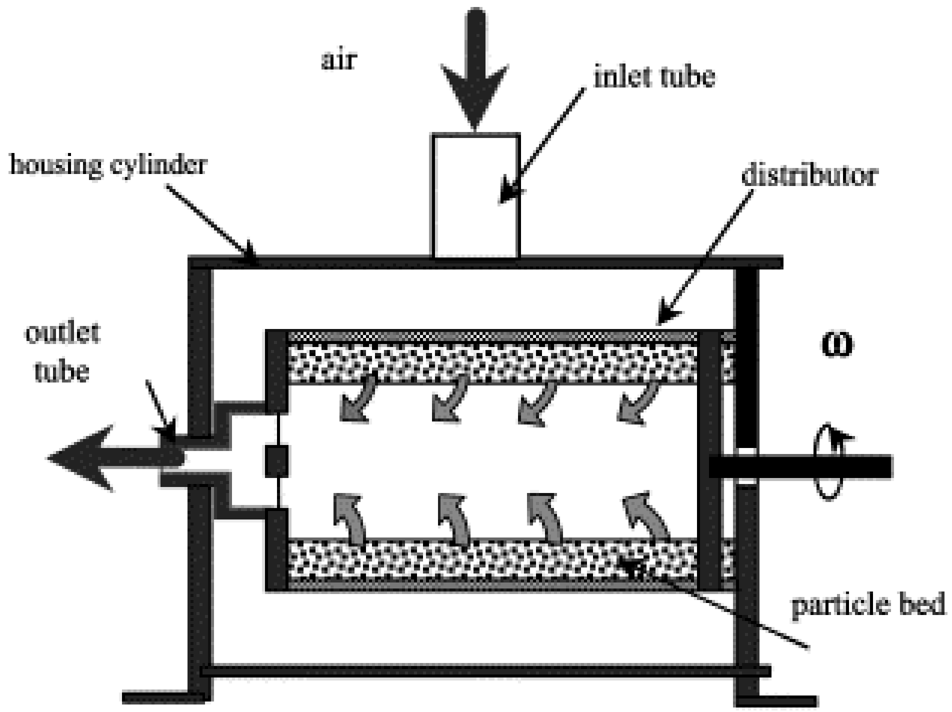
Discrete coating

Often carried out as dry powder coating.

Several devices are used to mix host particles and guest particles, for example:



magnetically assisted impaction coater

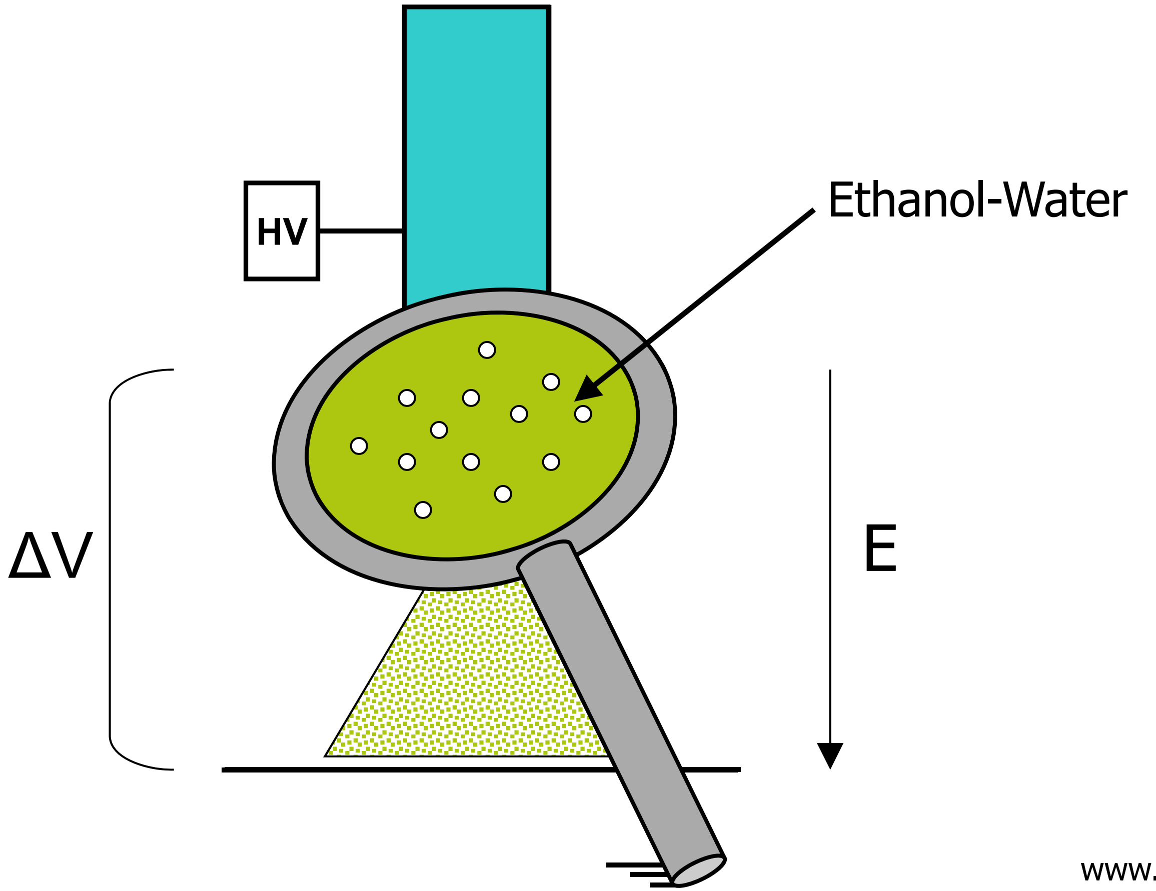


rotating fluidized bed coater

Pfeffer et al., Powder Technol 117 (2001) 40

Electrospraying

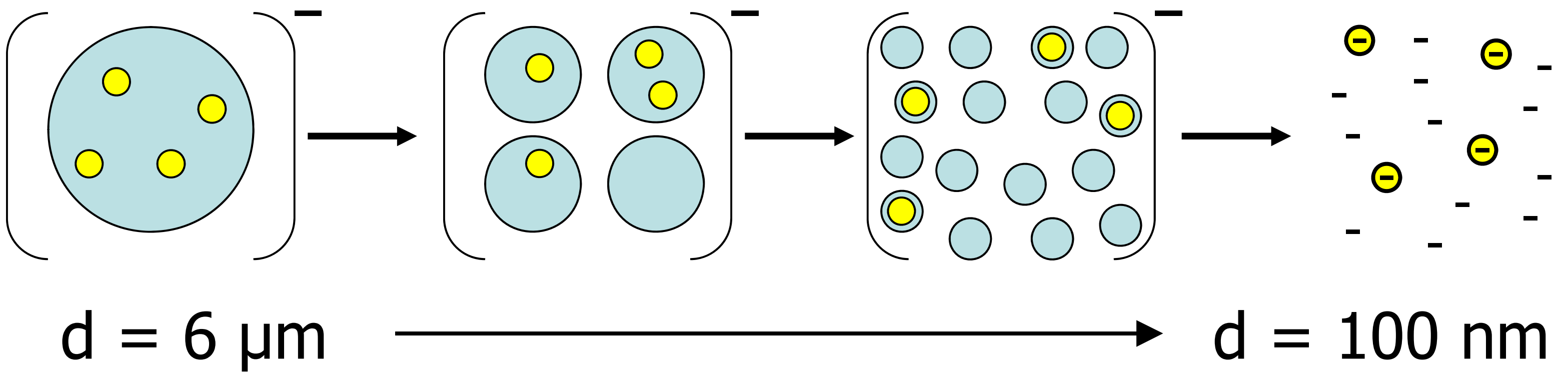
Alternative for discrete coating using mixing.



www.eng.yale.edu/eng150/timeline/1990.html

More precise, but limited to smaller amounts

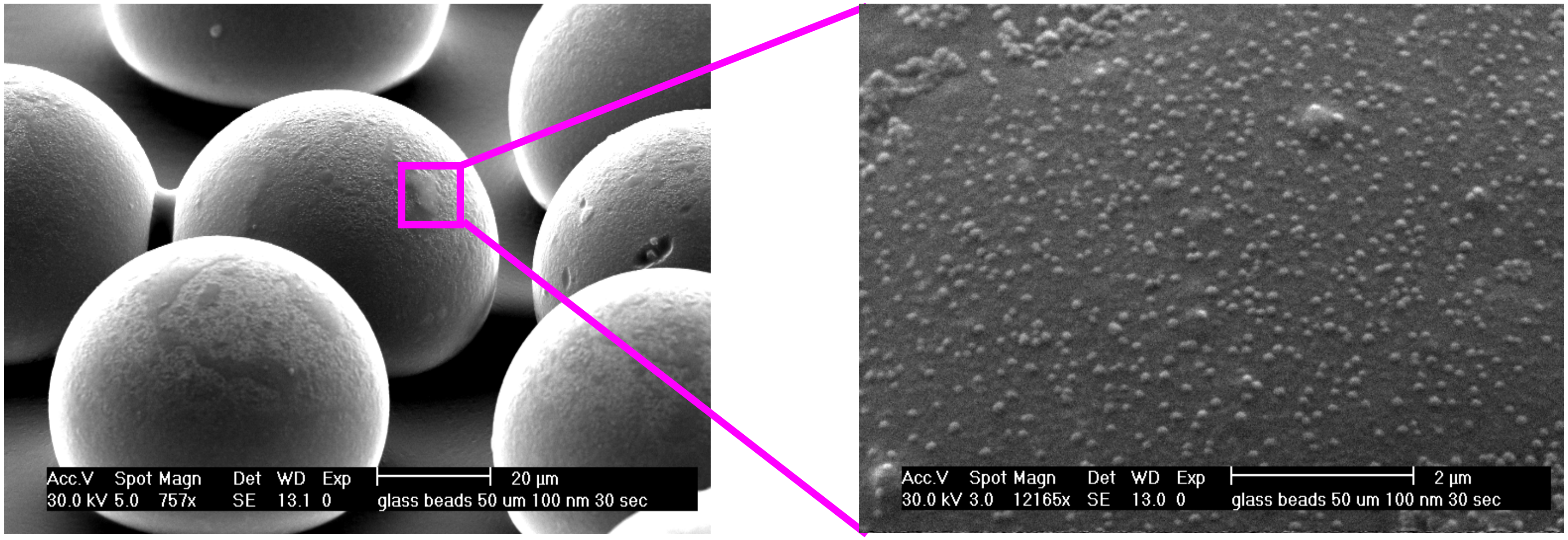
Electrospraying



- Volatile liquid evaporates
- Droplet breaks up at Rayleigh limit
- Negative voltage provides negative charge

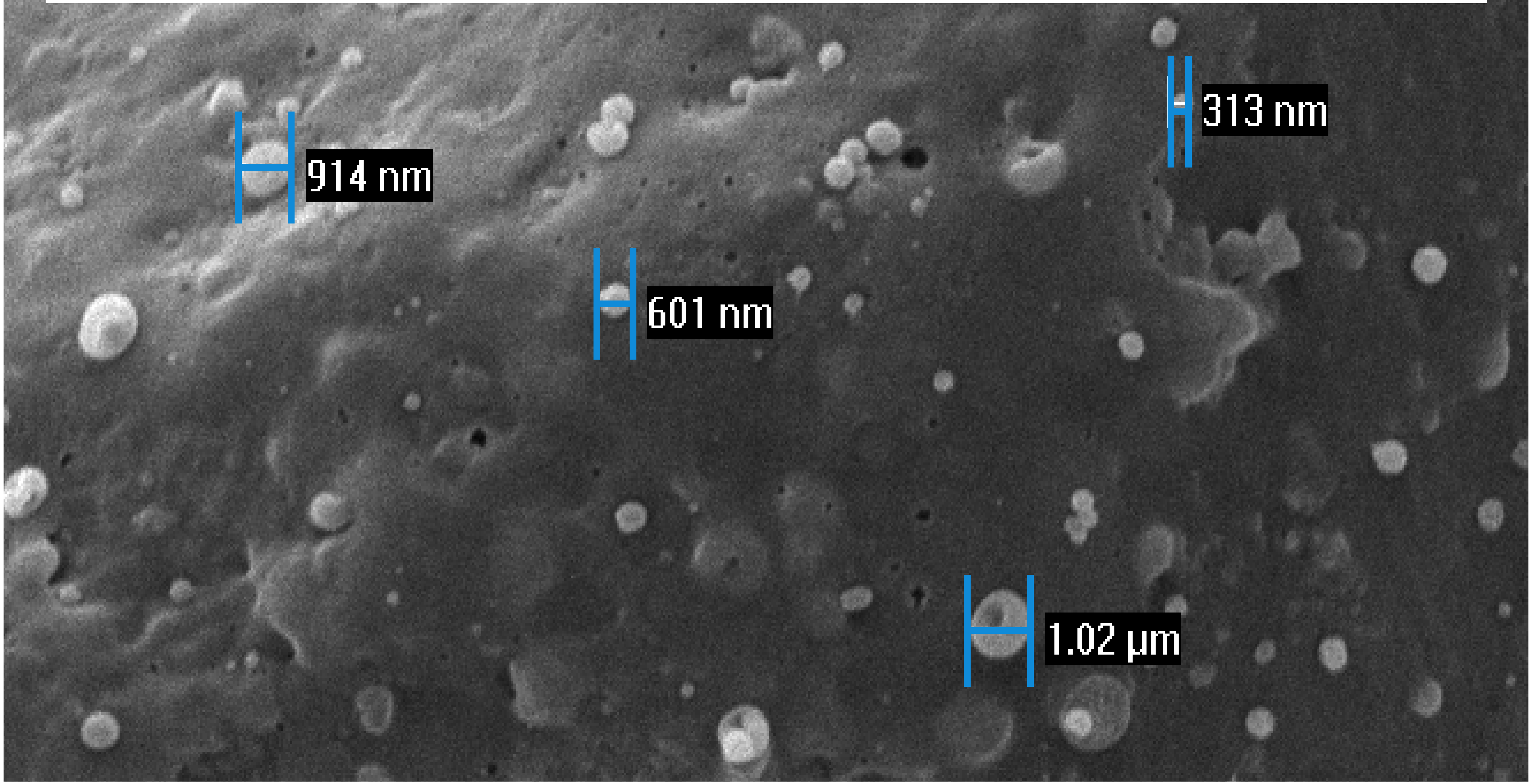
Results: SEM images

100 nm polystyrene particles on 50 μm glass beads (stationary)



See also: Elliset al., Chem Eng J 181 (2012) 798

Electrospraying Bovine Serum Albumin



Lactose coated with Bovine Serum Albumin
by electrospraying a solution of the protein in ethanol and acetic acid

Tavares Cardoso et al., Int. J. Pharmac. 414 (2011)

Nanoparticles with continuous coating

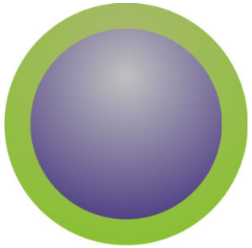
coating, overcoating, film deposition, …

Wide variety of applications:

- Li ion batteries
- Catalysts
- Biomarkers
- Pharma: controlled release
- Absorber in sunscreen
- Dental materials

and many more

Core-shell nanoparticles (NPs)



Diameter (incl. coating) 20 nm
Coating thickness 1 nm

Question:

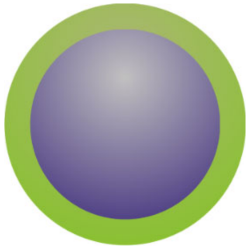
What is the volume fraction of the coating?

Answer:

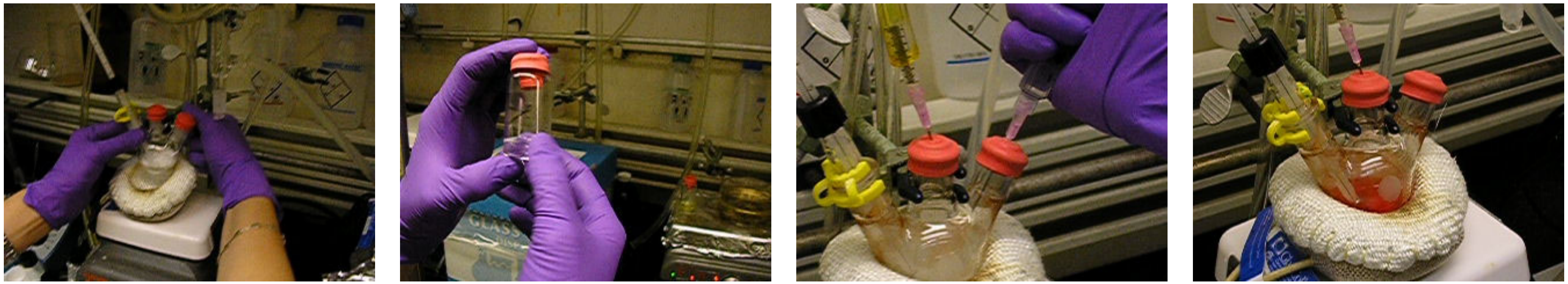
$$f = \frac{\delta \cdot 4\pi r^2}{4/3\pi r^3} = \frac{3\delta}{r} = 0.3$$

Synthesis of core-shell nanoparticles (NPs)

Diam. 5 -100 nm
coating 1-10 nm



Standard batch synthesis in liquid phase



chemgroups.northwestern.edu/odom/

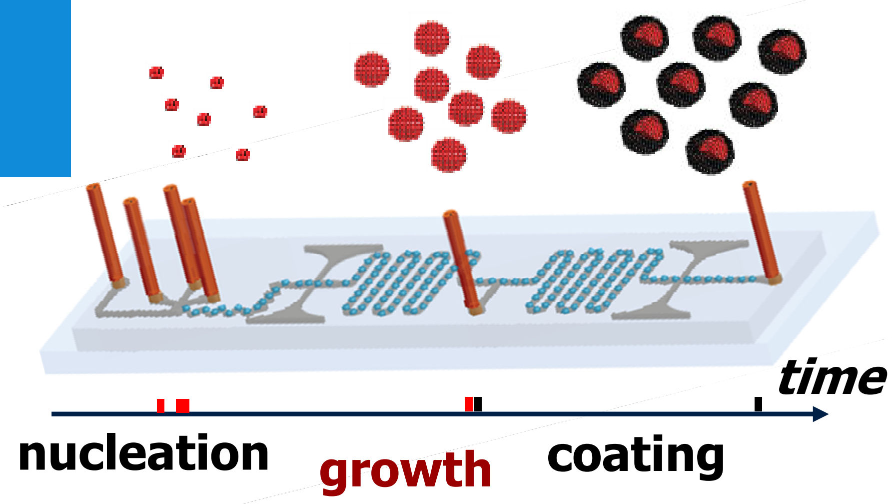
Disadvantages:

- **Poor control over process conditions**
- **Unsuitable to scale up**

TU Delft - Product & Process Engineering
is investigating two alternative approaches

Synthesis of core-shell nanoparticles (NPs)

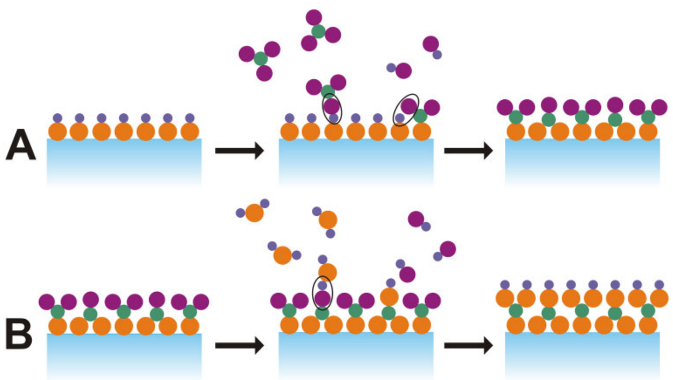
Alternative 1



Microfluididic synthesis:

- **Excellent control over process conditions**
- **Well suited to investigate mechanisms**

Alternative 2

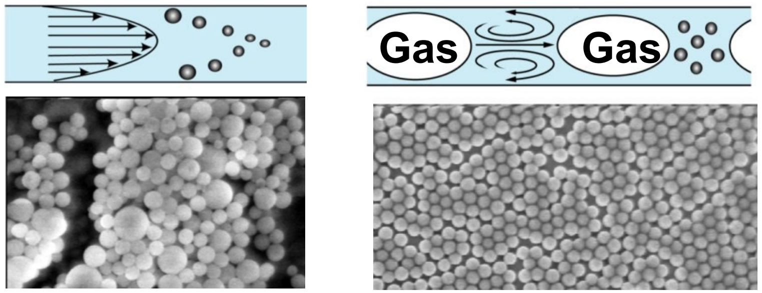


Fluid bed atomic layer deposition:

- **Major reduction of waste**
- **Well suited to scale up**

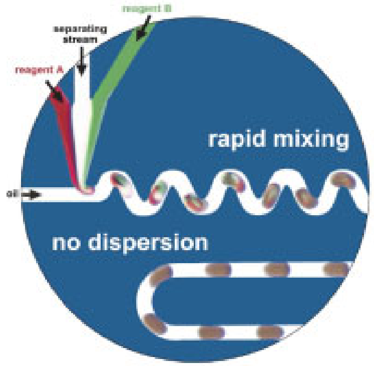
properties of microfluidic devices

Defined residence time



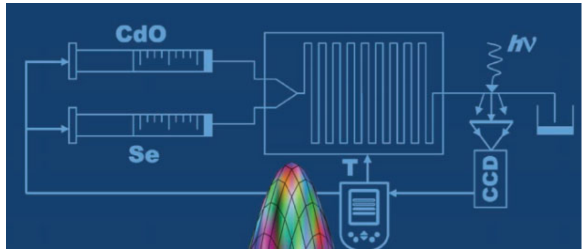
Colloidal Silica. Khan *Langmuir* 2005

Fast mixing



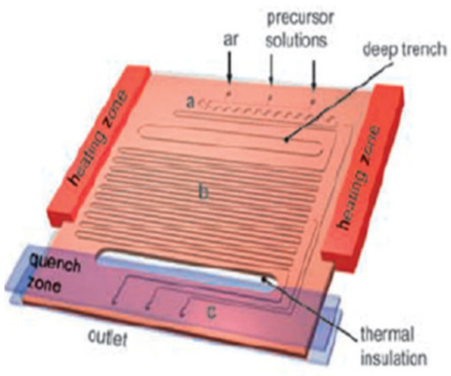
Song, Angew., 2003, 42,767.

In-line optimization



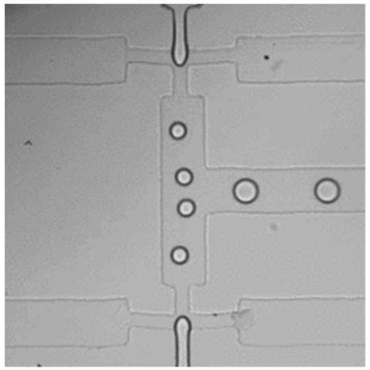
Krishnadashan, Lab Chip, 2007, 7, 1434.

Quenching



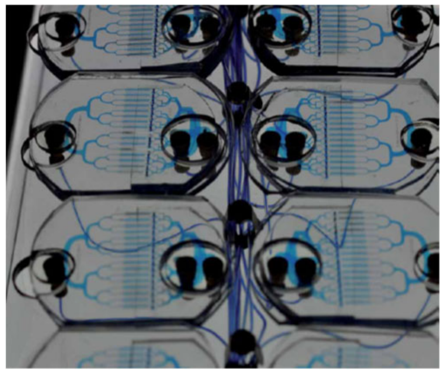
Yen, Angew.,2005,44,5447

Addition of reagents



Link, Lab Chip, 2006

Scale-up??



Li, Lab Chip, 2009, 9, 2715

TUDelft

Gas phase coating

- PVD: physcial vapour deposition
  deposit thin film by condensation of a vaporized form of the material onto surface; normally not used for particles
- CVD: chemical vapour deposition
  reactions are taking place simultaneously
- ALD: atomic layer deposition
  CVD split in half reactions

Gas phase coating

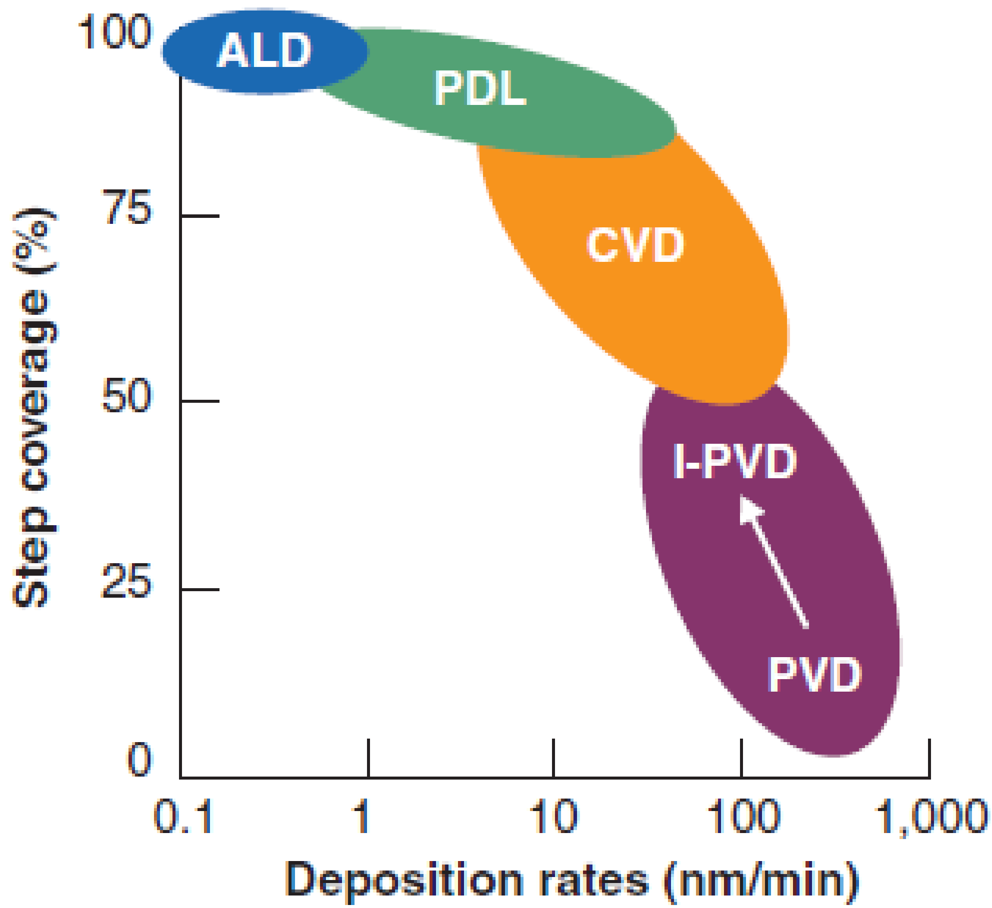
Method	ALD	MBE	CVD	Sputter	Evapor	PLD
Thickness Uniformity	good	fair	good	good	fair	fair
Film Density	good	good	good	good	poor	good
Step Coverage	good	poor	varies	poor	poor	poor
Interface Quality	good	good	varies	poor	good	varies
Number of Materials	fair	good	poor	good	fair	poor
Low Temp. Deposition	good	good	varies	good	good	good
Deposition Rate	fair	poor	good	good	good	good
Industrial Applicability	good	fair	good	good	good	poor

ALD = atomic layer deposition, MBE = molecular beam epitaxy.
CVD = chemical vapor deposition, PLD = pulsed laser deposition.

MBE and sputter: line of sight methods, not suited for particles

Source: Cambridge Nanotech 2005

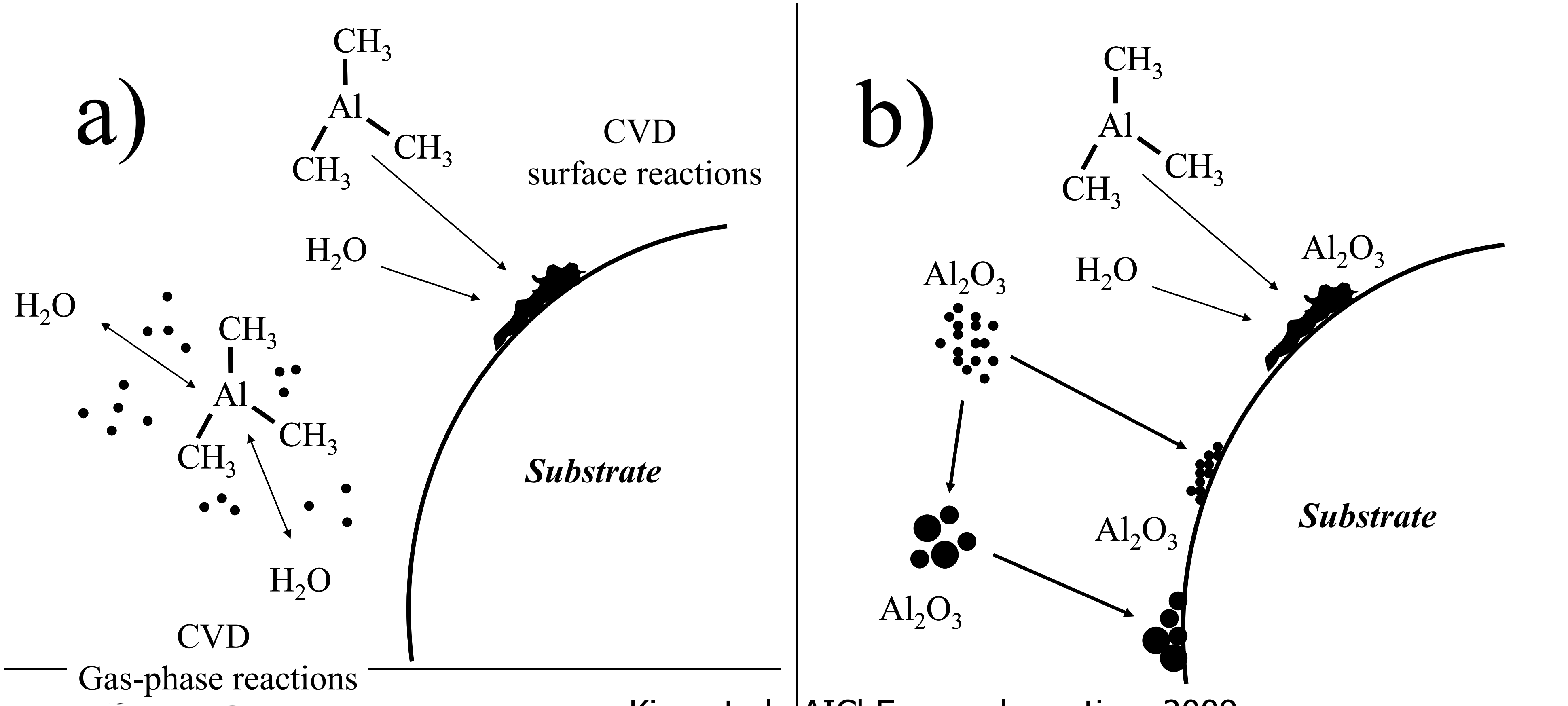
Gas phase coating



Source: ICKnowledge 2004

Chemical Vapor Deposition process mechanism

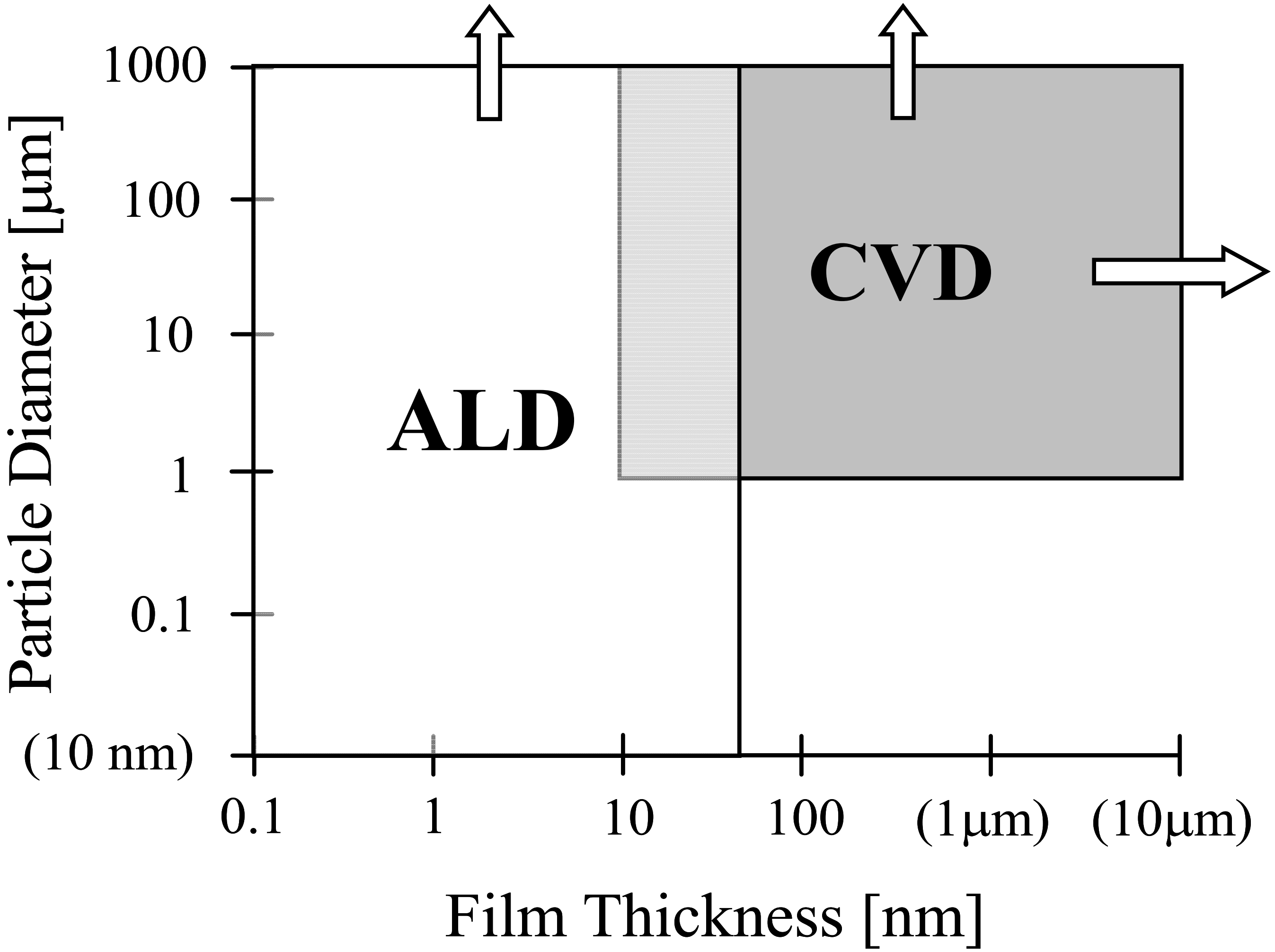
Al_2O_3 CVD: trimethylaluminum + H_2O



King et al., AIChE annual meeting, 2009

Adapted from: Powell et al., *J. Mater. Res.* **12** (1997) 552

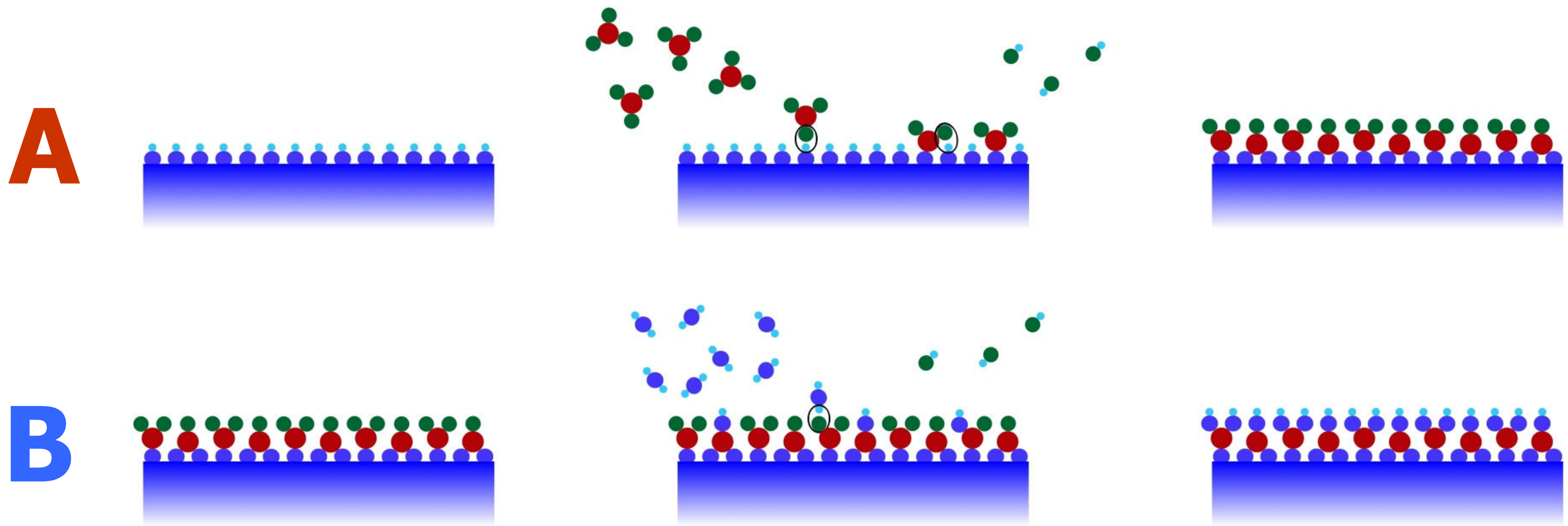
Process window for ALD vs. CVD



TU Delft

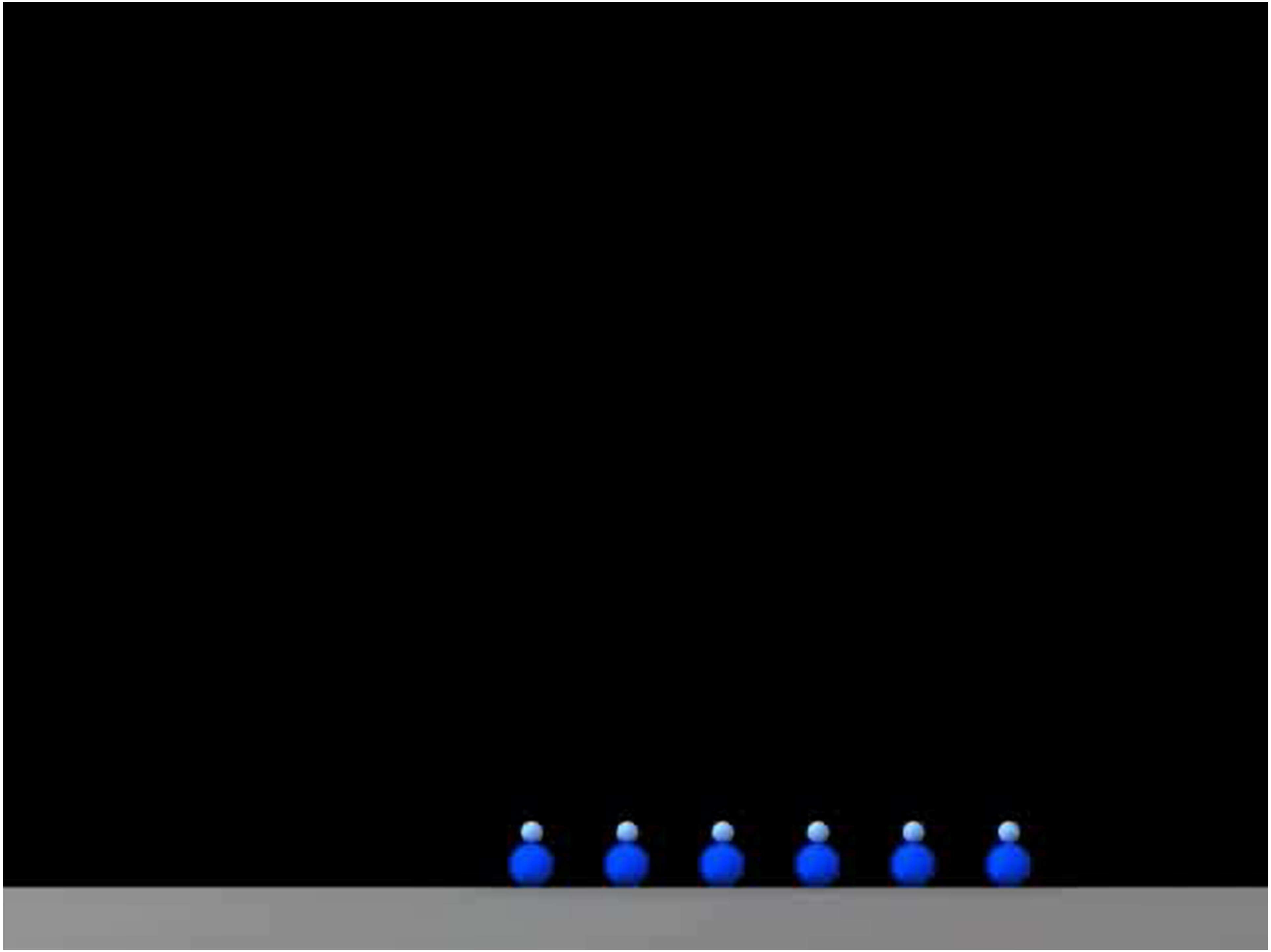
King et al., AIChE annual meeting, 2009

Atomic Layer Deposition (ALD)



A – B – A – B – A – B – A – B – … etc.

Number of cycles determines layer thickness



Atomic Layer Deposition (ALD)

Deposition of alumina layer using tri-methyl aluminum (TMA) and water:

A

$\|Al\text{-}OH + Al(CH_3)_3\ (g) \rightarrow \|Al\text{-}O\text{-}Al(CH_3)_2 + CH_4\ (g)$

$2\|Al\text{-}OH + Al(CH_3)_3\ (g) \rightarrow (\|Al\text{-}O)_2\text{-}Al\text{-}CH_3 + 2\ CH_4\ (g)$

B

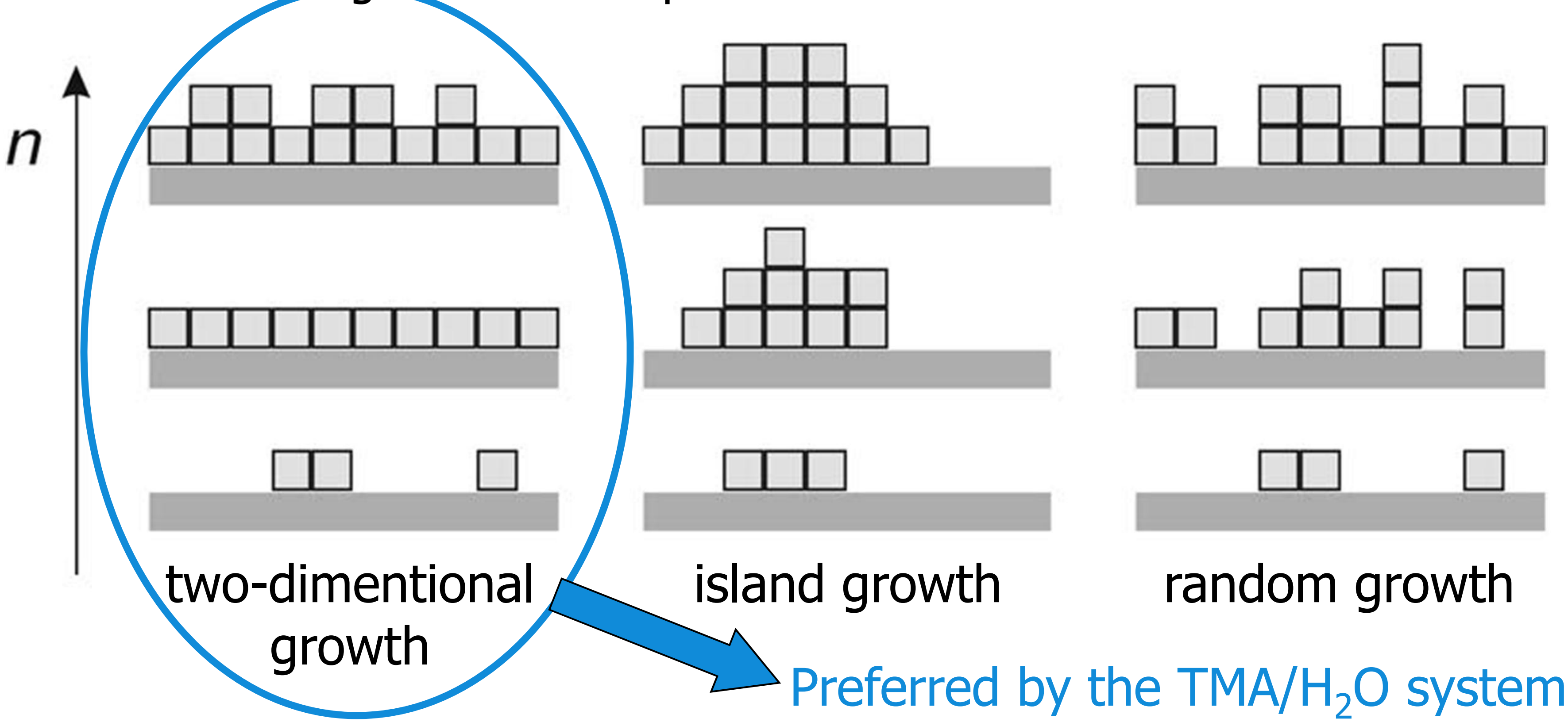
$\|Al(CH_3)_2 + 2H_2O(g) \rightarrow \|Al(OH)_2 + 2\ CH_4\ (g)$

$\|Al\text{-}CH_3 + H_2O\ (g) \rightarrow \|Al\text{-}OH + CH_4\ (g)$

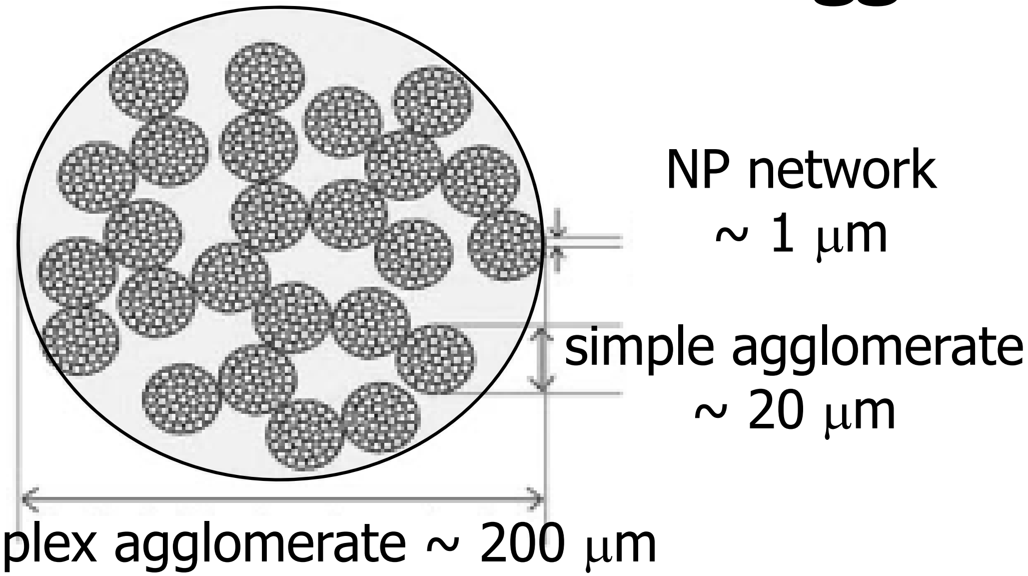
A – B – A – B – A – B – A – B – … etc.

Thickness control of coating

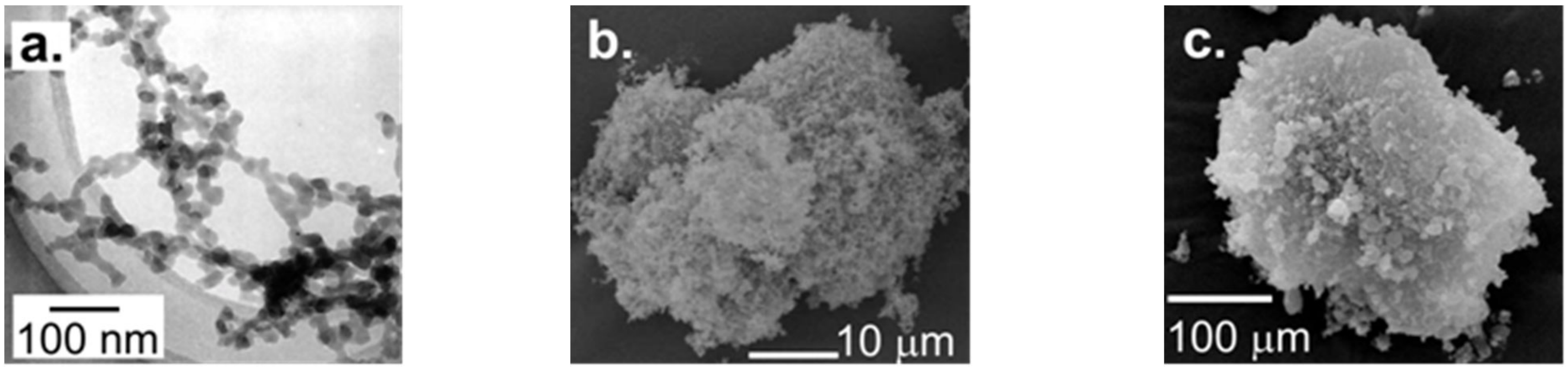
- 3 different growth modes possible:



Nanoparticles are fluidized as agglomerates!



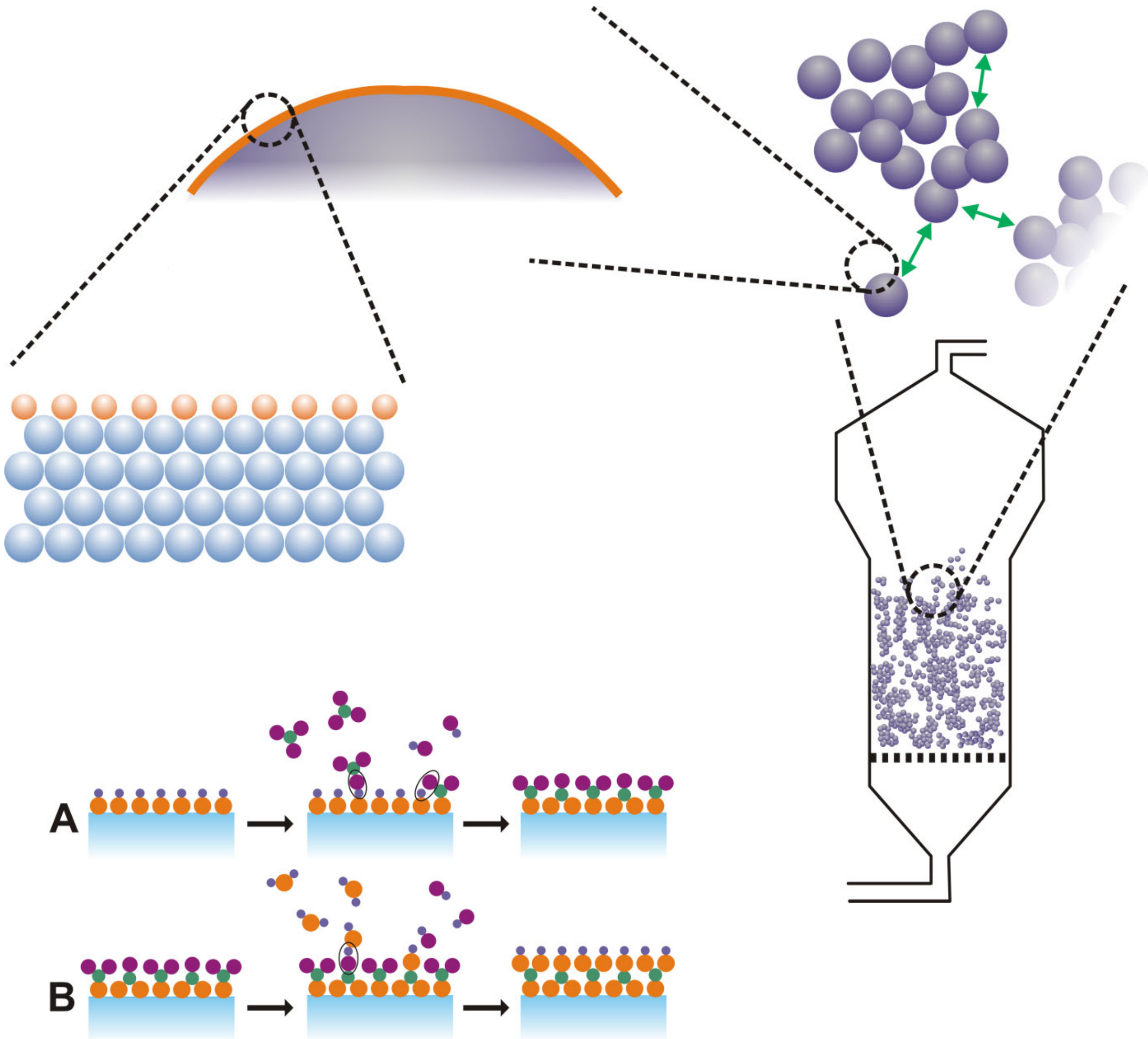
Wang et al., Powder Technol. 124 (2002) 152:



TEM NP network | SEM simple agglomerate | SEM complex agglomerate

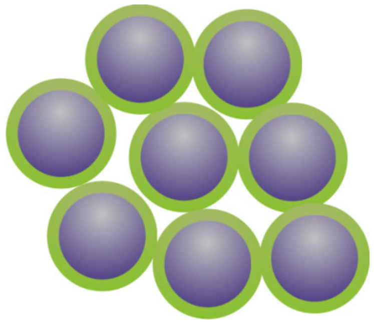
van Ommen et al., *J Nanopart Res* **14** (2012) 1

Fluidized bed reactor for ALD

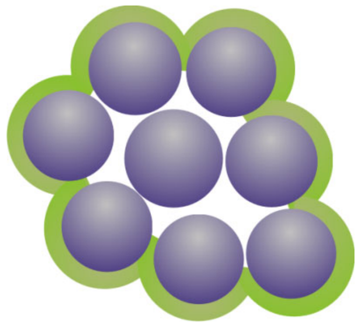


Question:

can we indeed coat individual particles?

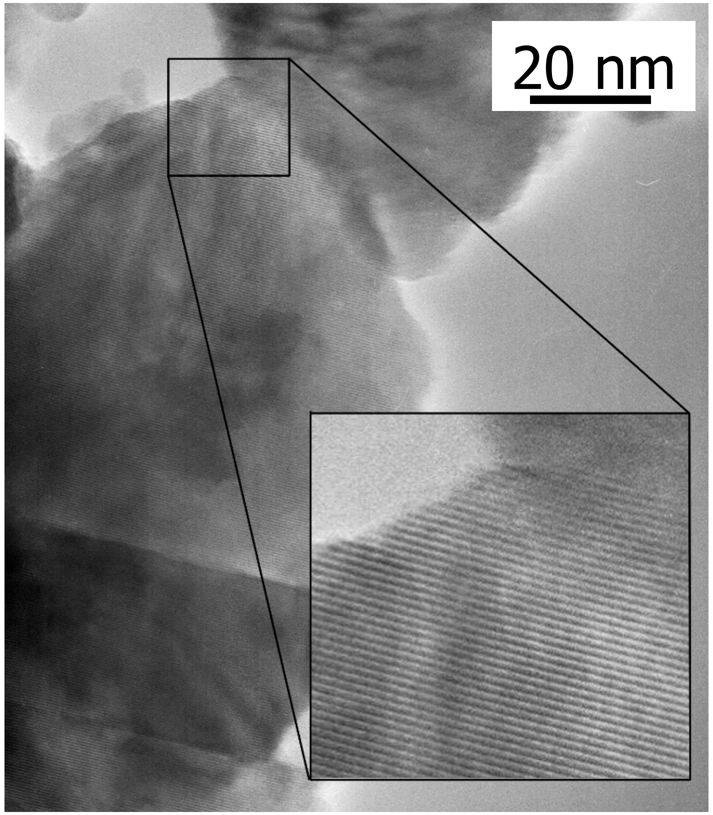


or

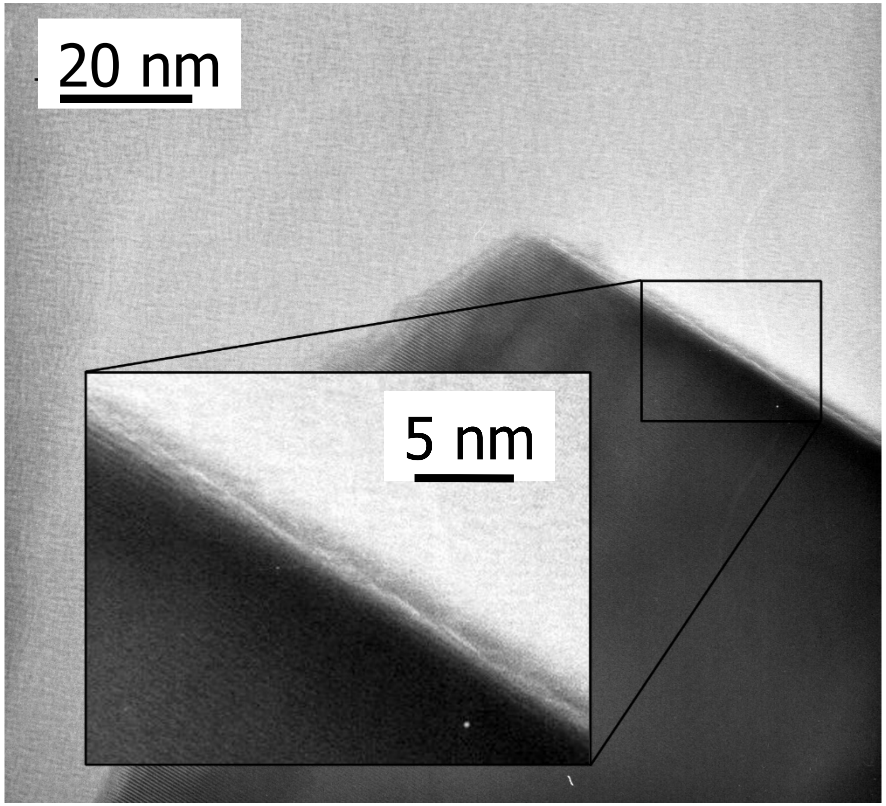


?

TEM pictures of results



Uncoated

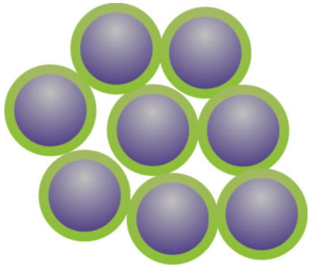


Coated (5 ALD cycles)

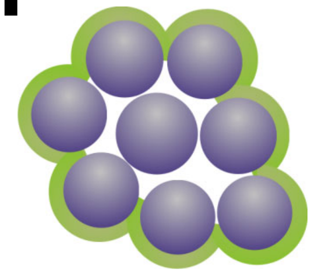
Obtained at atmospheric pressure!

Beetstra et al, *Chem. Vap. Dep.* **2009**

Results: BET analysis



or

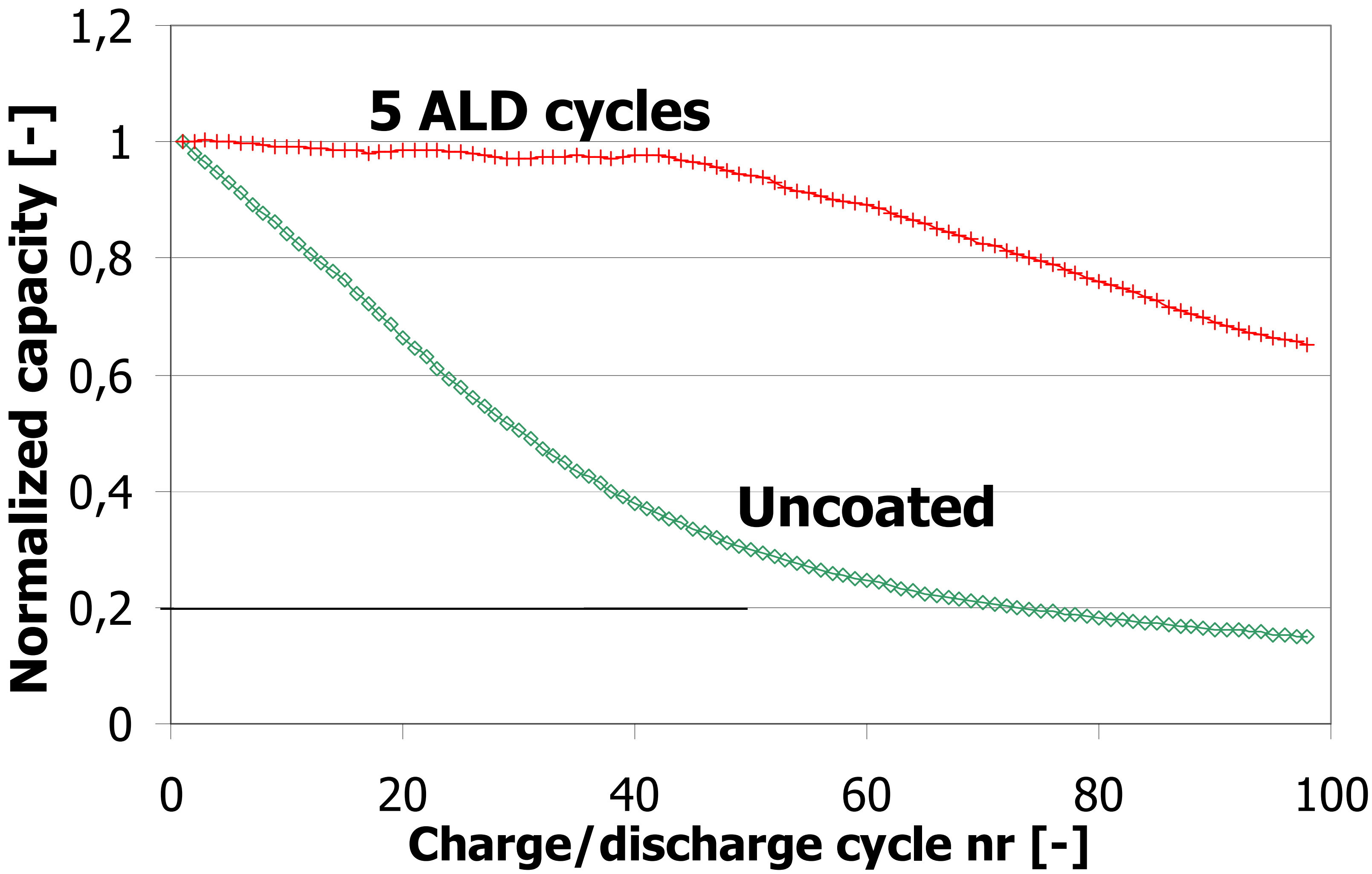


# ALD Cycles	Surface area [m^2/g]	D_{equiv} [nm]
0	1.9	730
5	1.7	820
11	1.5	930
28	1.3	1070

Primary particles of 100-500 nm; Agglomerates of 30-50 μm

The results show that we are mainly coating primary particles, not just the outer surface of the agglomerates

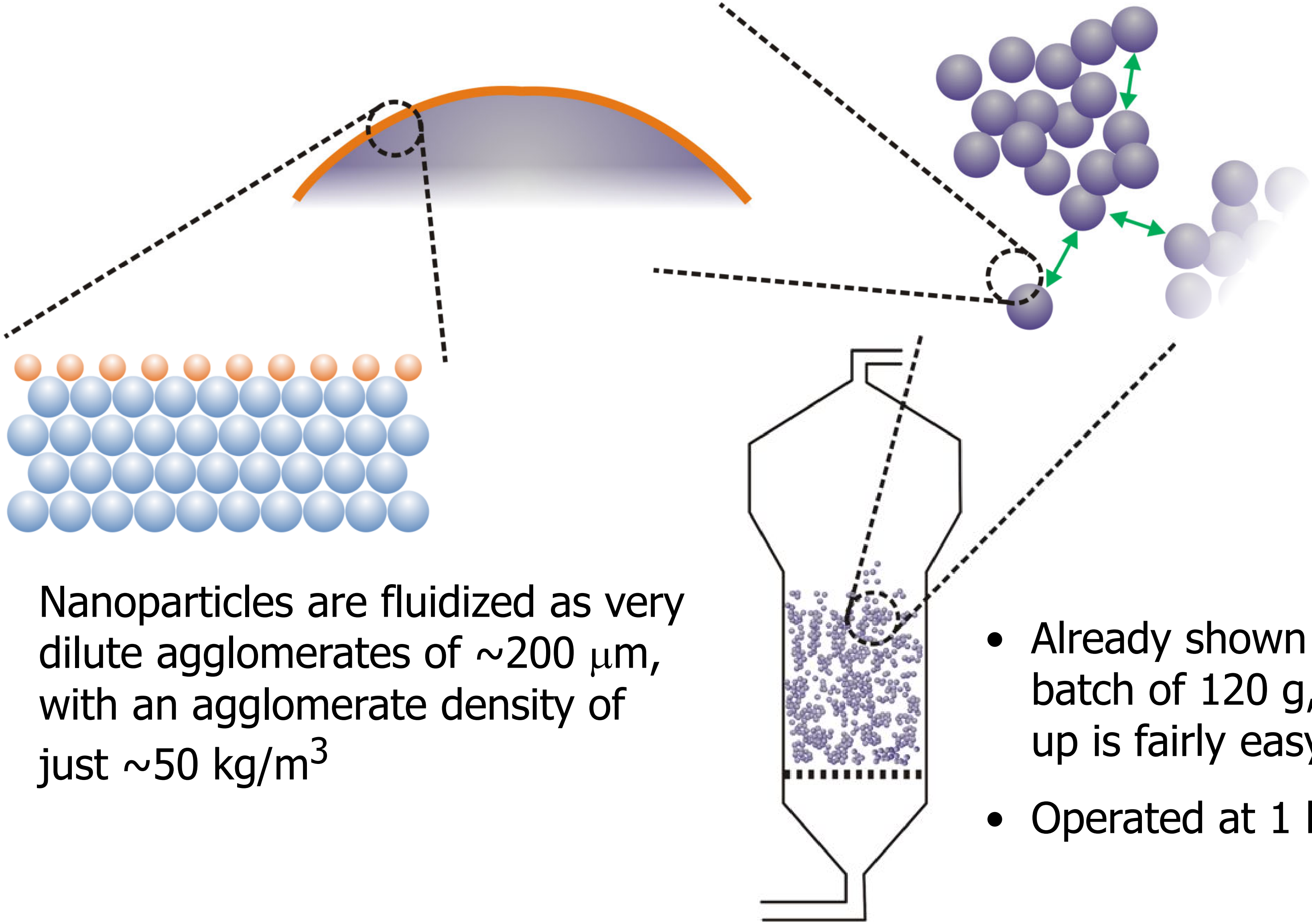
Results: battery tests at 60°C



in cooperation with Erik Kelder

TU Delft

ALD fluidized bed reactor



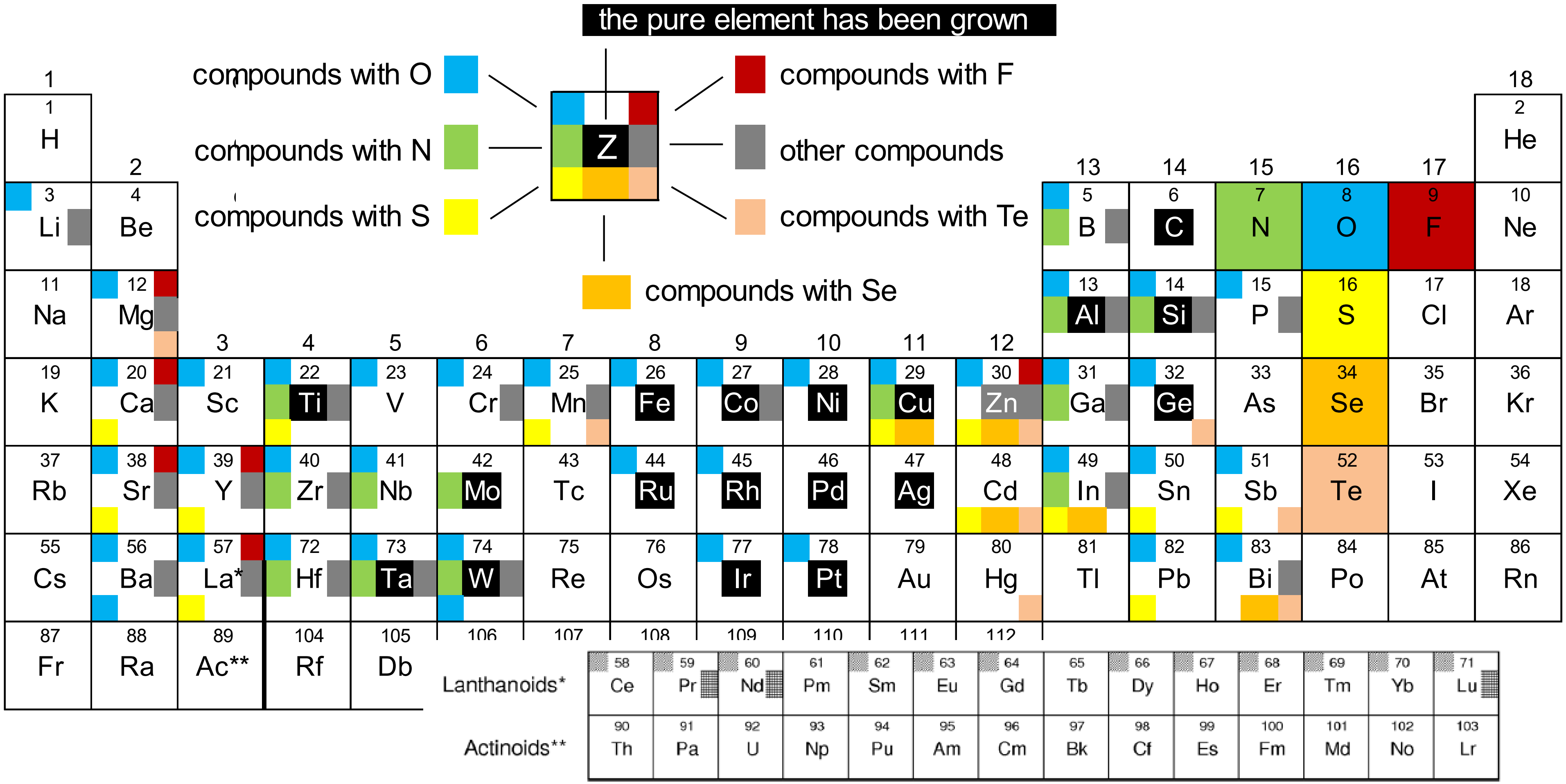
Nanoparticles are fluidized as very dilute agglomerates of ~200 μm, with an agglomerate density of just ~50 kg/m^3

- Already shown for batch of 120 g, scale-up is fairly easy
- Operated at 1 bar!

Wide range of coatings possible

'Periodic table of ALD'

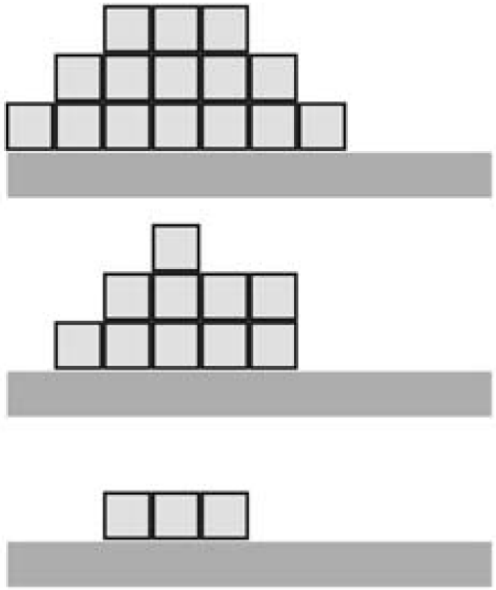
Miikkulainen et al., J. Appl. Phys. 113 (2013) 021301; Status Dec. 2010

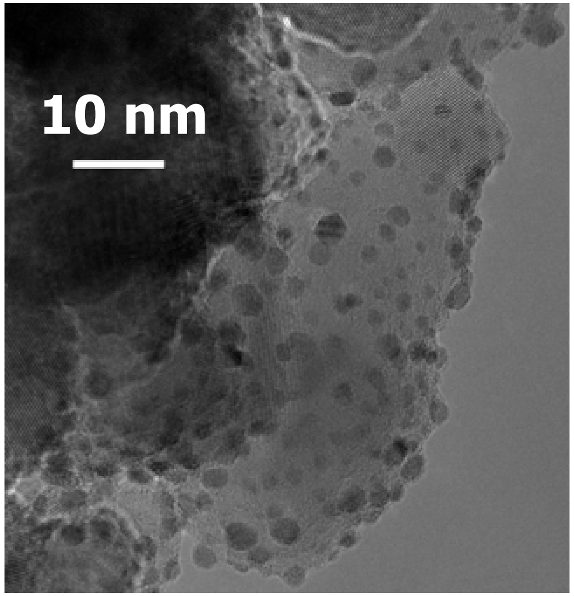


Pt deposition

TiO_2 particles “coated” with Pt (5 ALD cycles) at atmospheric pressure

Island growth!

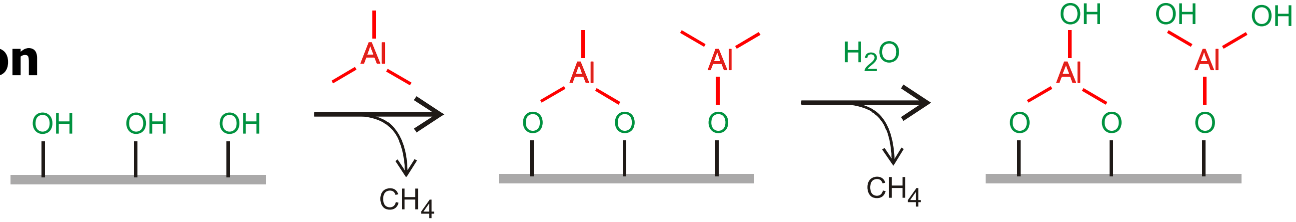




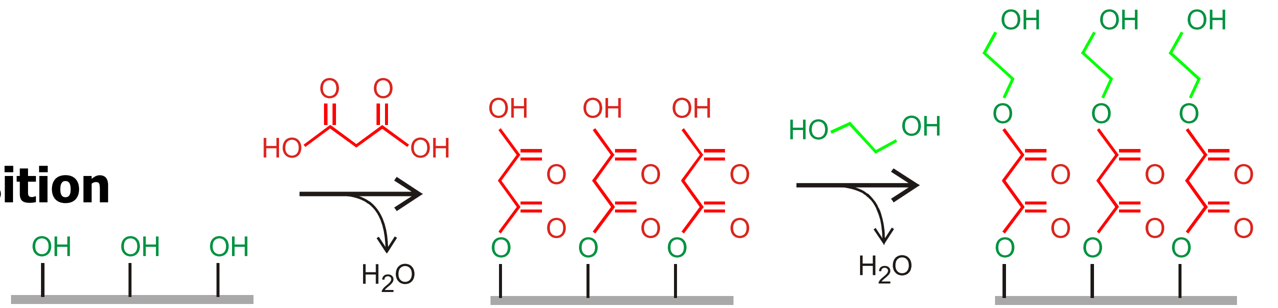
Pt on TiO_2

Vapour-phase coating

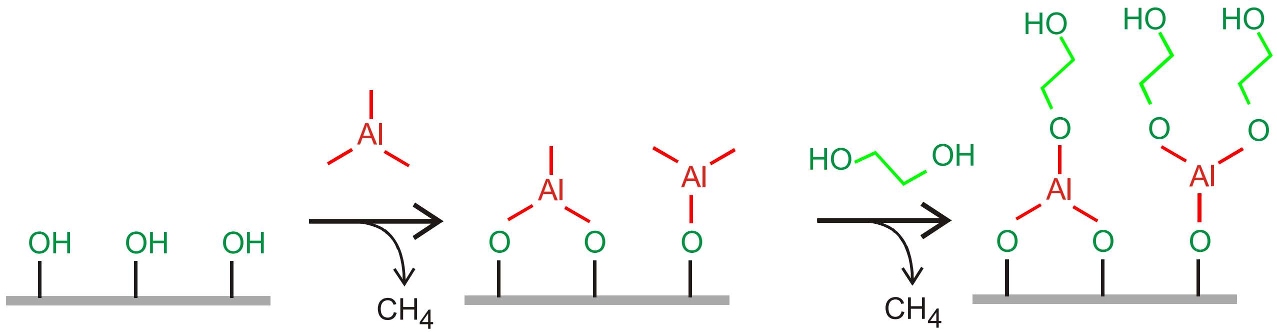
atomic layer deposition
(ALD; inorganic)



molecular layer deposition
(MLD; organic)



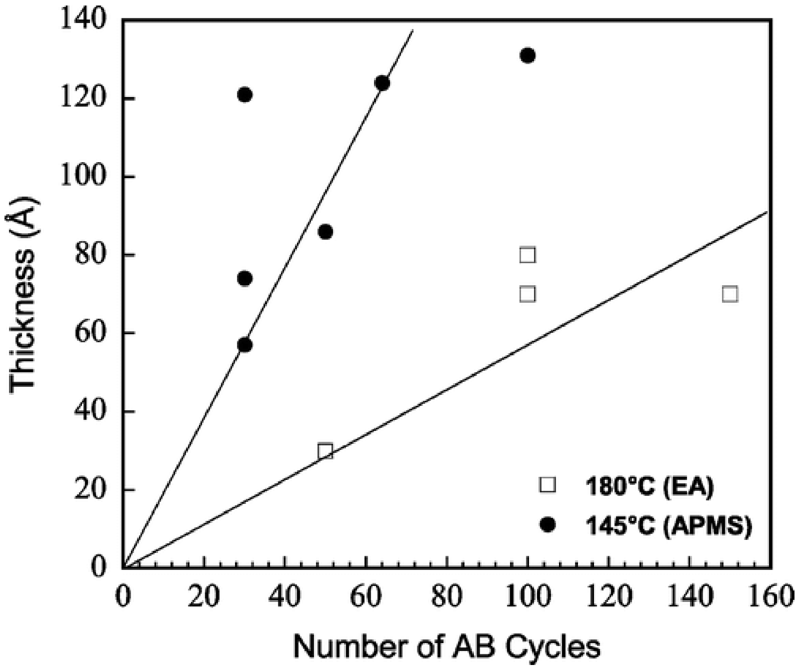
hybrid ALD/MLD
(mixed)

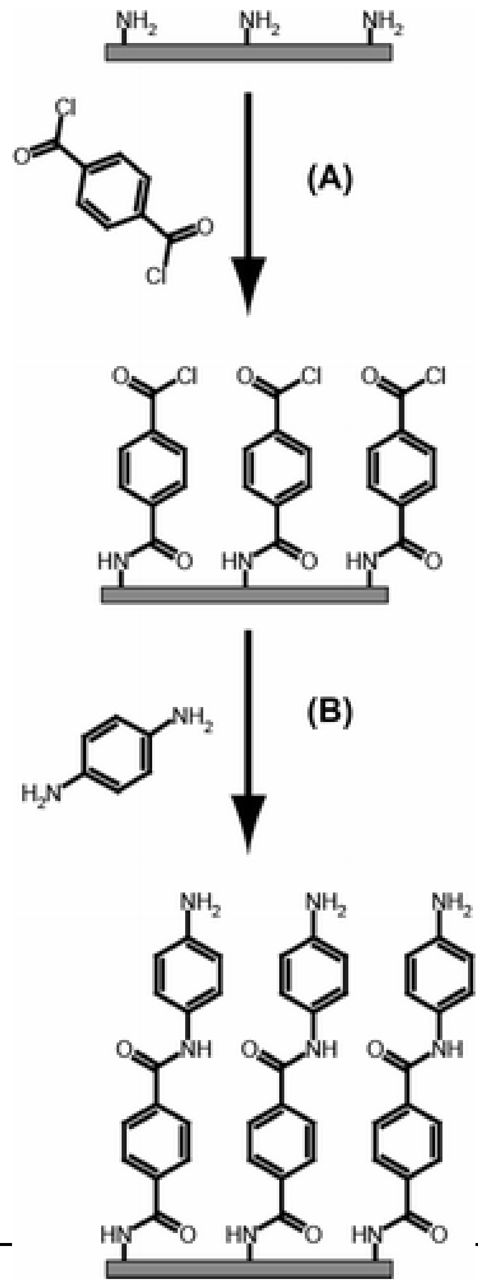


Bui et al., *Chem Comm* **53**(2017) 45

MLD

Molecular layer deposition: same approach as ALD, but now with organic molecules.





Adamczyk et al., Langmuir 24 (2008) 2081

Basic properties of nanoparticles

Gas phase production of nanoparticles

Sizing & forces on single particles

Particle-particle forces

Particle coating

Applications

Applications of Nanoparticles

- **Pigment**
  - Carbon black, TiO_2
- **Medicine**
  - diagnostics, drug delivery
- **Chemistry**
  - catalysis
- **Energy**
  - batteries, hydrogen storage, photovoltaic cells, LEDs
- **Construction**
  - nanostructured materials
- **Food**
  - ingredients, packaging
- **Personal care**
  - sunscreens
- …

This list is not complete!

Carbon Black

- Produced by the incomplete combustion of heavy petroleum products such as FCC tar, coal tar, ethylene cracking tar,

- Large surface area: typically nanoparticles of 20 – 200 nm

- 70% used in tyres (20% in other rubber application):
  - pigment
  - reinforcement
  - increase of heat transfer

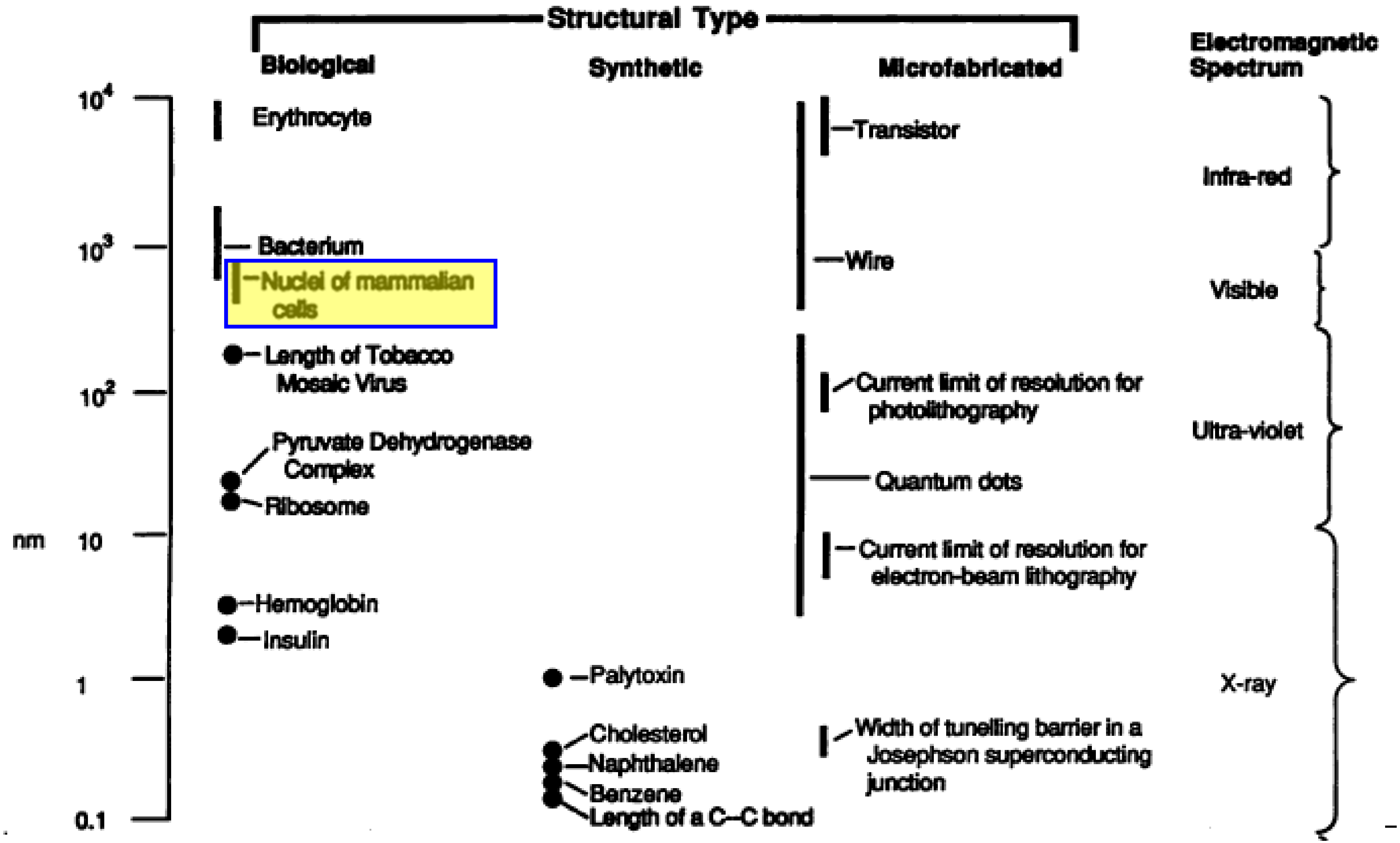
- Top 50 industrial chemicals manufactured worldwide, based on annual tonnage. Worldwide production is about 8.1 million metric tons (2006).

Titanium dioxide (=Titania)

- Titanium dioxide occurs in nature as the minerals rutile, anatase and brookite; there are some other crystal forms as well.
- Main application: pigment; also: photocatalyst, UV-blocker
- Most particles produced in the range 200-300 nm, but also in finer grades
- Production: Crude ore (containing at least 70% TiO_2) is reduced with carbon, and oxidized with chlorine to give $TiCl_4$. This is distilled, and re-oxidized with oxygen to give pure TiO_2 while regenerating chlorine.
- Worldwide production is about 4.4 million metric tons (2004).

Applications in medicine

Relevant sizes



Whitesides, G.M., et al. (1991). *Science* **254**: 1312

Definition of Nanomedicine

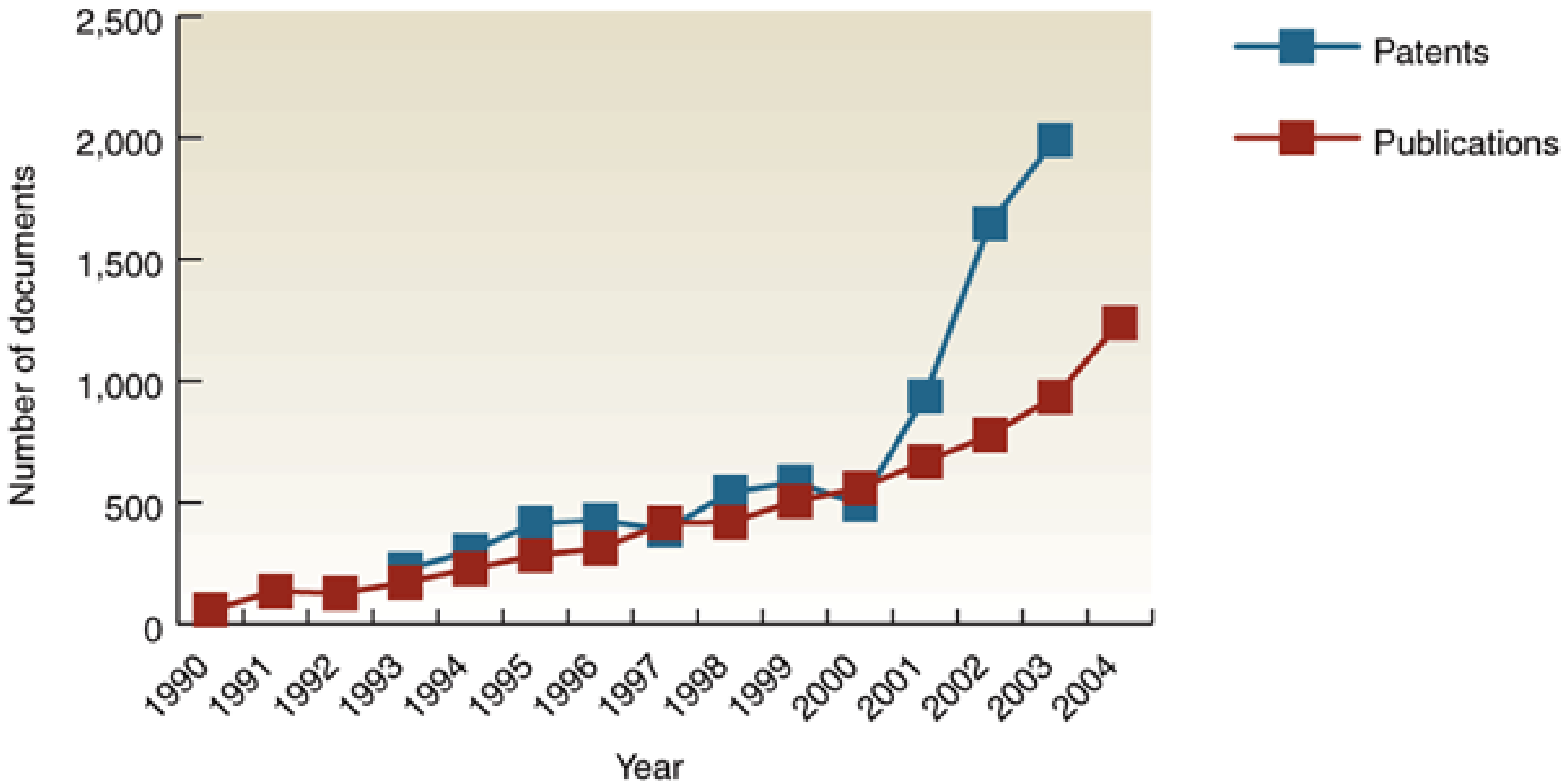
Definition 1 (broad): pharmaceutical technology that uses molecular tools and knowledge of the human body for medical diagnosis and treatment.

Definition 2 (narrower): pharmaceutical technology that makes use of physical effects occurring in nanoscale objects that exist at the interface between the molecular and macroscopic world in which quantum mechanics still reigns.

Wagner et al., Nature Biotechnology 24 (2006) 1211

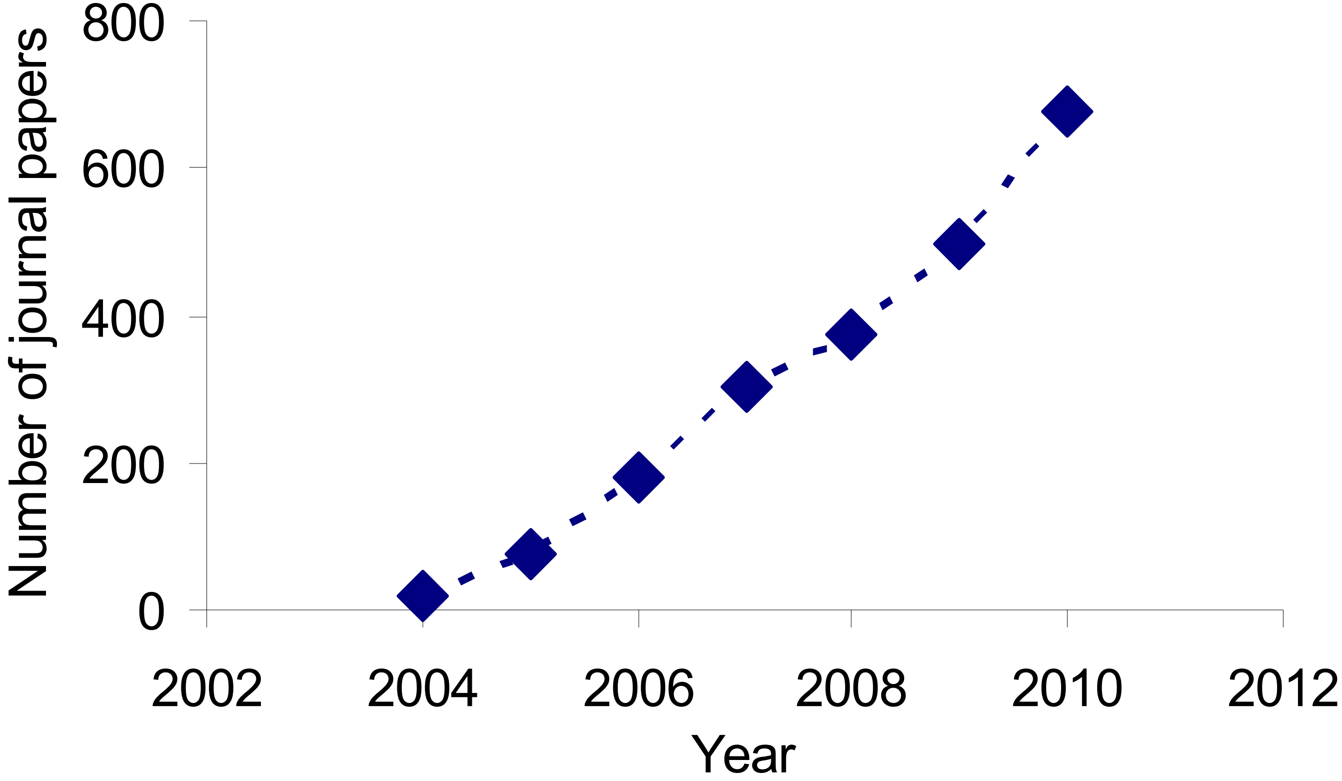
Nanomedicine: strongly growing

Nanomedicine publications and patents worldwide



Wagner et al., *Nature Biotechnology* 24 (2006) 1211

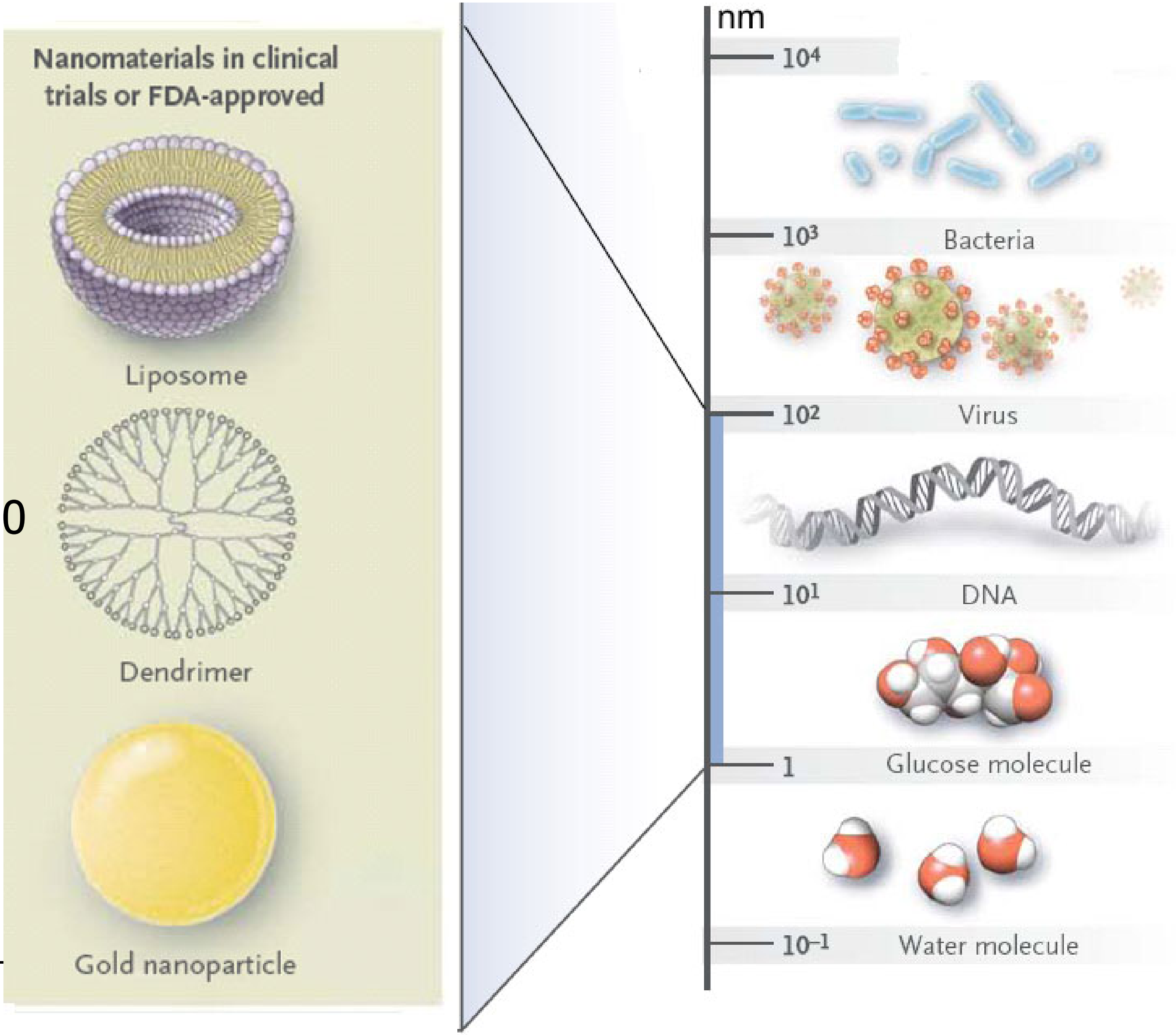
The growth continues…



In contrast with previous slide, just papers than have "nanomedicine" in title, abstract or keywords. Source: SCOPUS

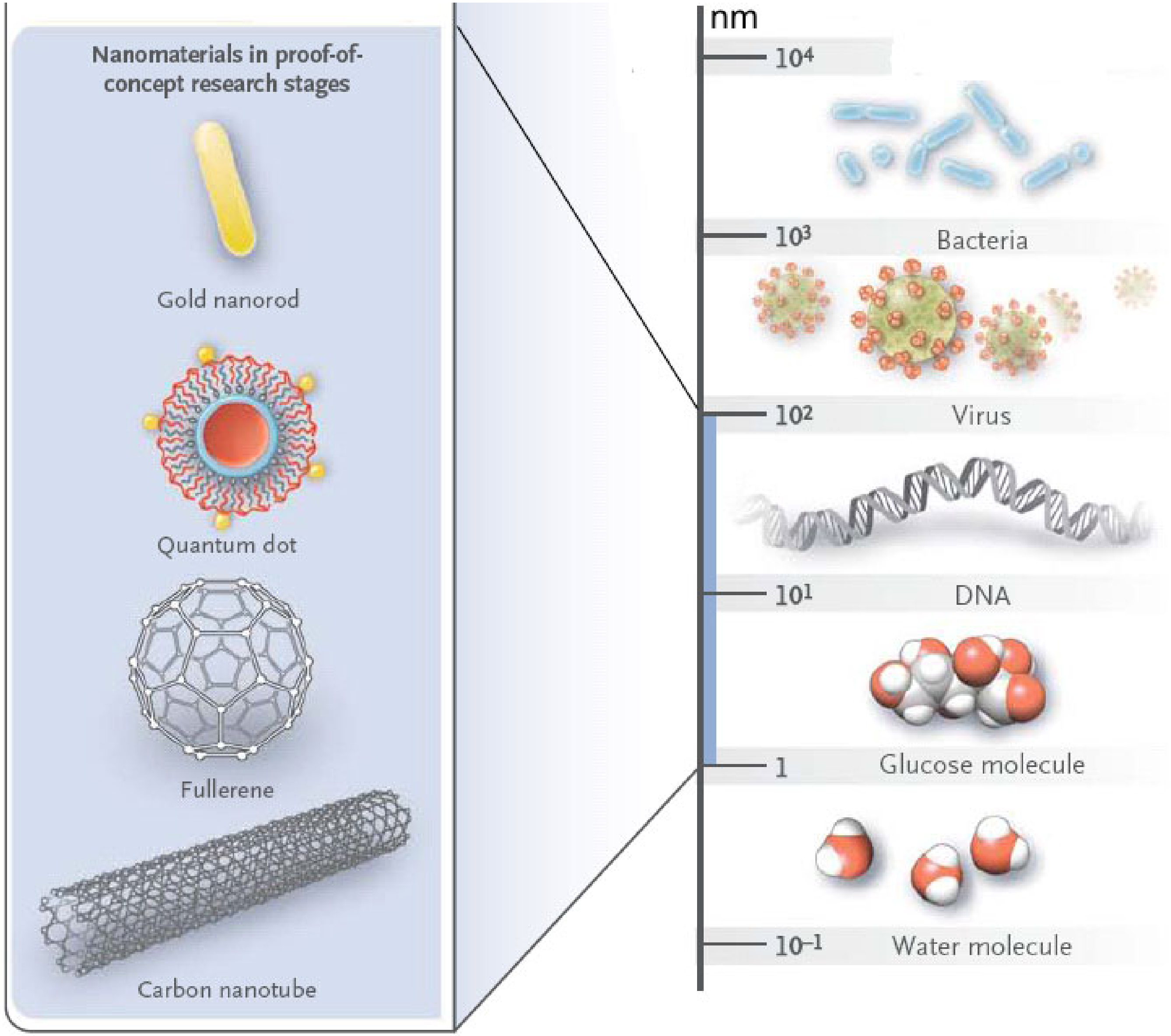
Nanomaterials in clinical trials or FDA-approved

Kim et al.,
N Engl J Med 2010
363: 2434.



Nanomaterials in proof-of-concept research stages

Kim et al.,
N Engl J Med 2010
363: 2434.

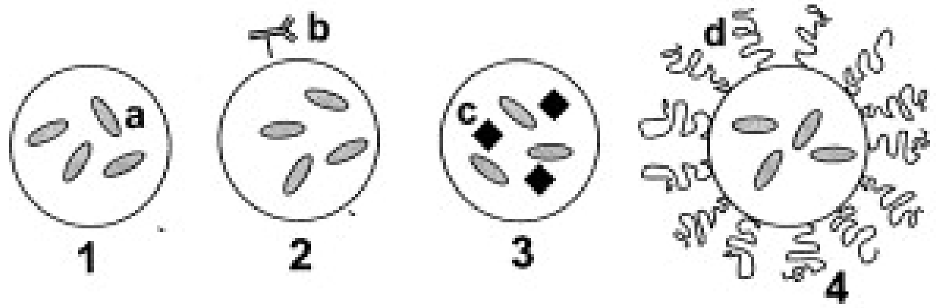


Commercial efforts in nanomedicine

	# products	Sales ($ billions)	Total	Advanced stages*	Companies
Drug delivery	23	5.4	98	9	113
Biomaterials	9	0.07	9	6	32
In vivo imaging	3	0.02	8	2	13
In vitro diagnostics	2	0.78	30	4	35
Active implants	1	0.65	5	1	7
Drugs & therapy	0	0	7	1	7
Total	38	6.8	157	23	207
Sales numbers of nanomedicines are estimates **for the year 2004**.					
*Drugs where the product is in clinical phase 2/3 or 3 and for all other products where market introduction is expected within two years.					

Wagner et al., *Nature Biotechnology* 24 (2006) 1211

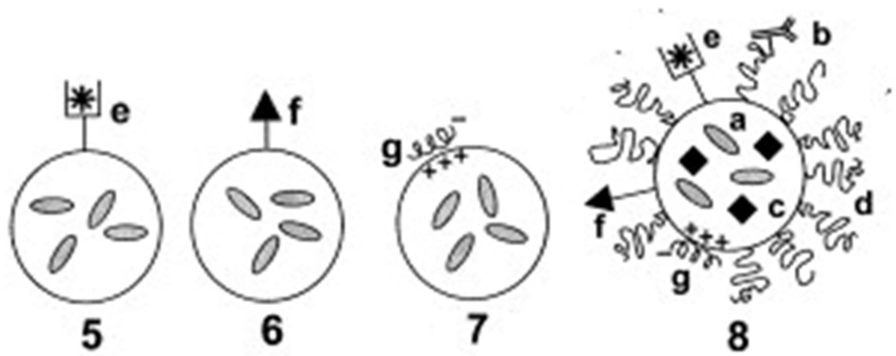
Pharmaceutical nanocarriers



- 1 – **Traditional "plain" nanocarrier** (a – drug loaded into the carrier);
- 2 – **Targeted nanocarrier** or immunocarrier (b – specific targeting ligand, usually a monoclonal antibody, attached to the carrier surface);
- 3 – **Magnetic nanocarrier** (c – magnetic particles loaded into the carrier together with the drug and allowing for the carrier sensitivity towards the external magnetic field and its use as a contrast agent for magnetic resonance imaging);
- 4 – **Long-circulating nanocarrier** (d – surface-attached protecting polymer (usually PEG, Polyethylene glycol) allowing for prolonged circulation of the nanocarrier in the blood);

Torchilin, *Advanced Drug Delivery Reviews* 58 (2006) 1532

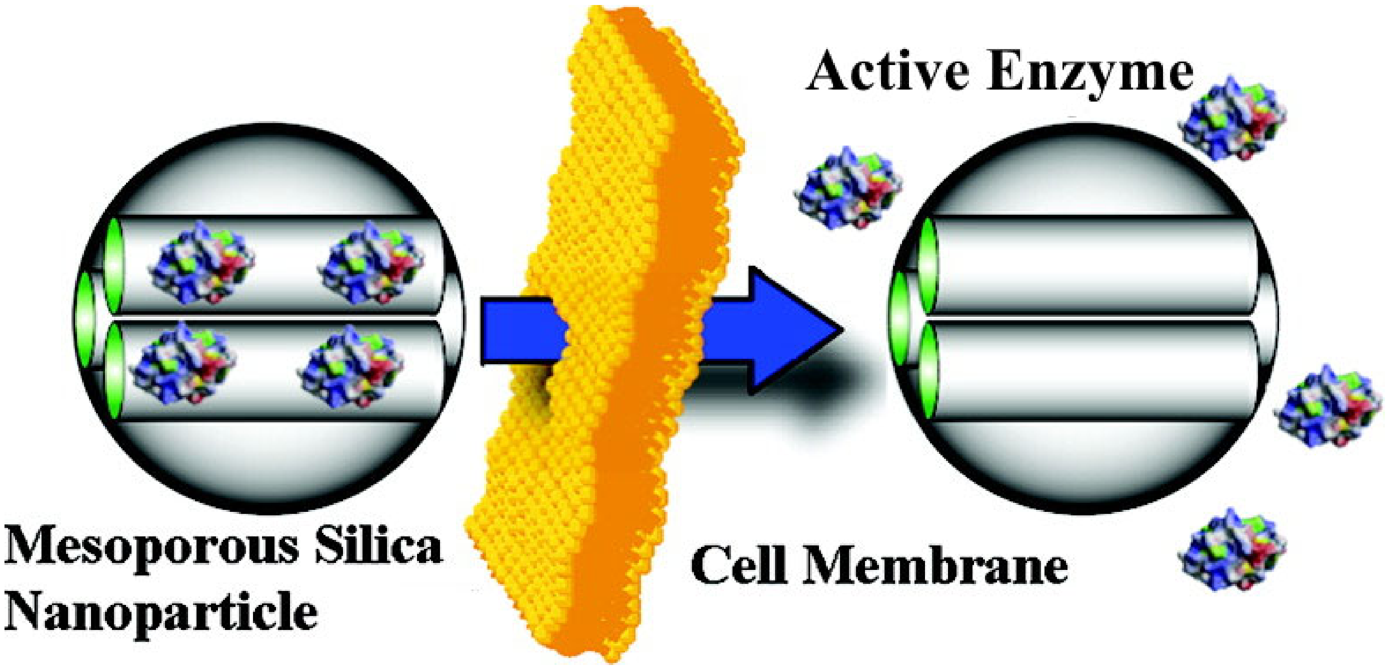
Pharmaceutical nanocarriers



- 5 – **Contrast nanocarrier** for imaging purposes (e – heavy metal atom – 111In, 99mTc, Gd, Mn – loaded onto the nanocarrier via the carrier-incorporated chelating moiety for gamma- or MR imaging appl.);
- 6 – **Cell-penetrating nanocarrier** (f – cell-penetrating peptide, CPP, attached to the carrier surface and allowing for the carrier enhanced uptake by the cells);
- 7 – **DNA-carrying nanocarrier** such as lipoplex or polyplex (g – DNA complexed by the carrier via the carrier surface positive charge);
- 8 – **Hypothetical multifunctional pharmaceutical nanocarrier** combining the properties of the carriers # 1–7.

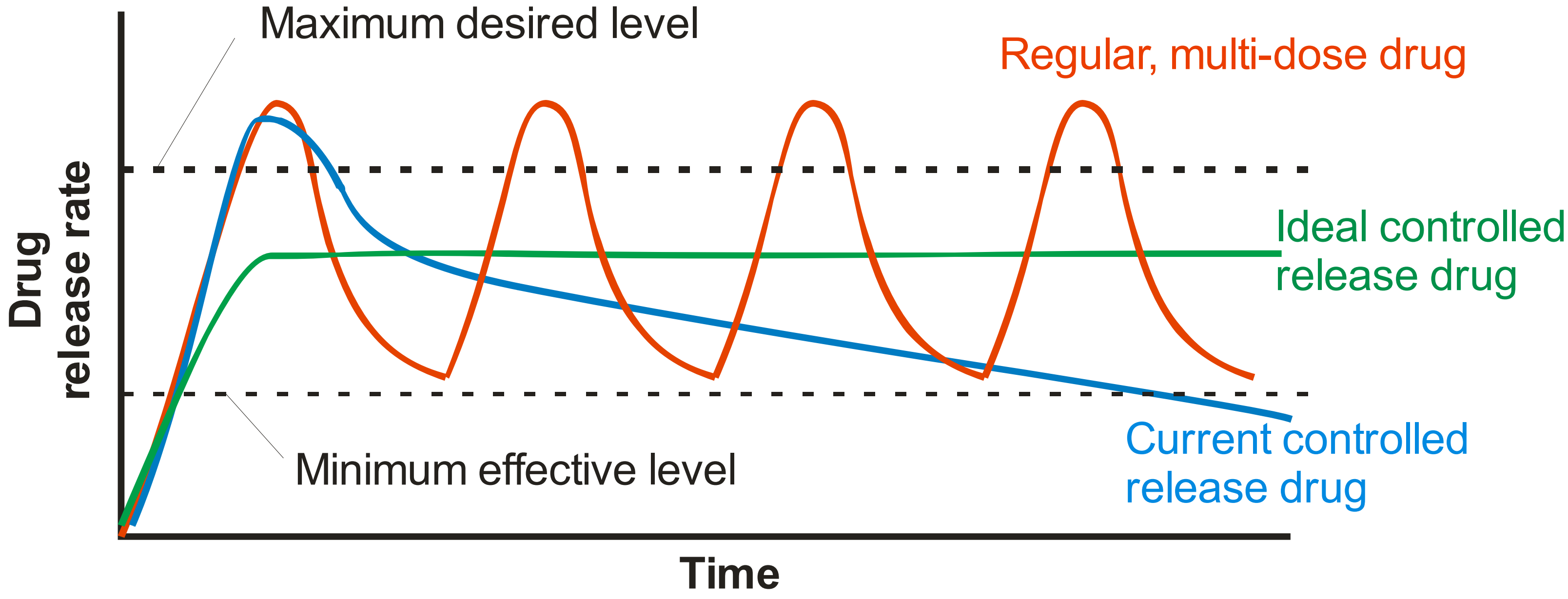
Torchilin, *Advanced Drug Delivery Reviews* 58 (2006) 1532

Nanoparticle as transport vehicle



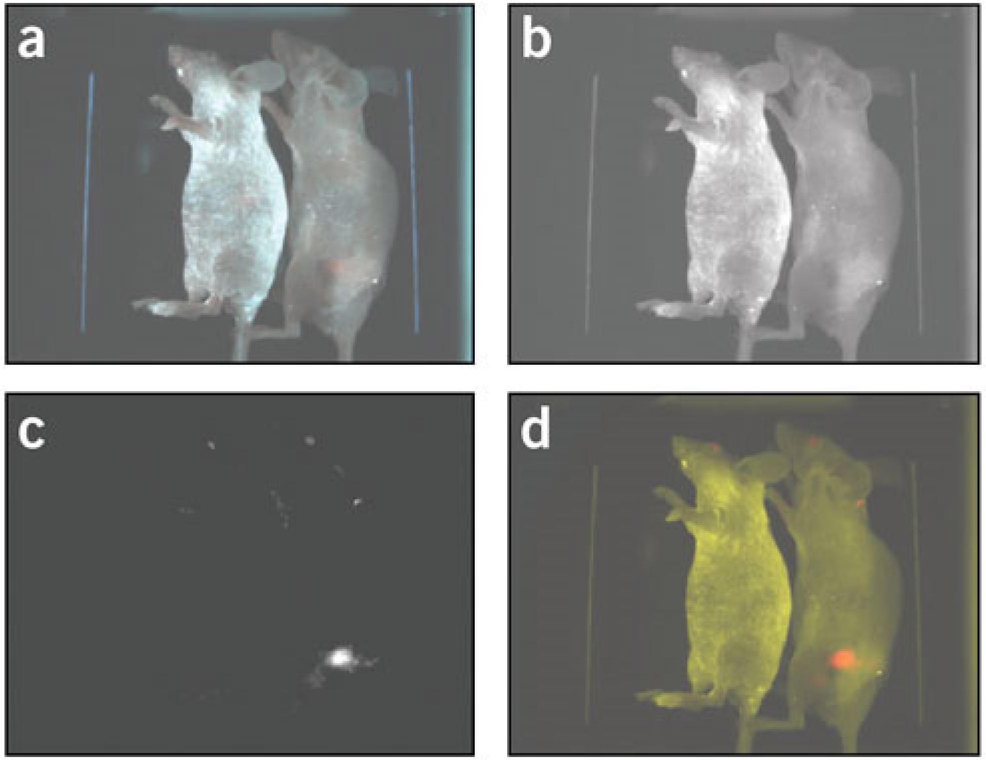
Schematic representation of a nanoparticle transporting an active enzyme through the cell membrane and releasing it into the cytoplasm (adapted from: Slowing et al., 2007).

Controlled release



Use of Quantum Dots

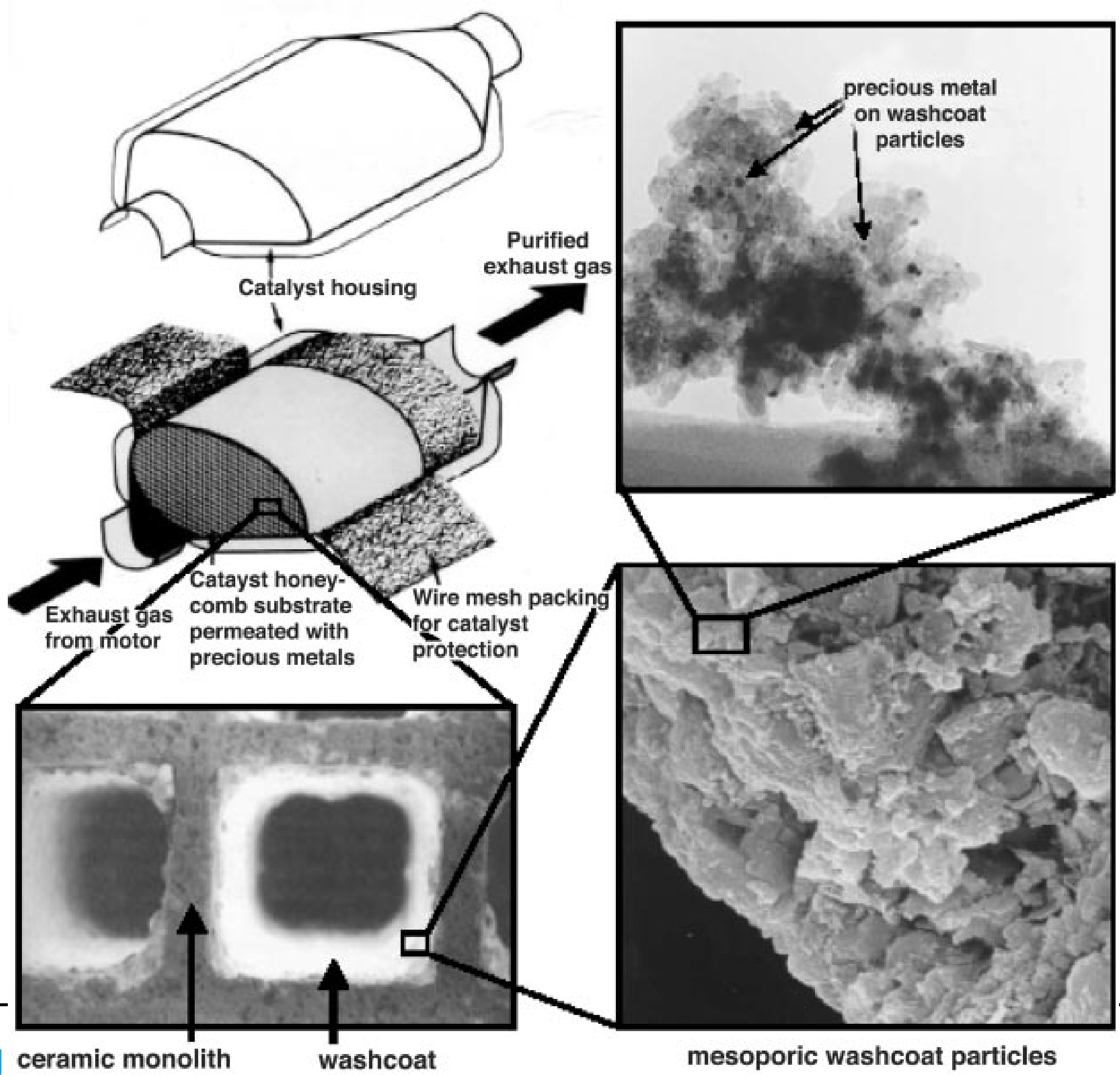
Detection of prostate tumor in a mouse using quantum dots.



Gao et al., Nat. Biotech. **2004**

Applications in catalysis

Example: three-way catalytic converter

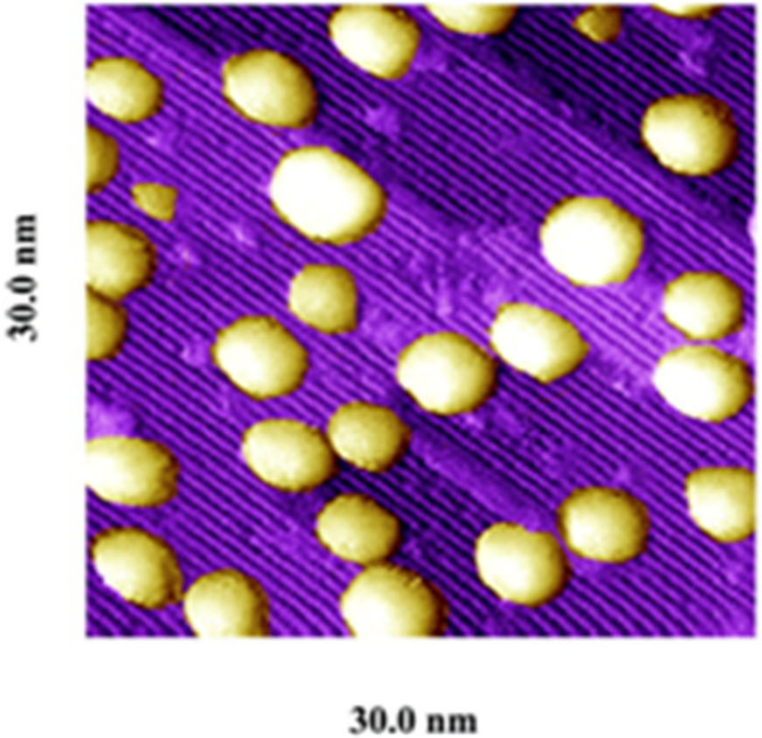


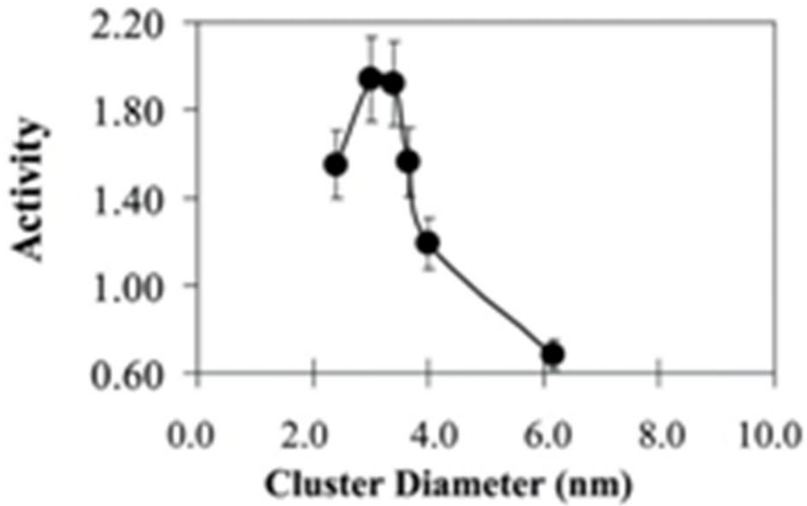
The alumina washcoat is impregnated with nanoparticles of Pt, Rh, Ce, zirconia, lanthana, …

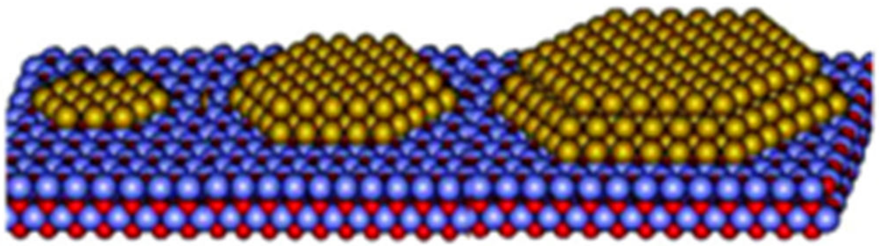
Bell, Science 299 (2003) 1688

Influence of particle diameter

$CO + \frac{1}{2} O_2 \rightarrow CO_2$



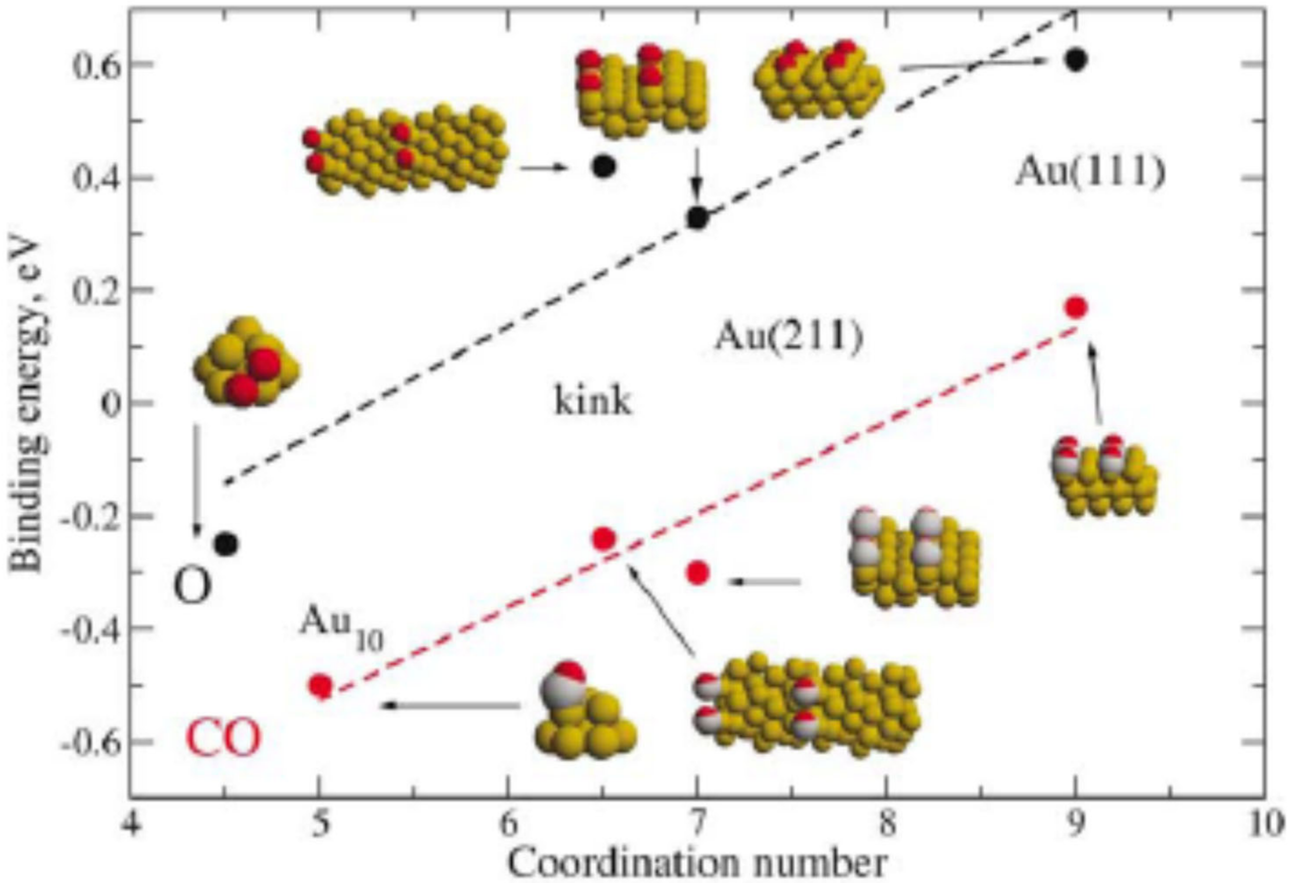




Effect ascribed to oxidation of Au atoms in contact with the support

Bell, Science 299 (2003) 1688

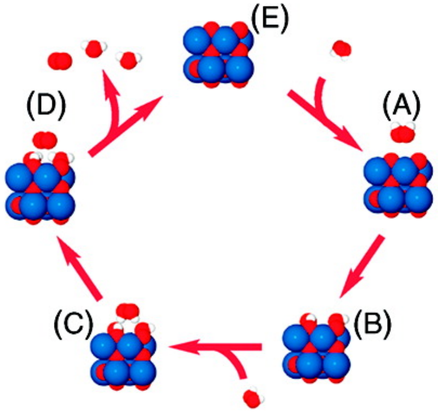
Influence of coordination number



Lopez et al., Journal of Catalysis 223 (2004) 232

Sabatier principle

Example reaction:



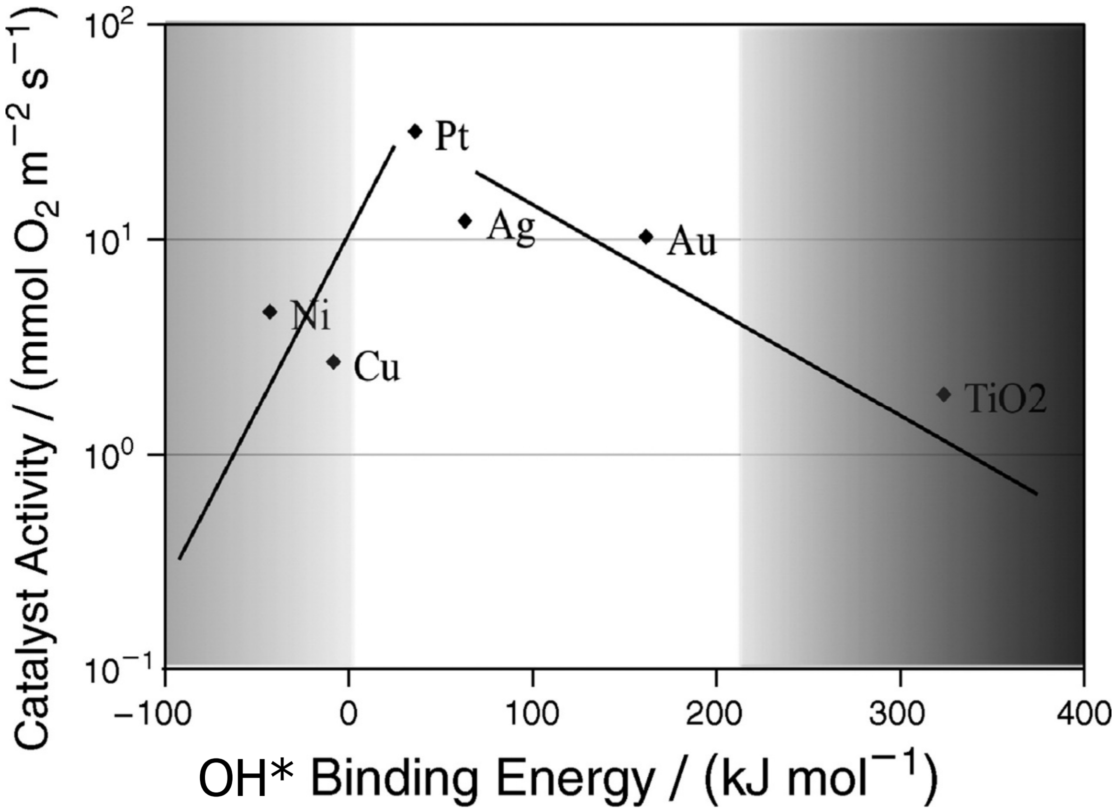
$H_2O_2(aq) + 2^* \longrightarrow 2OH^*$ (E) to (B)

$2OH^* + H_2O_2(aq) \longrightarrow 2H_2O^* + O_2(g)$ (B) to (D)

$2H_2O^* \longrightarrow 2H_2O(l) + 2^*$ (D) to (E)

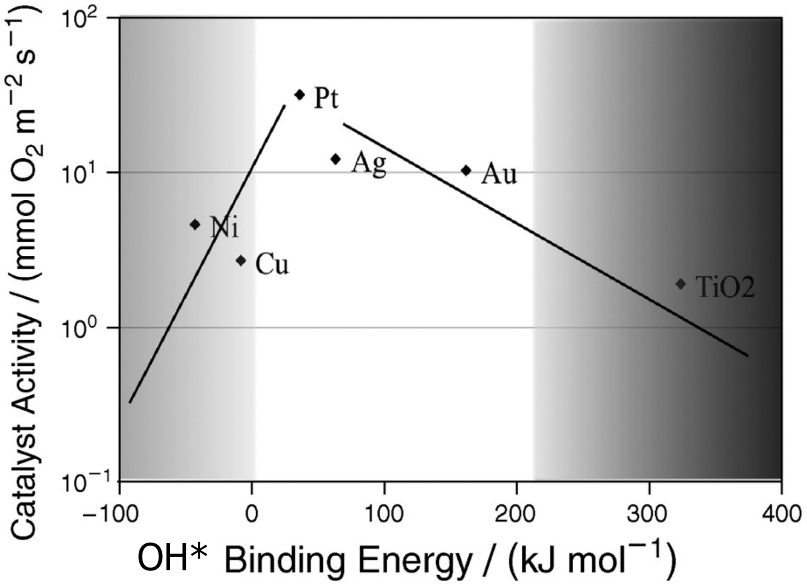
$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$

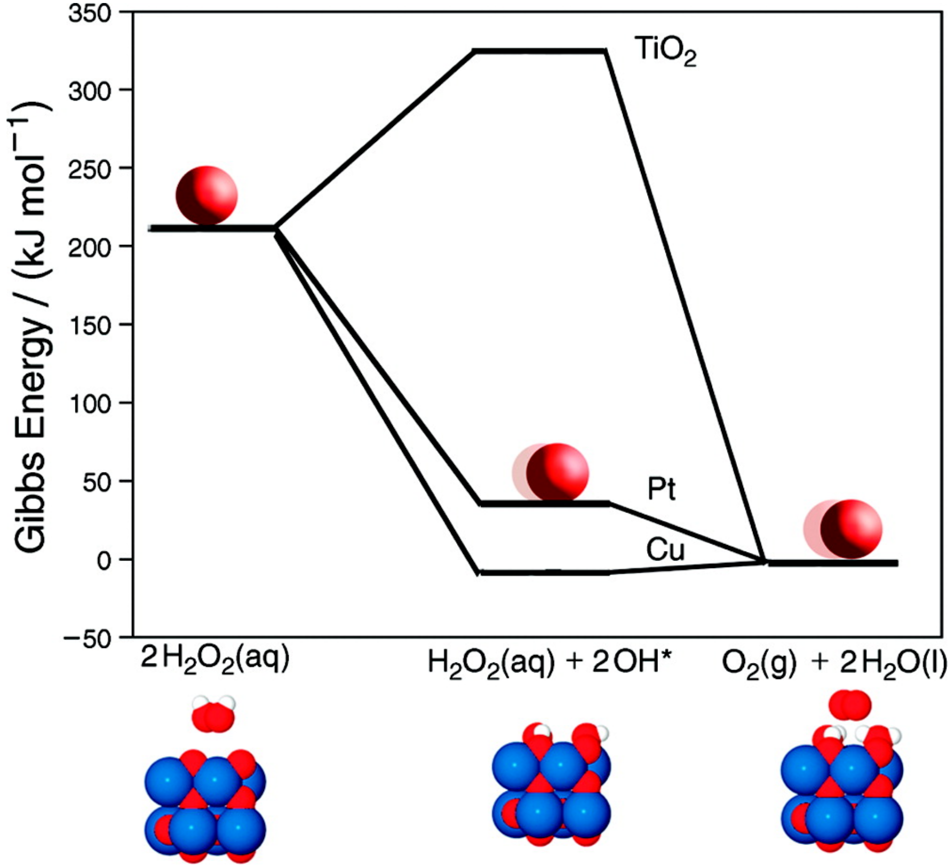
Volcano plot:



Laursen et al., *J. Chem. Educ.* **2011,** 88, 1711-1715

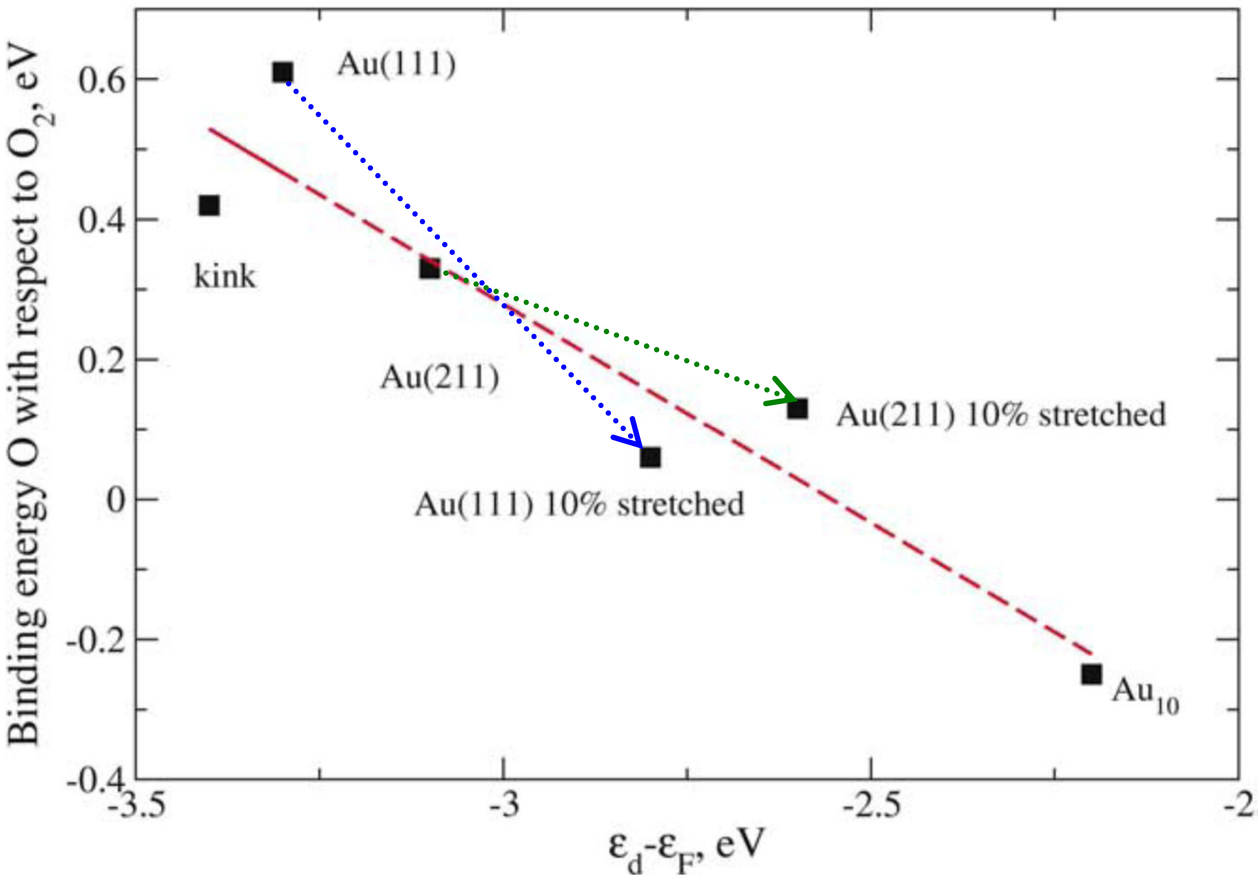
Sabatier principle





Laursen et al., *J. Chem. Educ.* **2011,** 88, 1711-1715

Influence of stretching



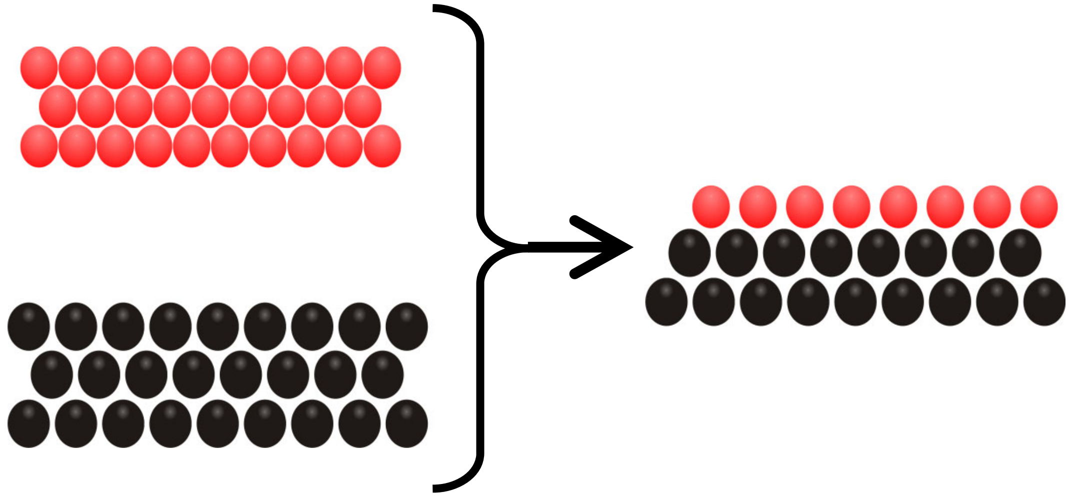
Lopez et al., Journal of Catalysis 223 (2004) 232

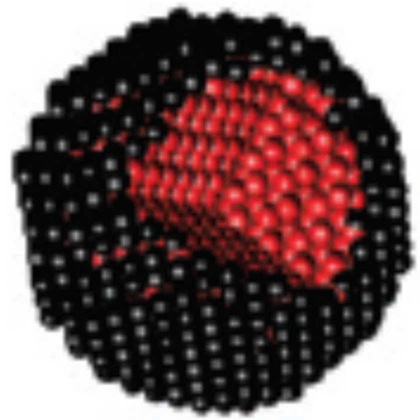
How to stretch the atoms

in a catalyst particle?

Stretching atoms in a catalyst particle

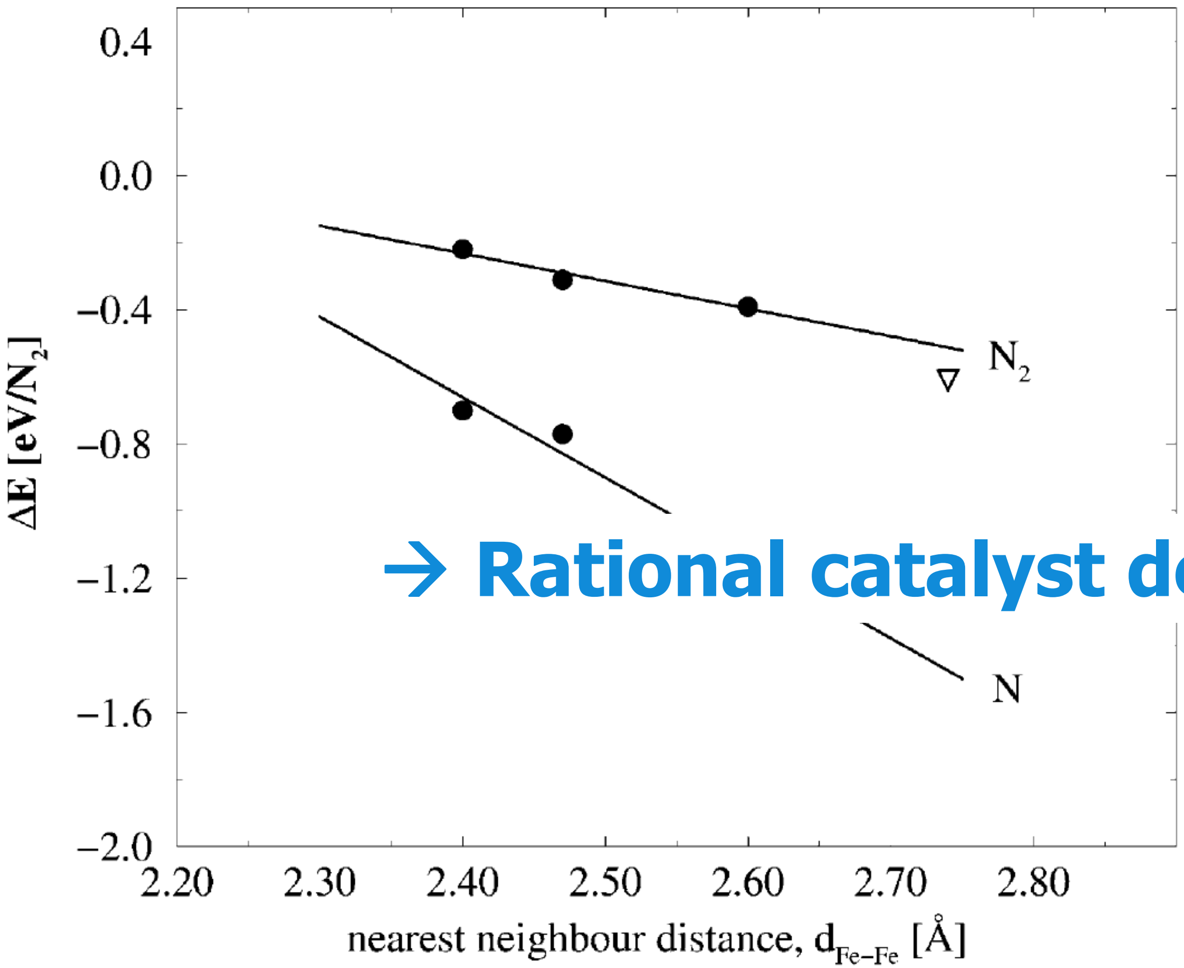
Place a coating of only 1 (or max 2-3) atom-layers thick on a different metal





Ru core with Pt shell

Alayoglu et al., Nature Mater. (2008)



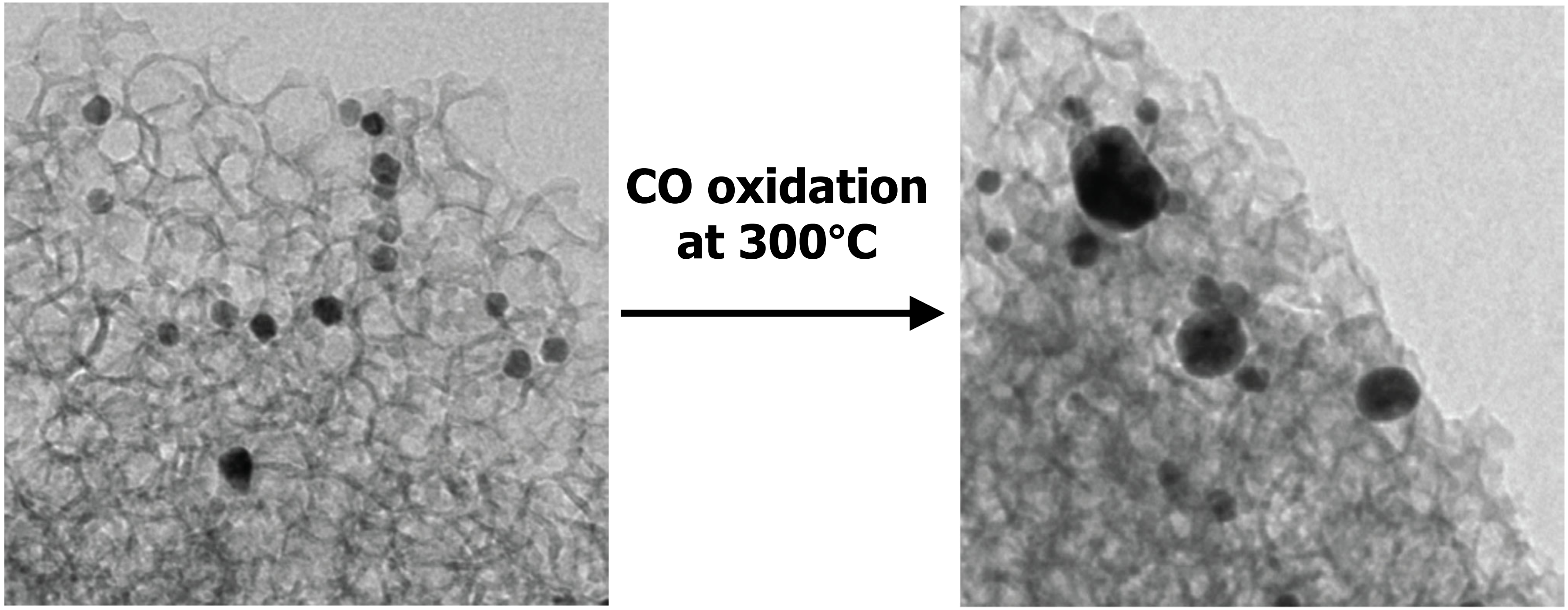
→ Rational catalyst design!

The adsorption energy of N and N_2 on an fcc-Fe(1 1 1) surface as a function of the nearest neighbour distance , d_{Fe-Fe}. The binding energies are compared to N_2 (g) and a clean metal surface. The triangles give the energies in the case of a monolayer of Fe on Ru (0 0 0 1).

TU Delft

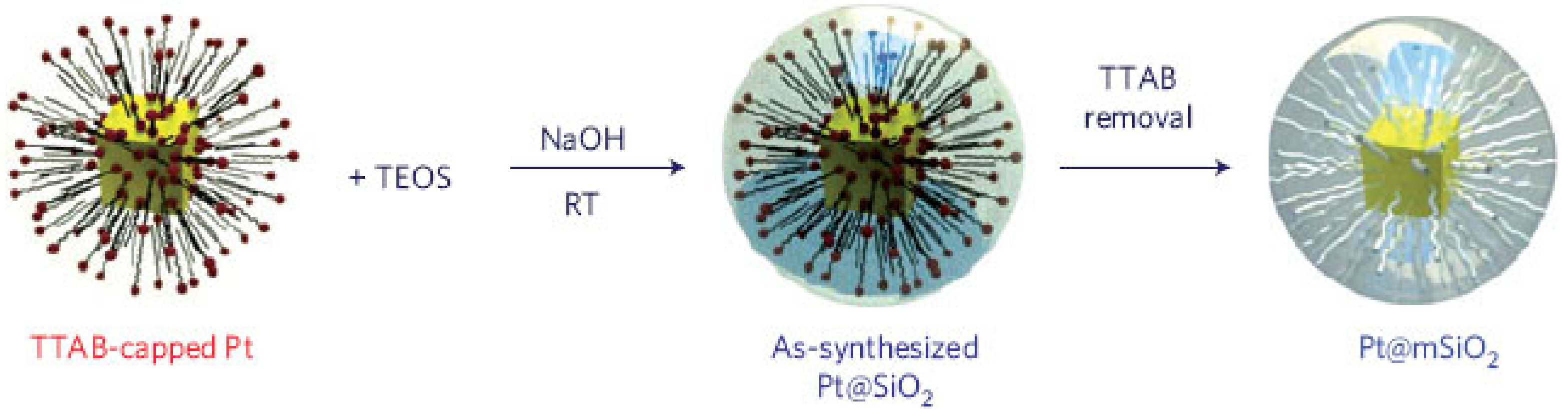
Logadottir, A., Nørskov, J.K., Surface Science 489, 135-143 (2001)

Core-shell NPs for thermal stability



Joo et al., Nature Mat. 8 (2009) 126

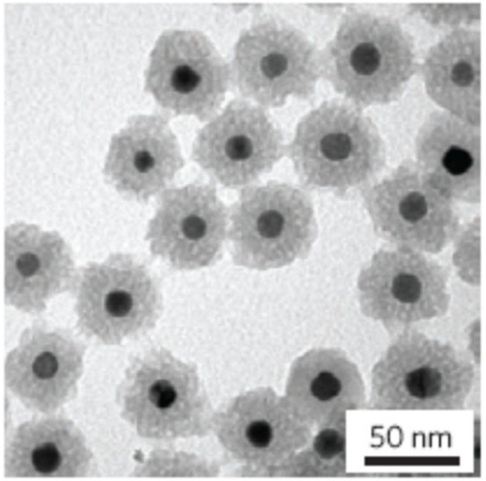
Core-shell NPs for thermal stability

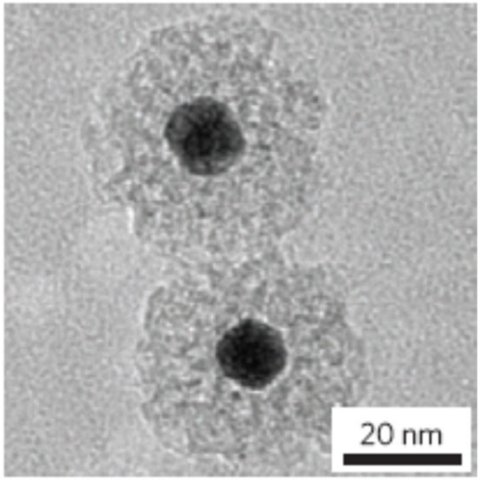


Schematic representation of the synthesis of Pt@mSiO2 nanoparticles
(Pt NPs coated with mesoporous silica)

Core-shell NPs for thermal stability

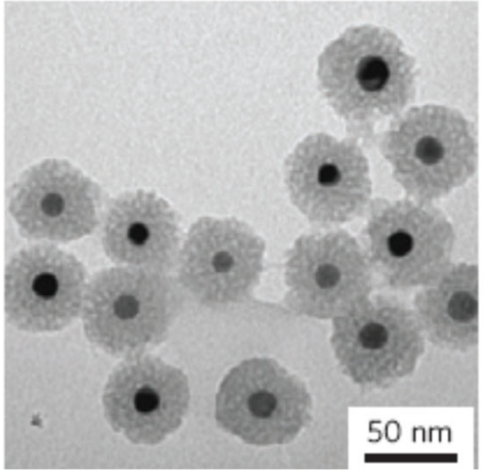
T=350°C

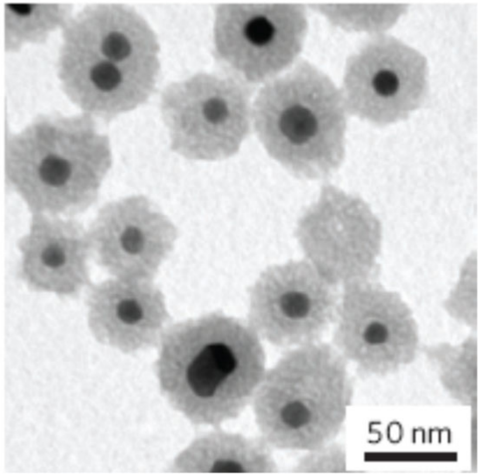




T=350°C

T=550°C





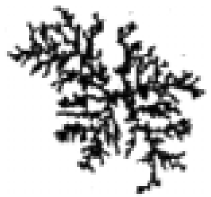
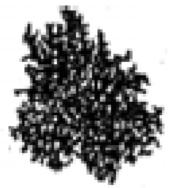
T=750°C

Is sintering always a problem in catalysis?

At low temperatures it is not a problem. Example: photocatalysis!

However, agglomeration / aggregation can still play a role.

Kinetic growth models in a 2-D

Diffusion-limited	Ballistic	Reaction-limited
 Particle-cluster ($D_f = 2.50$)	 Particle-cluster ($D_f = 3.00$)	 Particle-cluster ($D_f = 3.00$)
 Cluster-cluster ($D_f = 1.80$)	 Cluster-cluster ($D_f = 1.95$)	 Cluster-cluster ($D_f = 2.09$)

The mass fractal dimension D of their 3-D analogs are given

Friedlander, *Smoke, Dust, and Haze*, 2nd ed., Oxford Univ. Press, 2000

Sustainable energy solutions

Photovoltaic cell

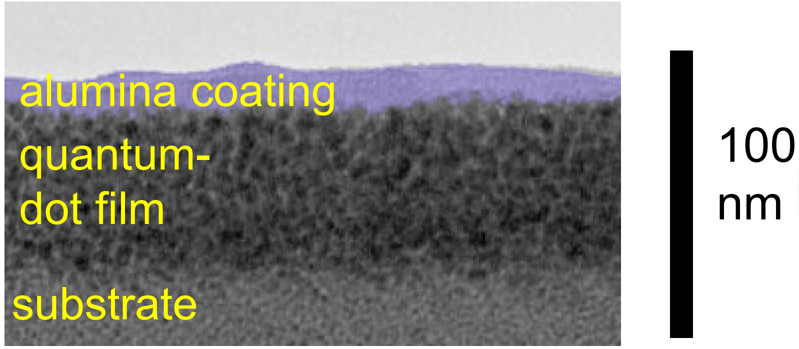
Fuel cell

Solar H_2 production

Li ion battery

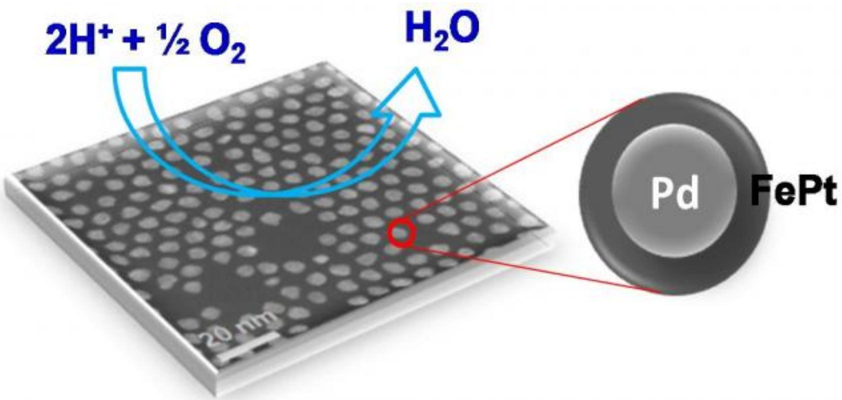
Nanotechnology for sustainable energy

Quantum dot film (→ PV cells?)



Valdesueiro et al., J Phys Chem C 120 (2016) 4266

Fuel cell

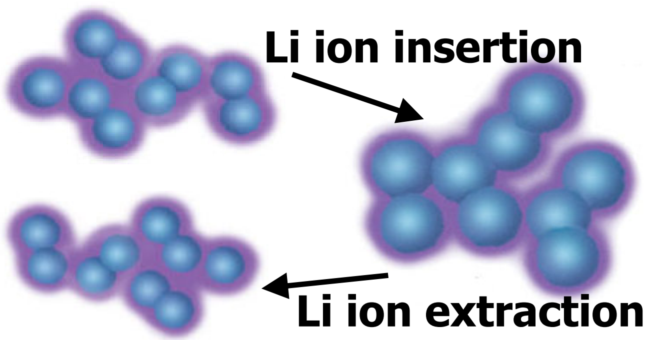


Mazumder & Sun, Brown University

Solar H_2 production

Maeda et al., Chem Eur J 16 (2010) 7750

Li ion battery



Lawrence Berkeley National Lab.

Many novel solutions rely on core-shell nanoparticles