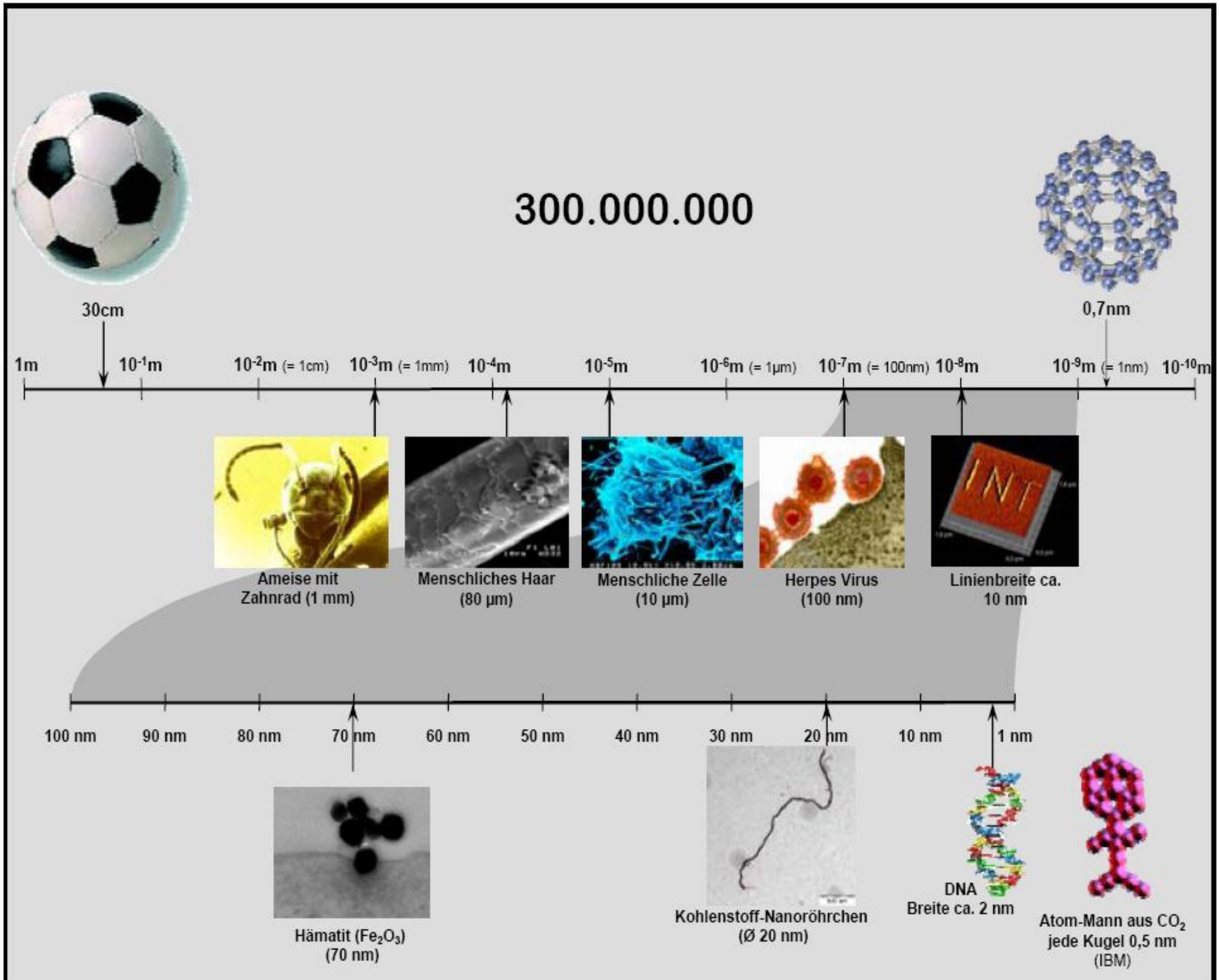
VL „Nanoparticle in the environment“ (Introduction)

Importance, Classification, Properties
Distribution in air and water
Aggregation
Transport
Transformation
Ecotoxicity (Toxicity)
Content of the course, literature sources

Size range of NP



Krug, 2007

Nature, November 2006:

Safe handling of nanotechnology

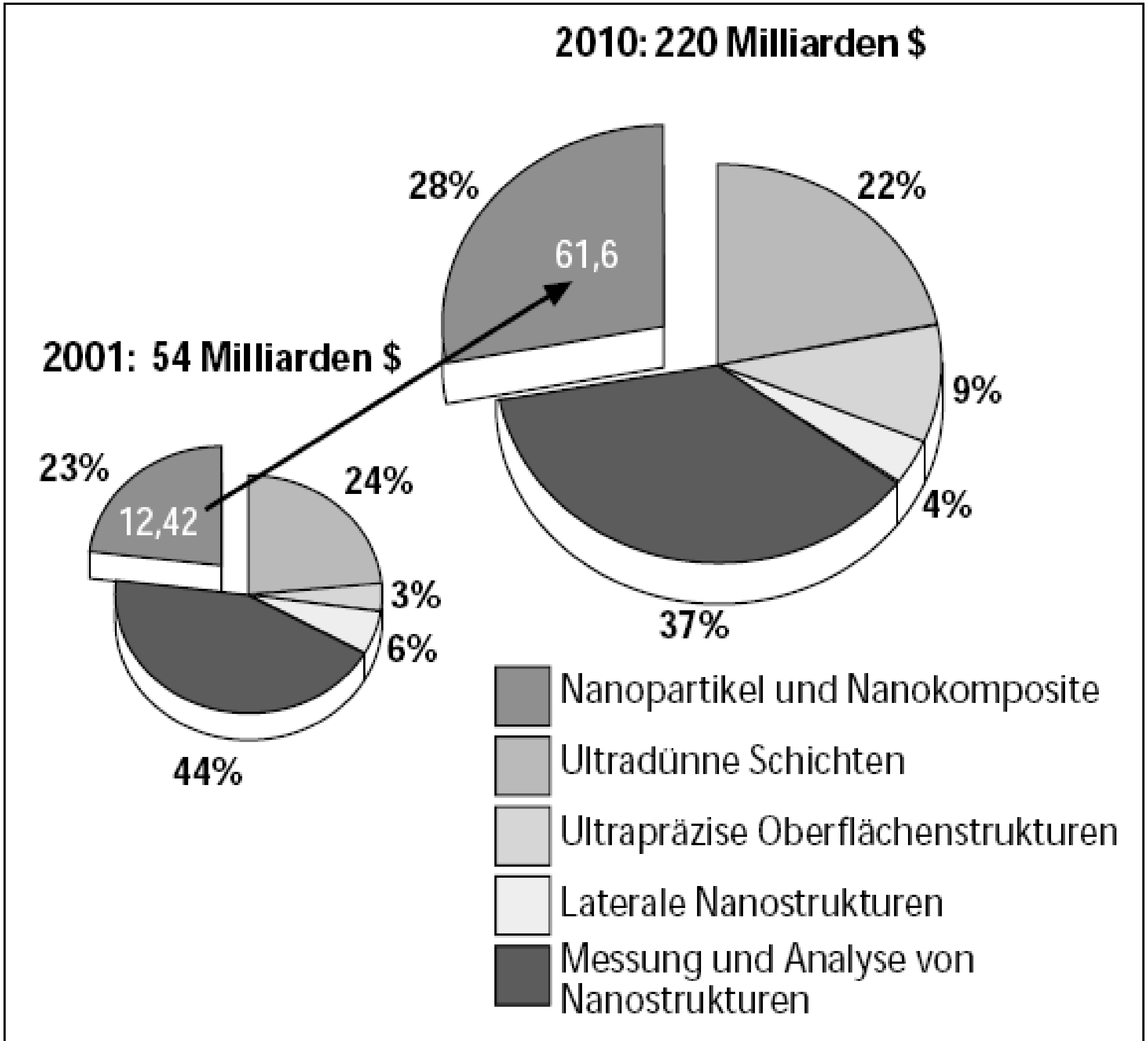
The pursuit of responsible nanotechnologies can be tackled through a series of grand challenges, argue **Andrew D. Maynard** and his co-authors.

When the physicist and Nobel laureate Richard Feynman challenged the science community to think small in his 1959 lecture 'There's Plenty of Room at the Bottom', he planted the seeds of a new era in science and technology. Nanotechnology, which is about controlling matter at near-atomic scales to produce unique or enhanced materials, products and devices, is now maturing rapidly with more than 300 claimed nanotechnology products already on the market[1]. Yet concerns have been raised that the very properties of nanostructured materials that make them so attractive could potentially lead to unforeseen health or environmental hazards[2].

The spectre of possible harm — whether real or imagined — is threatening to slow the development of nanotechnology unless sound, independent and authoritative information is developed on what the risks are, and how to avoid them[3]. In what may be unprecedented pre-emptive action in the face of a new technology, governments, industries and research

Potential health risks from exposure to engineered nanomaterials must be understood and minimized.

Nano materials: estimated forgalmi ertek



BAFU 2007

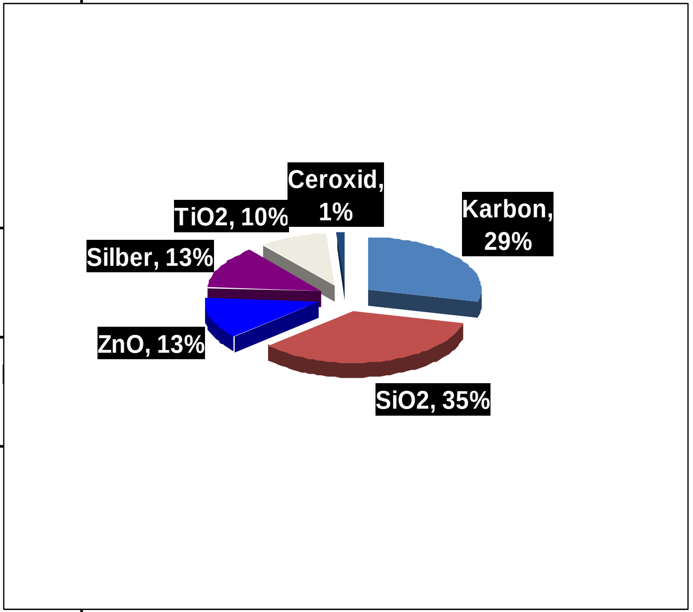
Natural und synthetic NP (NM) – Materials and applications

Natural NP: vulcanic ash, black carbon, clays, viruses, ferritin, Seesprays….

Synthetische NP und NM bzw. Produkte:

Typ	Produkte (Beispiele)
Metalloxide ♦ Siliziumdioxid (SiO_2) ♦ Titandioxid (TiO_2) ♦ Aluminiumoxid (Al_2O_3) ♦ Eisenoxid (Fe_3O_4, Fe_2O_3) ♦ Zirkonoxid (ZrO_2) ♦ Zinkdioxid (ZnO_2)	♦ Additive in Polymerkompositen ♦ UV-A Schutz ♦ Solarzellen ♦ Pharmazie / Medizin ♦ additive zu kratzresistenten Oberflächen
Kohlenstoffmodifikationen ♦ Carbon Black	♦ Autoreifen, Drucker, Kopierer
Fullerene ♦ Buckminsterfullerene (C_{60})	♦ Mechanische und tribologische Anwendunge ♦ Additive zu Schmierfetten
Kohlenstoffnanoröhrchen ♦ *Single-wall* Kohlenstoffnanoröhrchen ♦ *Multi-wall* Kohlenstoffnanoröhrchen	♦ Additive in Polymerkompositen ♦ Elektronische Feldemission Batterien Brennstoffzelle
Kohlenstoffnanodrähte ♦ verschiedene Konformationen	♦ Mechanische und tribologische Anwendungen Trägermaterial für Katalysatoren Additive in Polymerkompositen Elastische Schäume

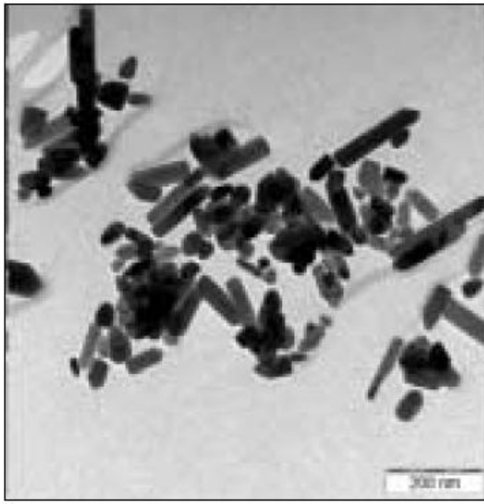
Materials:



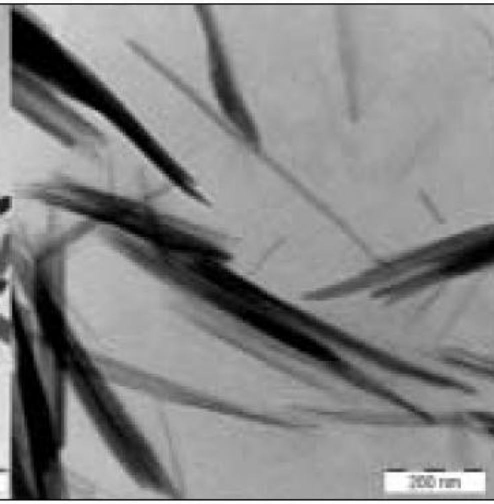
Krug UWSF, 2005; BAFU 2007

NP – different shapes

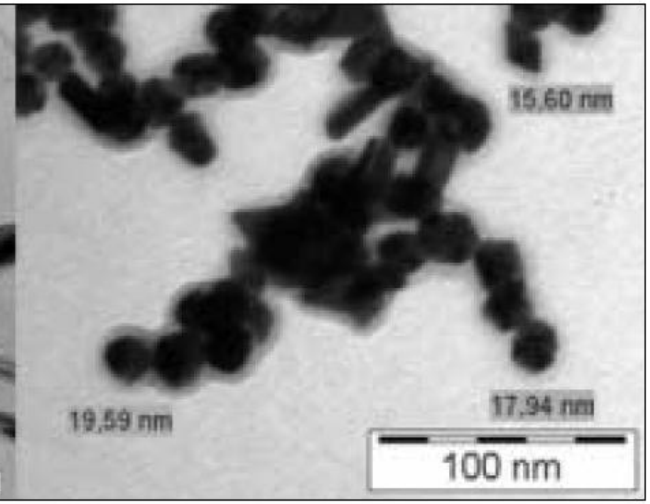
ZnO



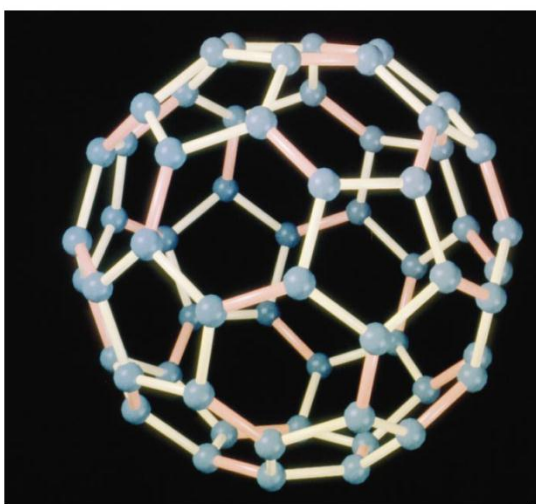
Vanadiumtrioxide



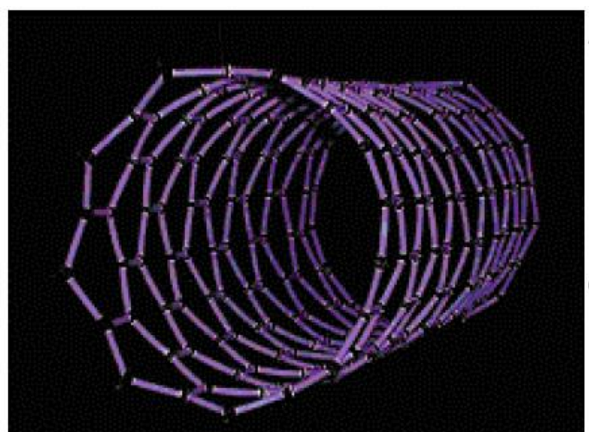
Palladium



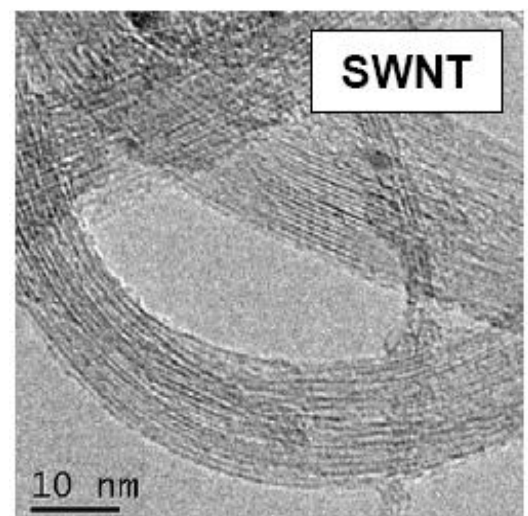
Fullerene



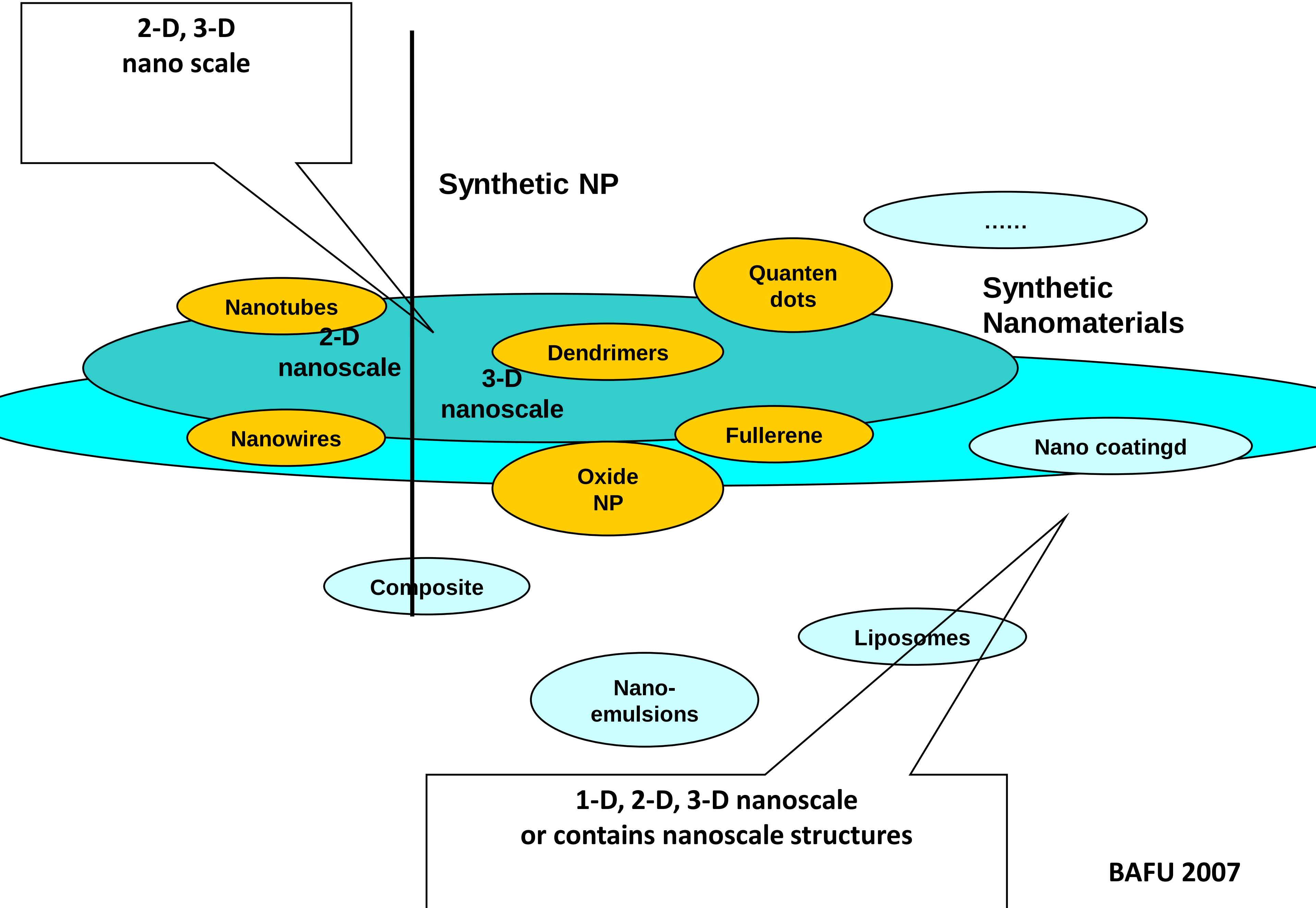
Carbon nanotubes



http://www.nccr-nano.org/ncc

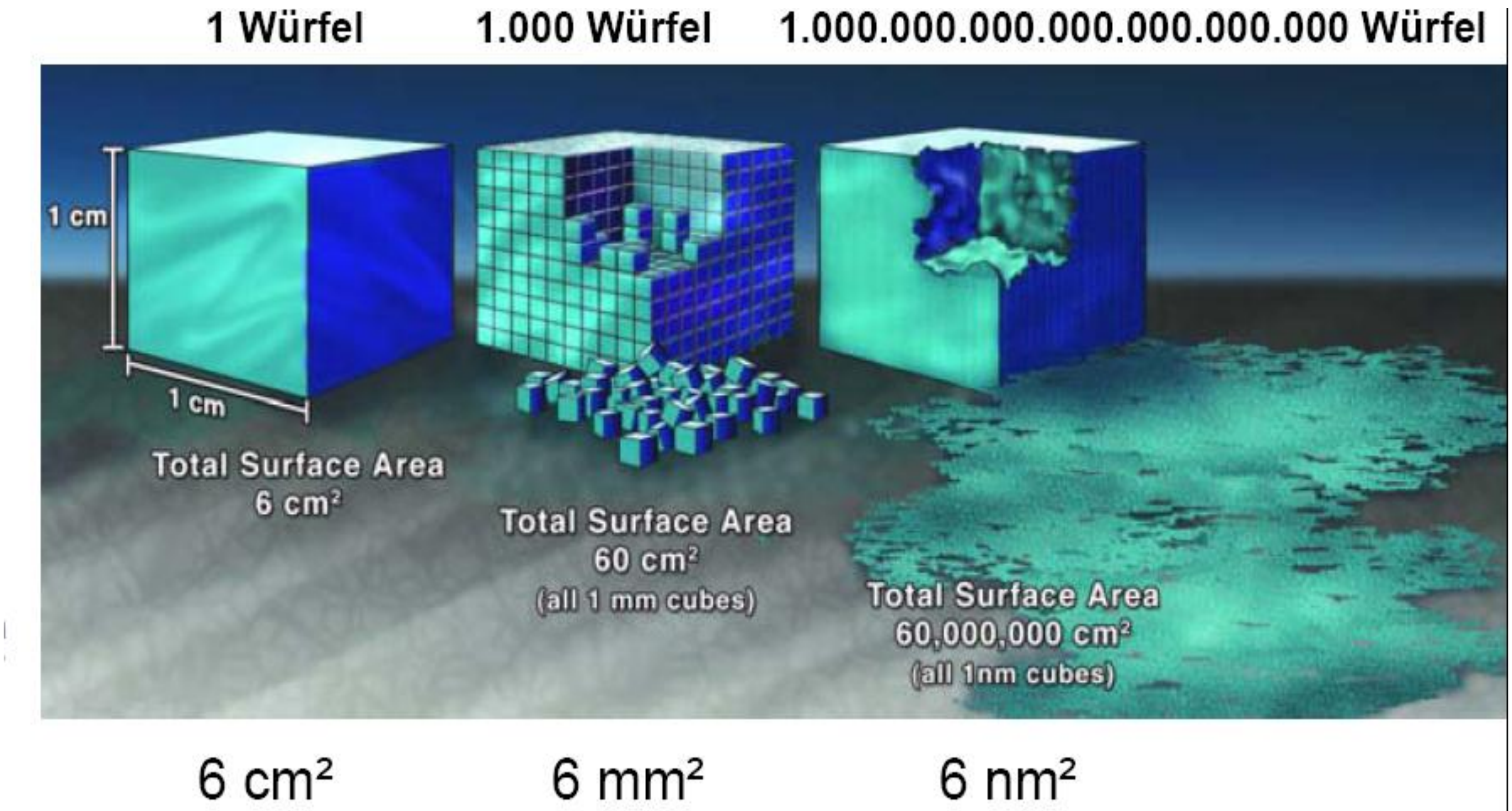


Classification of nanoparticles and nanomaterials



BAFU 2007

Particle size – specific surface area



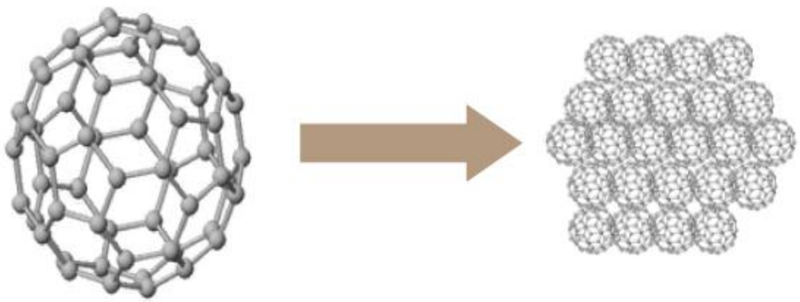
„Gott created the volume, der Teufel the surface!“ (*Wolfgang Pauli*)

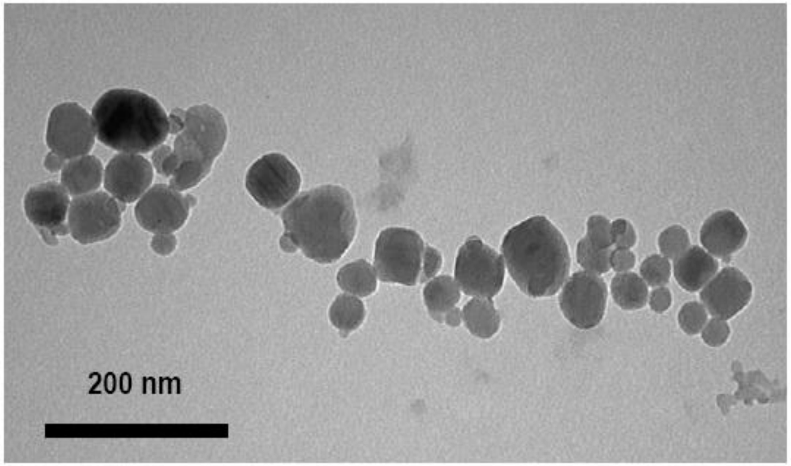
Würfel = cube

Functionalisation – fullerene & fullerene derivatives

Buckminsterfullerene C_{60}

nC_{60}





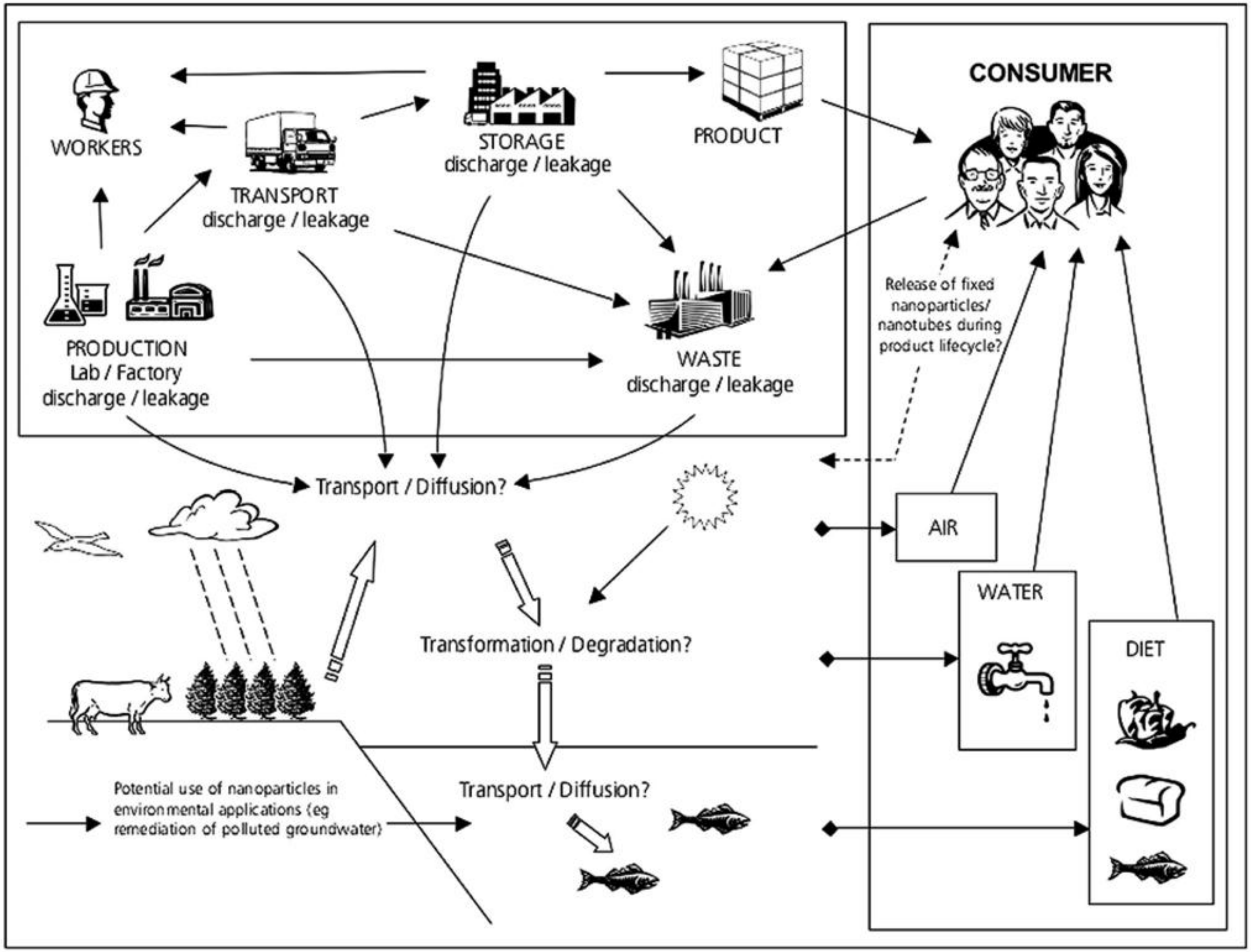
- C_{60} encapsulated in poly(vinyl-pyrrolidone), cyclodextrins, or poly(ethylene glycol)
- Hydroxylated fullerene
- Carboxyfullerene (malonic acid derivatives)
- Fullerene derivatives with pyrrolidine groups
- Other alkane derivatives of C_{60}
- Metallofullerene

Chen et al, JCIS 2006, Wiesner et al, ES&T 2006

Important properties of NP

- extremely high surface ara = reactivity
- Quantum mechanic begins to be valid – particular optical, magnetic and electric properties
- strong tendency to aggregate formation

NP in the environment



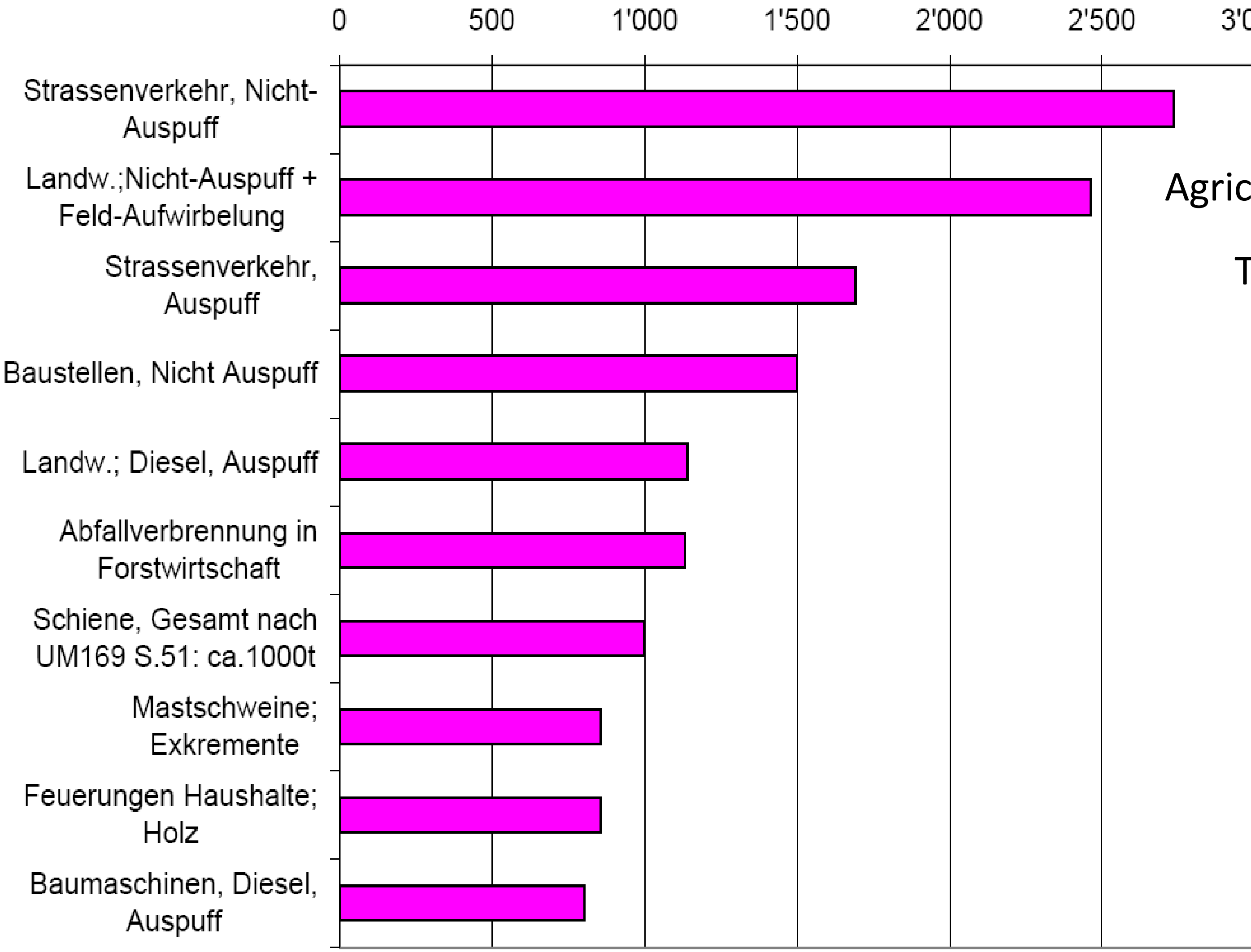
Direct input: e.g. in soil remediation, and waste water treatment

ROYAL SOCIETY, 2003

Concentrations in the air/atmosphere

Emissions of NP ???????

The„Top-10“ fine dust (<10µm)-Emmission sources in Swiss in 2000 (t/year)



Traffic without exhaust.

Agriculture without exhaust.

Traffic with exhaust.

EMPA, 2005

Distribution of NP via air

NP concentration in the air (in a city) = 10^{10} – $5x10^{10}$ NP/m³(*Sinner, 2006; Imhof, 2007*)

Behavior of NP in the atmosphere: Knowledge about soot particles can be useful

<u>Primary particles</u>:

High diffusion coefficients → frequent collisions → aggregation → sedimentation

Partikel Durchmesser [nm]	Halblebenszeit bei einer Konzentration von 1 g x m^{-3}	1 mg x m^{-3}	1 µg x m^{-3}	1 ng x m^{-3}
1	2,20 µs	2,20 ms	2,20 s	36,67 min
2	12,00 µs	12,00 ms	12,00 s	3,34 h
5	0,12 ms	0,12 s	2,00 min	33,34 h
10	0,70 ms	0,70 s	11,67 min	8,10 d
20	3,80 ms	3,80 s	63,34 min	43,98 d

Half lifes

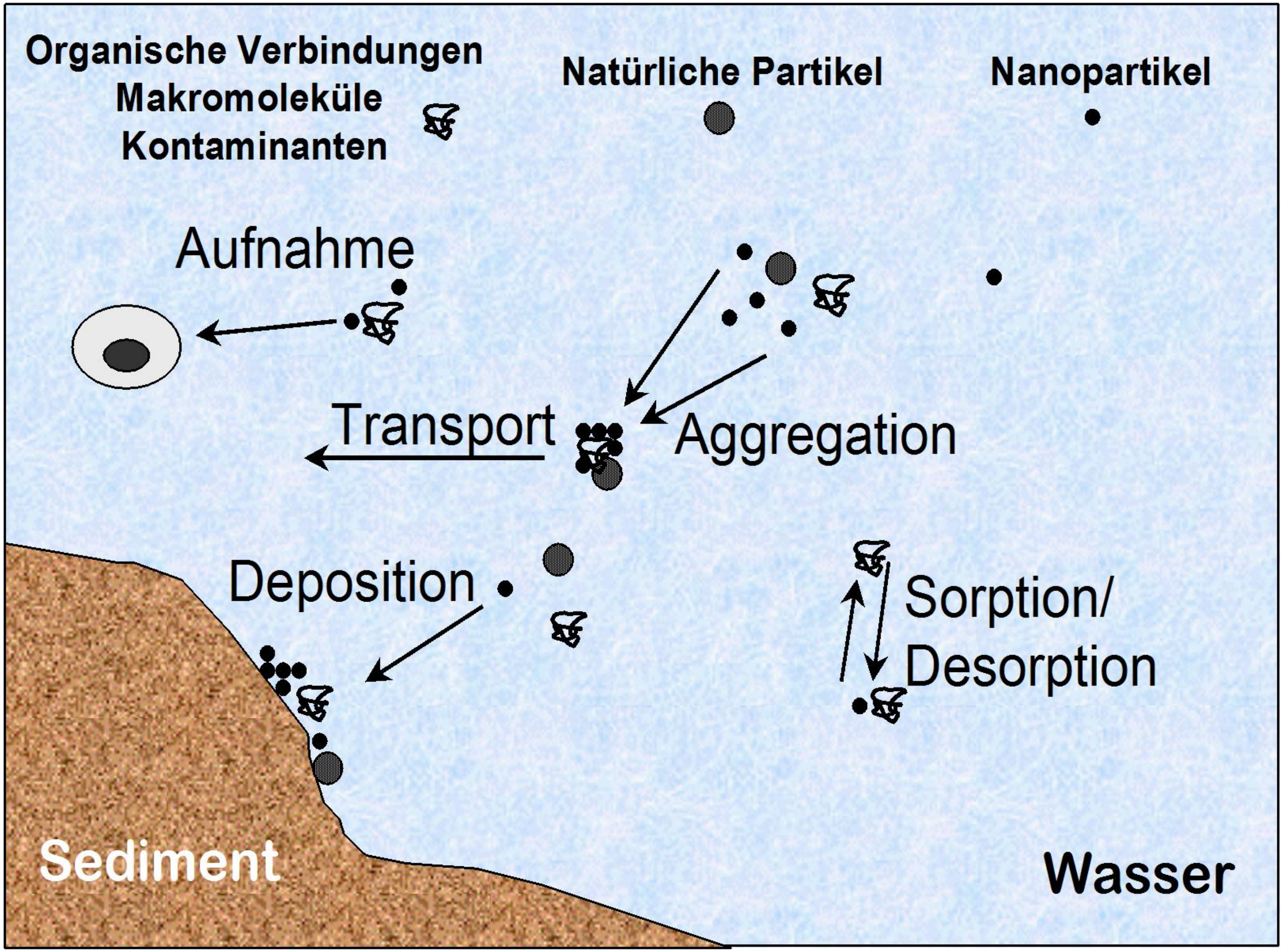
(Preining 1998)

Sedimentation von Fe^0 in air and water

size [nm]	Sedimentation rate in air [cm/h]	Sedimentation rate in H_2O [cm/h]
1000	$3x10^{-2}$	$7x10^{-4}$
100	$3x10^{-4}$	$7x10^{-6}$
10	$3x10^{-6}$	$7x10^{-8}$

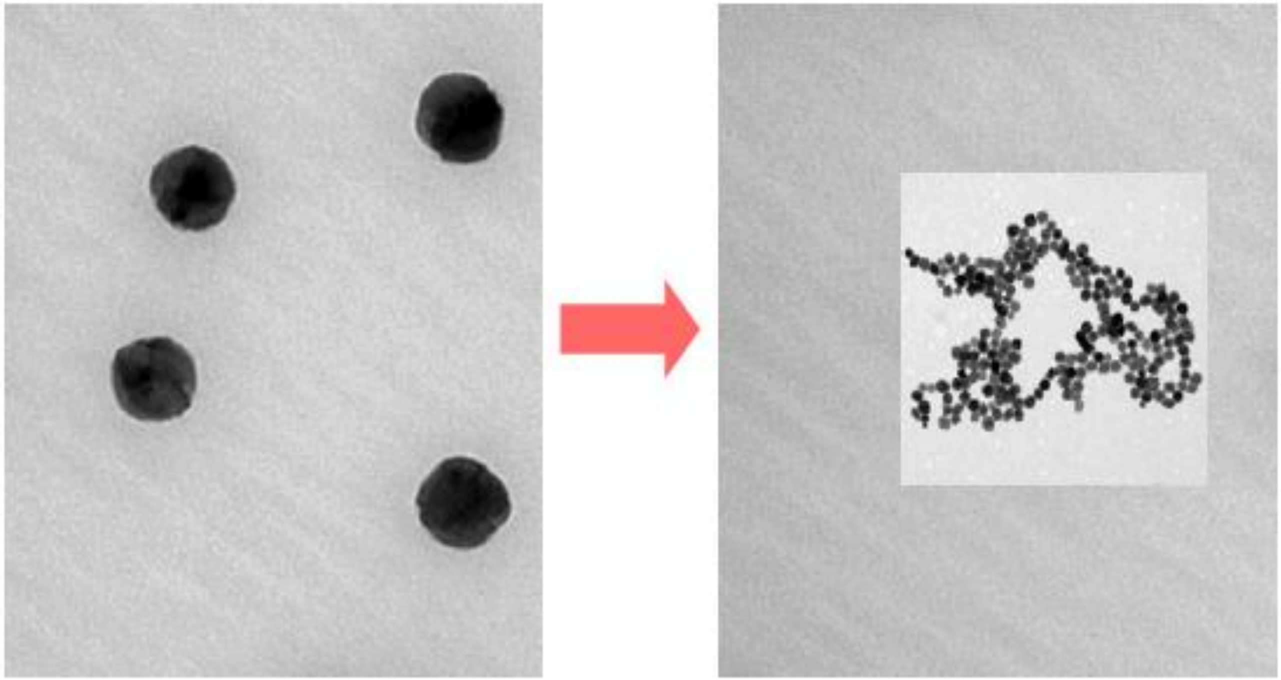
Sellers, 2007

Verteilung von NPn über das Wasser



Krug, 2005

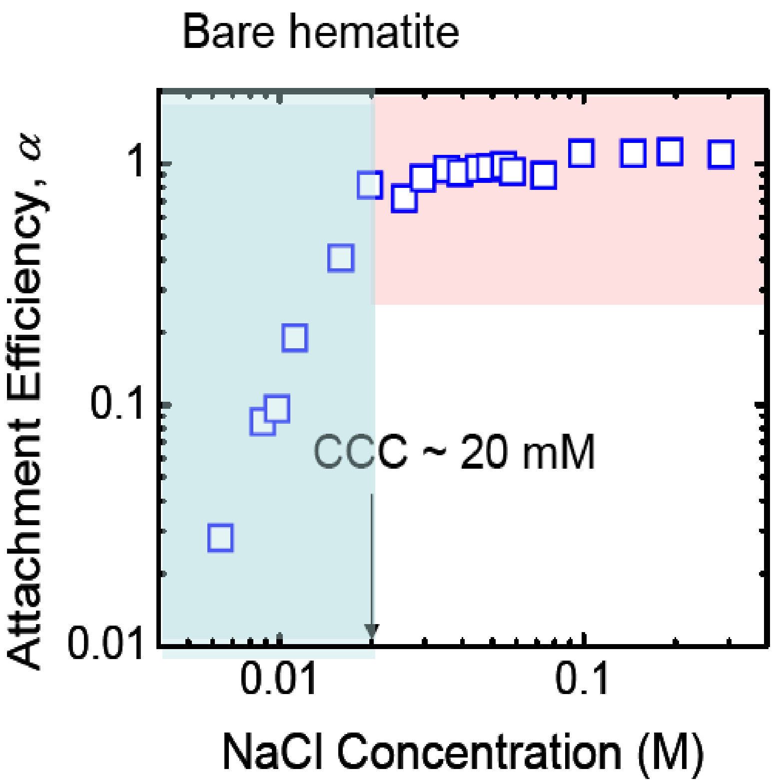
Aggregation of NP is a key process

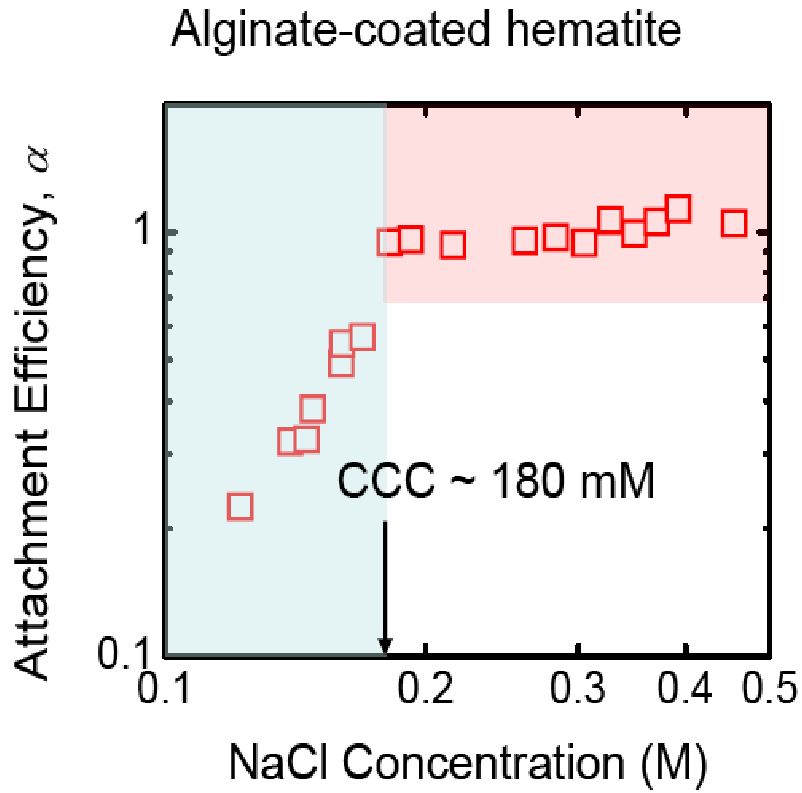


- **Aggregation influences the sedimentation, the transport and persistence of NP in aquatic systems**

- **Aggregation can influence the reactivity and toxicity of NP.**

Aggregation behavior of hematite (70 nm) in presence of DOM



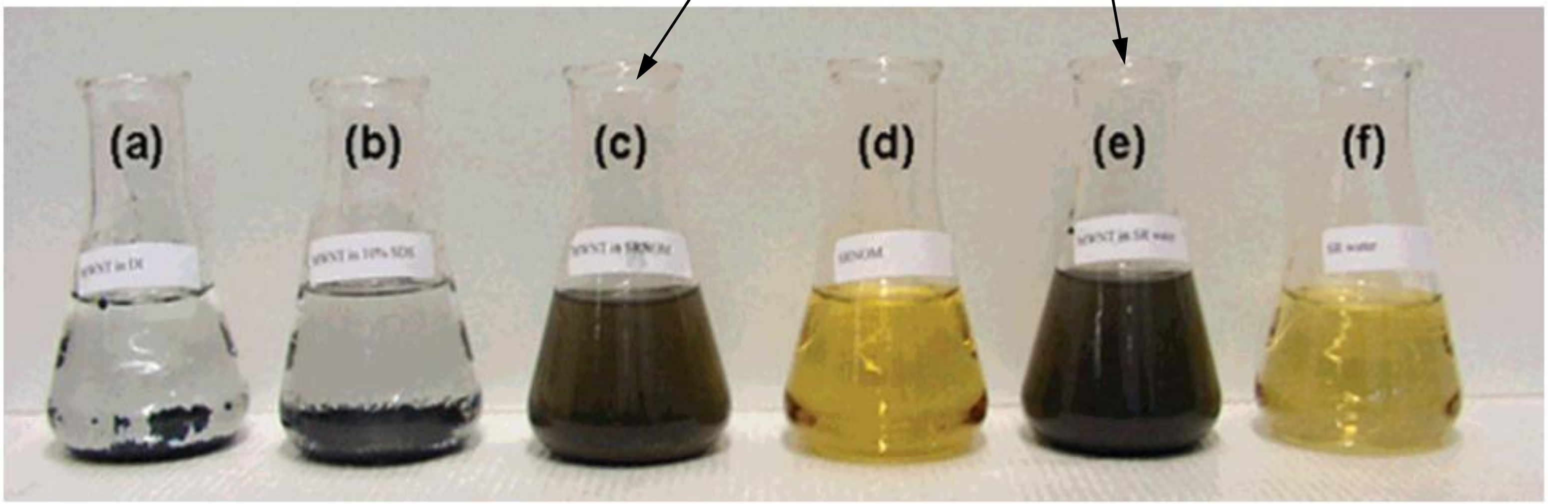


CCC (hematite) << CCC (alginate-hematite) ⟶ Steric stabilisation

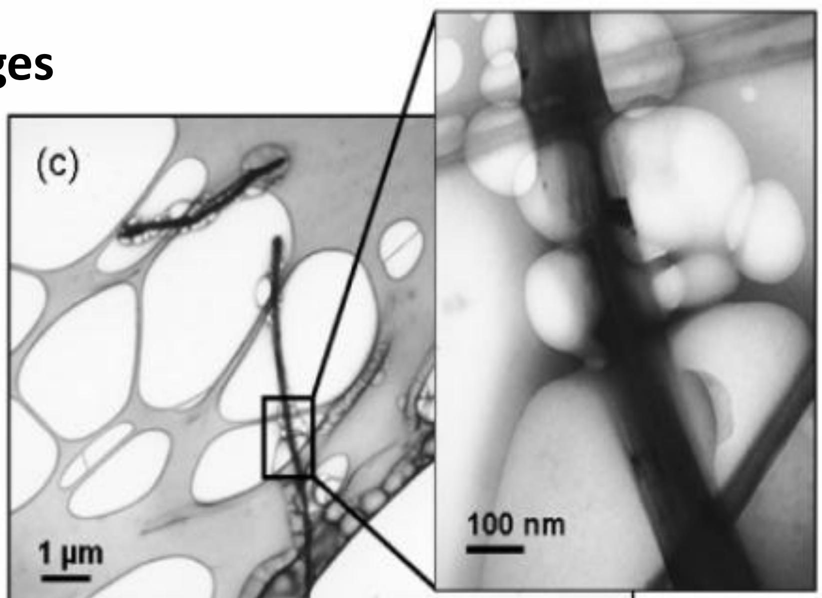
Chen et al, ES&T 2006

Aggregation behavior of C nanotubes in presence of DOM

100 mg/l and 500 mg/l Suwannee River organic matter



TEM images

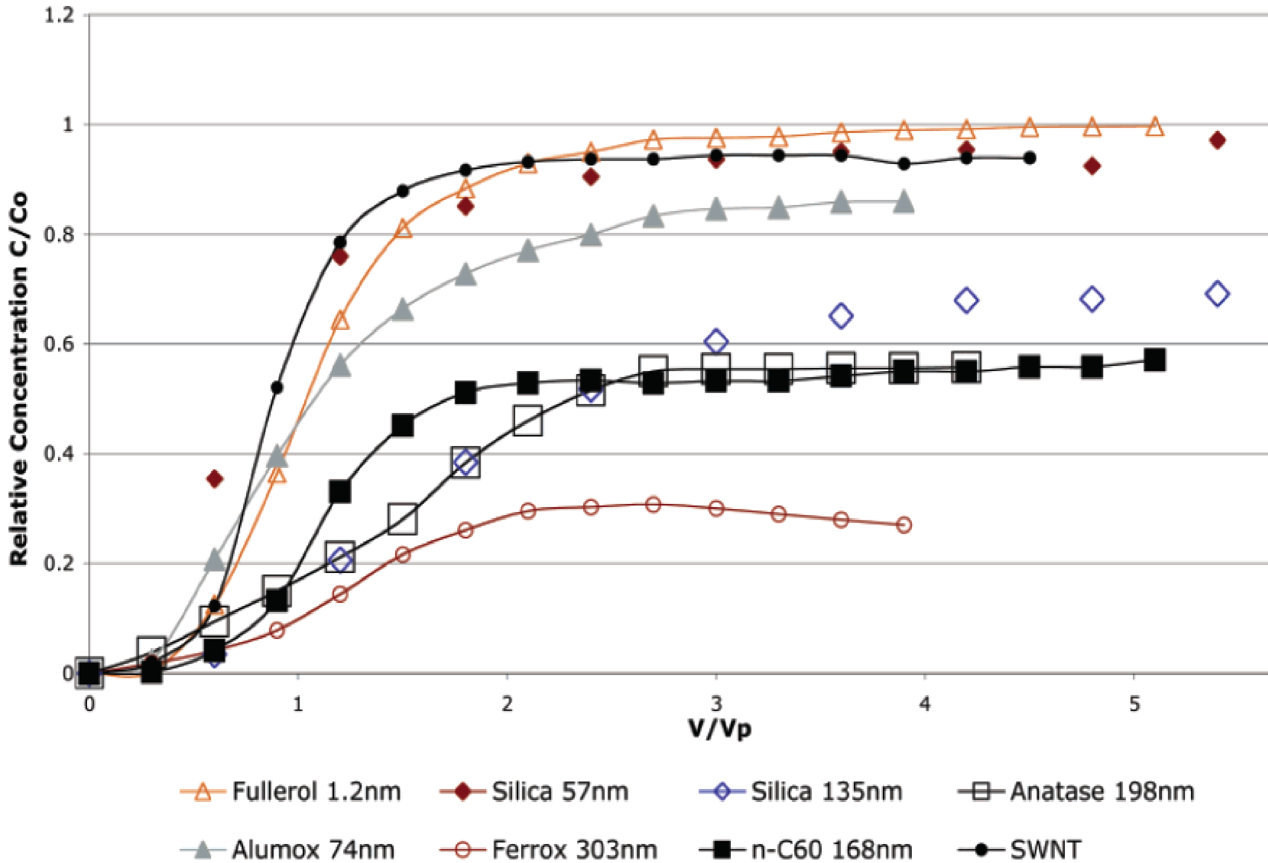


The NP suspensions with DOM remain stable for months

Hyung, ES&T 2007

Transport of NP – Breakthrough behavior in model sand

Nanomaterial	size (nm)	EM (10^{-8} $m^2s^{-1}V^{-1}$)
Fullerol	1,2	nd
Silica	57	-1,95
Silica	135	-2,58
Anatase (TiO2)	198	-0,27
Alumox* [(Al(O)(OH)]n	74	-2,45
Ferrox* (FeOOH)	303	-0,43
n-C60	168	-1,99
C nanotubes (SWNT)	0,7x80 1,2x200	-3.98

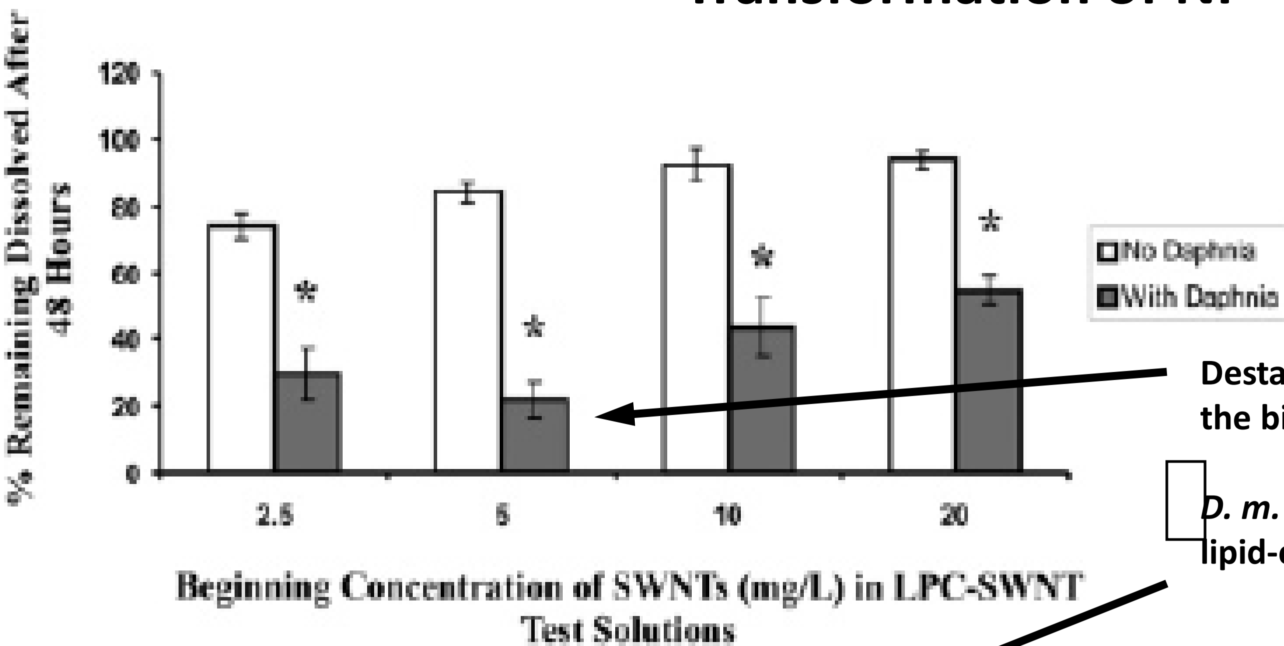


Glas-perls d=355µm
Column L= 10cm, D=2,5 cm
Darcy velocity.: 2,4 cm/min
Zeta-Potential: -29,8 mV

EM = elektrophoretic mobility
***coated by acetic acid**

Lecoanet et al, ES&T 2004

Transformation of NP

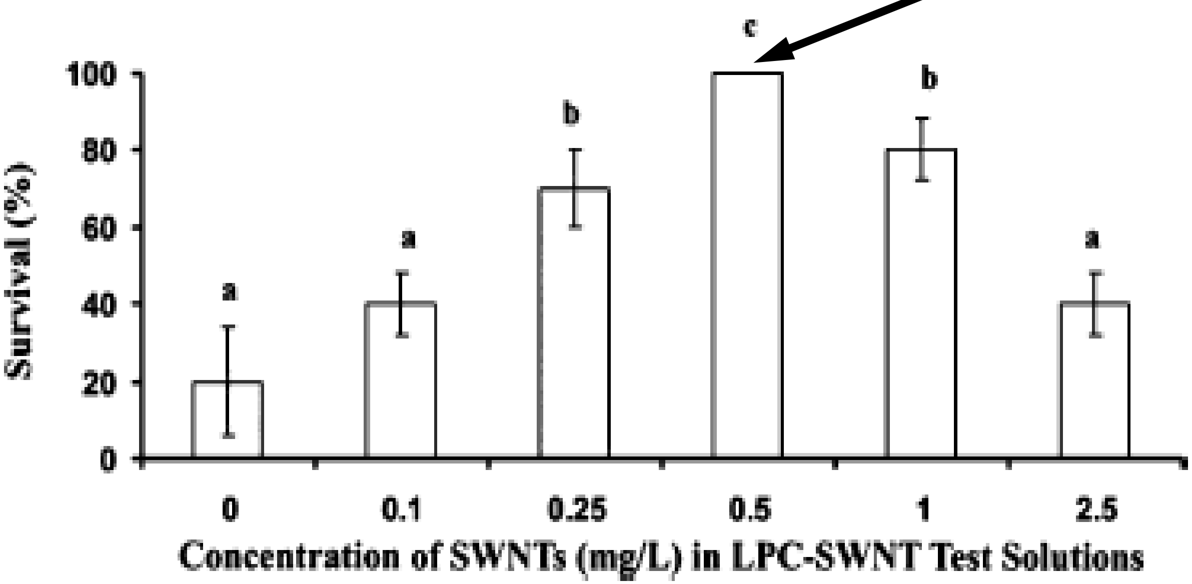


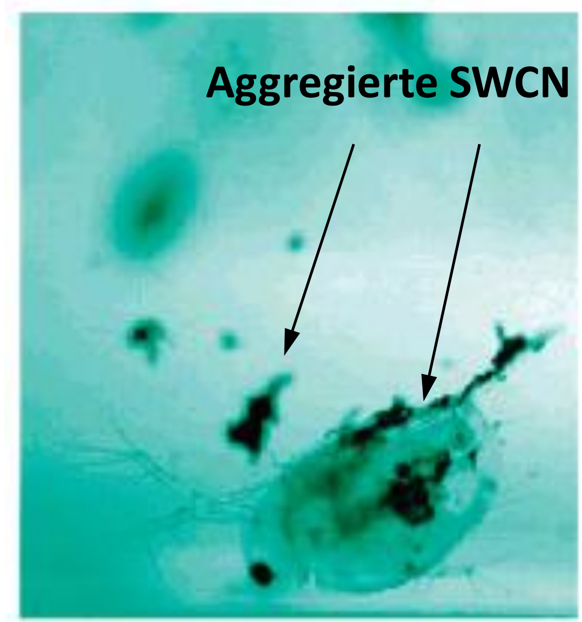
<u>*D. magna* modifies in vivo lipid-coated C-Nanotubes</u>

Roberts, ES&T 2007

Destabilisation of dispersed SWCN through the biodegradation of lipid coating

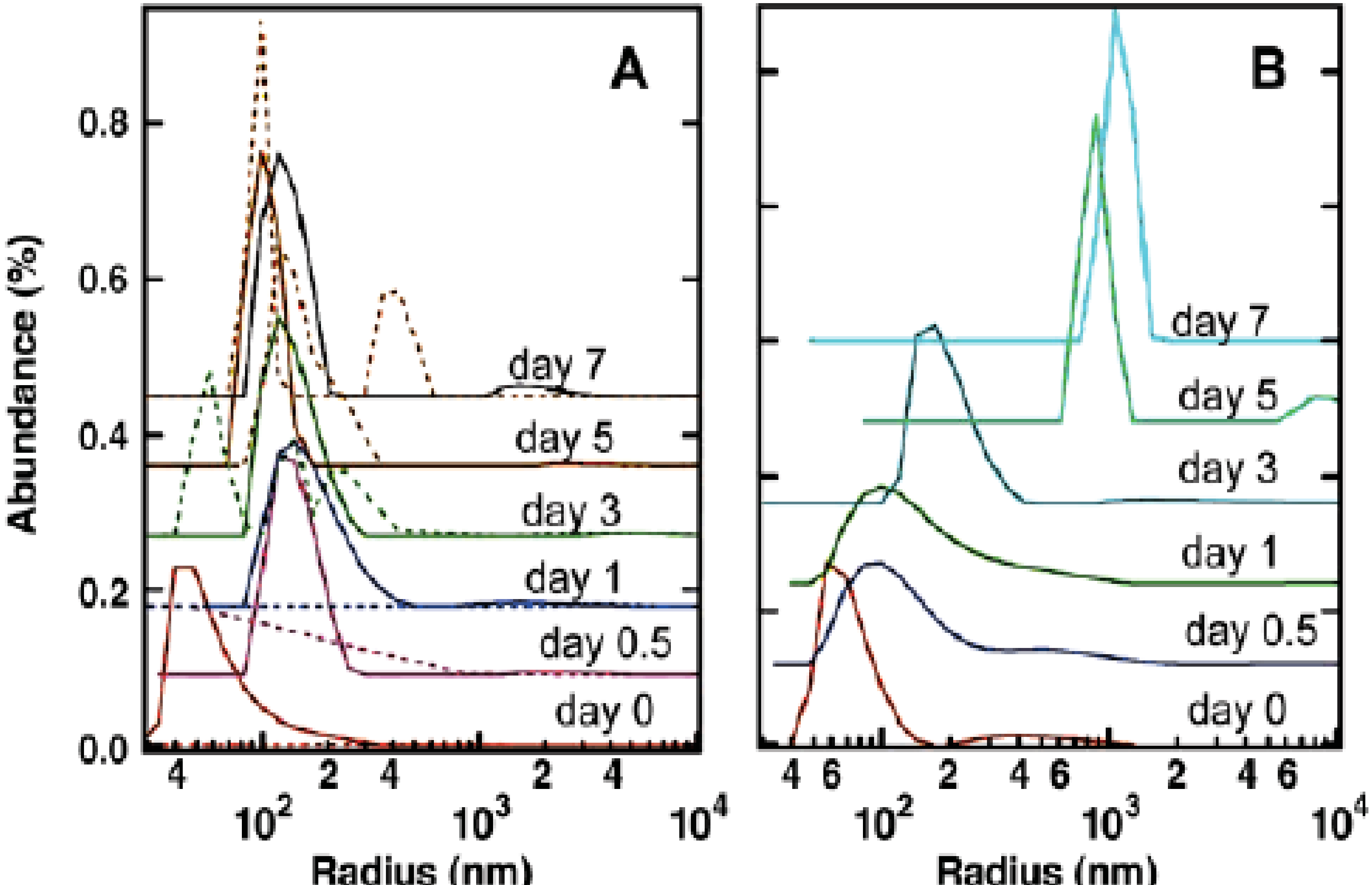
→ *D. m.* growth at < 0,5 ppm lipid-coated SWCN.





Transformation of NP

Extracellular proteins limit the dispersal of biogenic NP



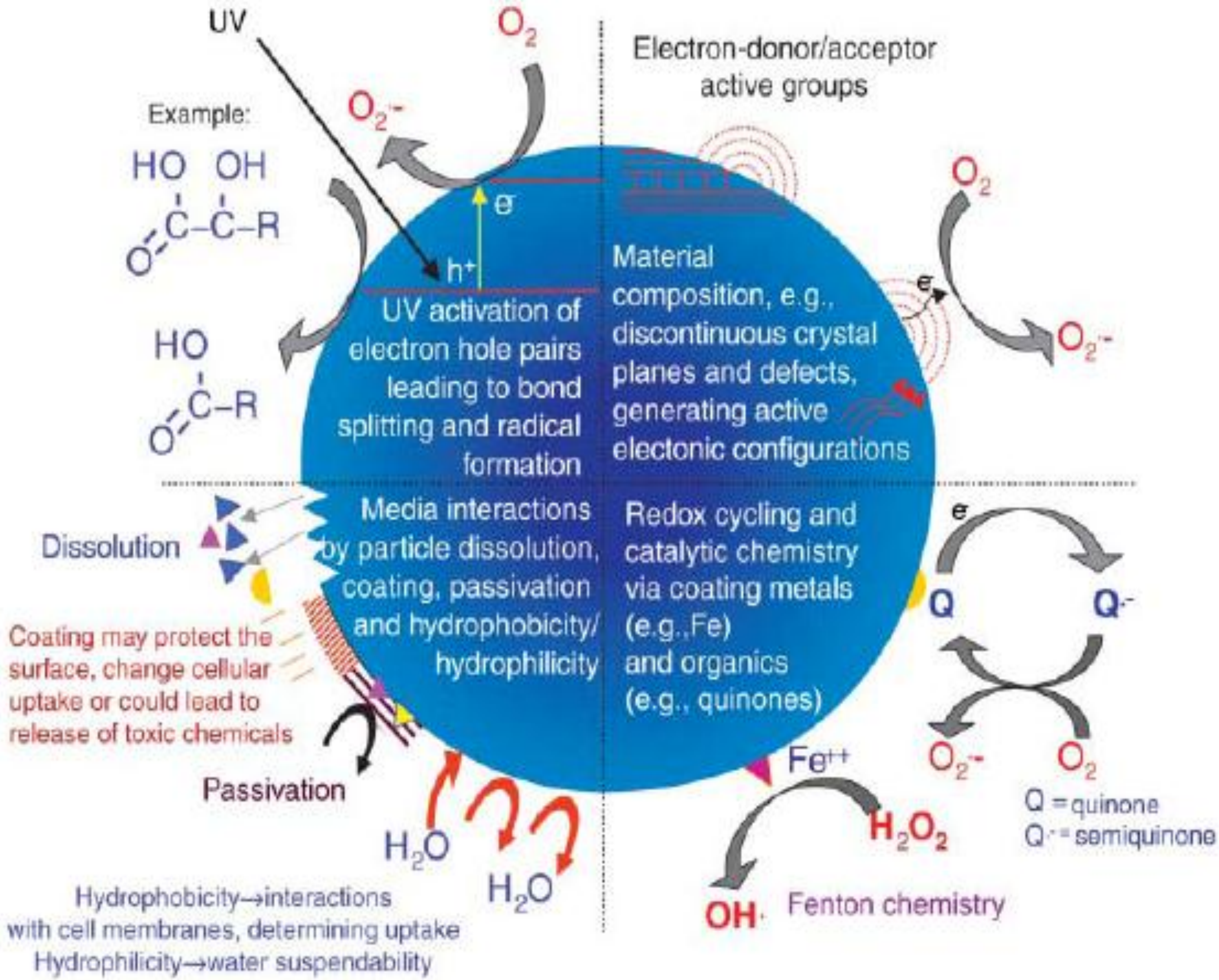
A) ZnS NP suspension forms aggregates after 0.5 day.

B) Destabilisiation of 10 µM dispersed ZnS NP through 100 µM Cystein.

Moreau et al, Science, 2007

Toxicity of NP: „great potential“ (review in Science 2006, Nel et al.)

Possible interaction mechanisms of NP with biological tissue



<u>Important factors</u>:

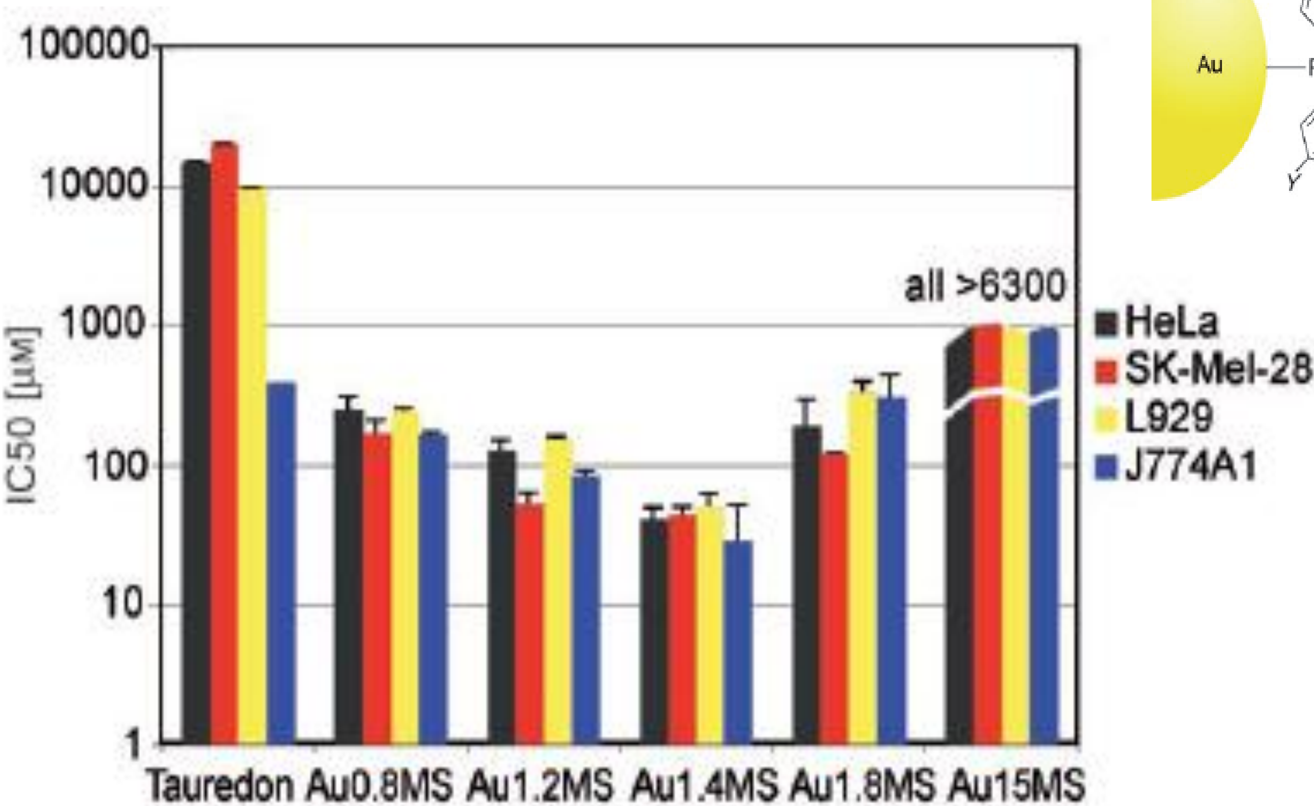
composition
Electric structure
Bond species
Coating (passiv/activ)
Solubility
Interaction with UV

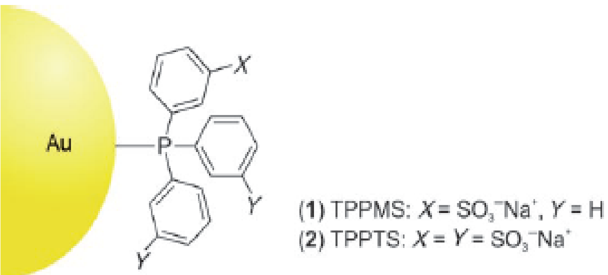
size??? shape???

Nel et al., Science 2006

Toxicity - Role of particle size

Size-dependant toxicity of Au-NP





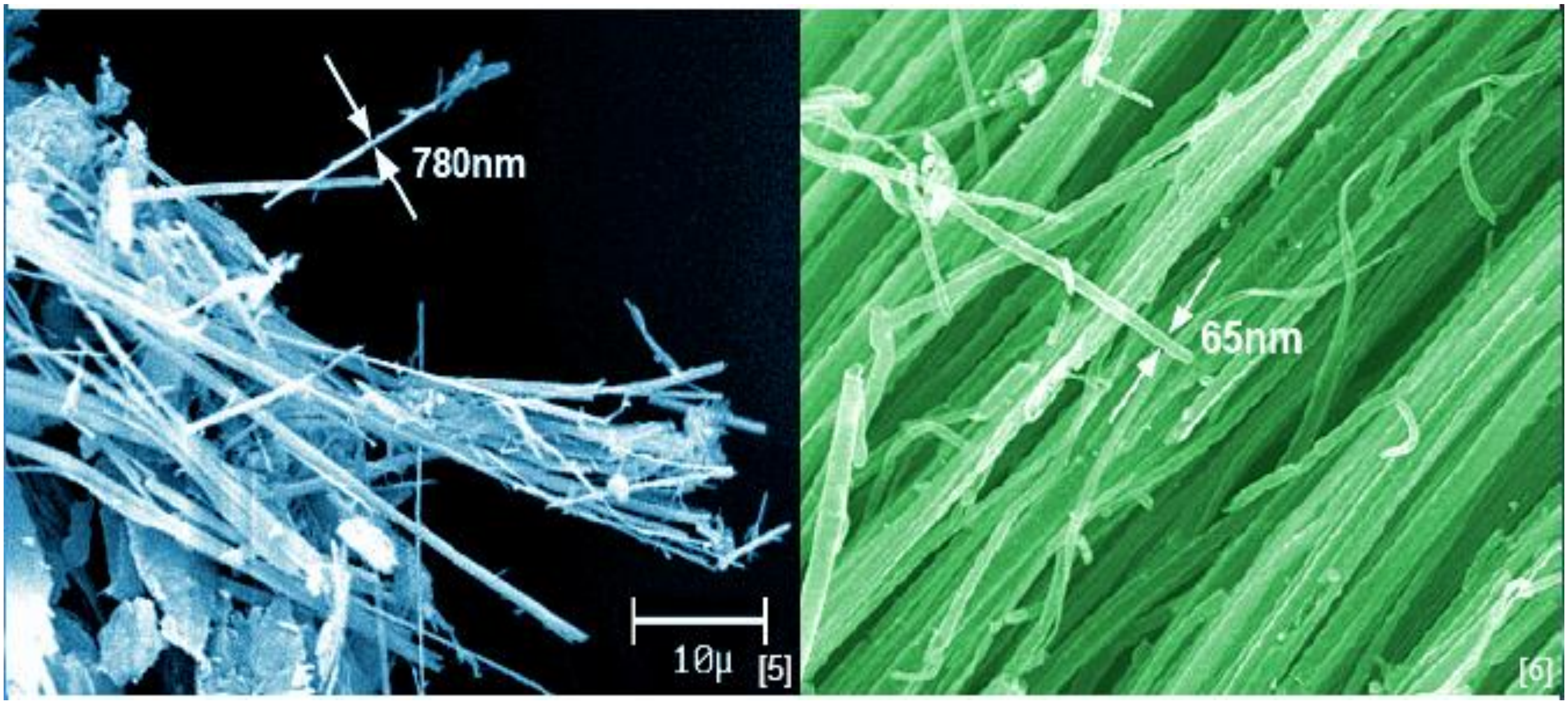
Triphenylphosphine

Highest toxic impact (IC_{50}) in the size range 1-2 nm.
Toxicity depends mostly on the size and not on the functional group

Pan et al., Small 2007

Toxicity - Role of NP-shape

Symbolic comparison: Asbestos versus carbon nanotubes

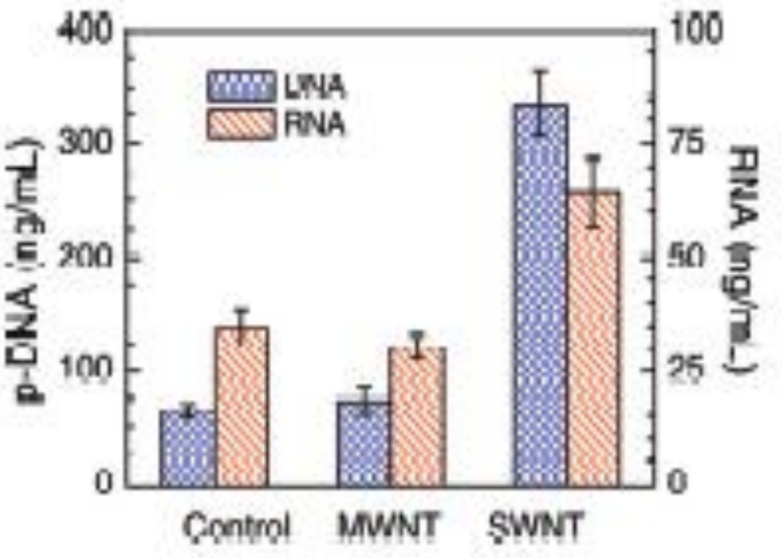


Asbestos: Vorbidden after 100 years use

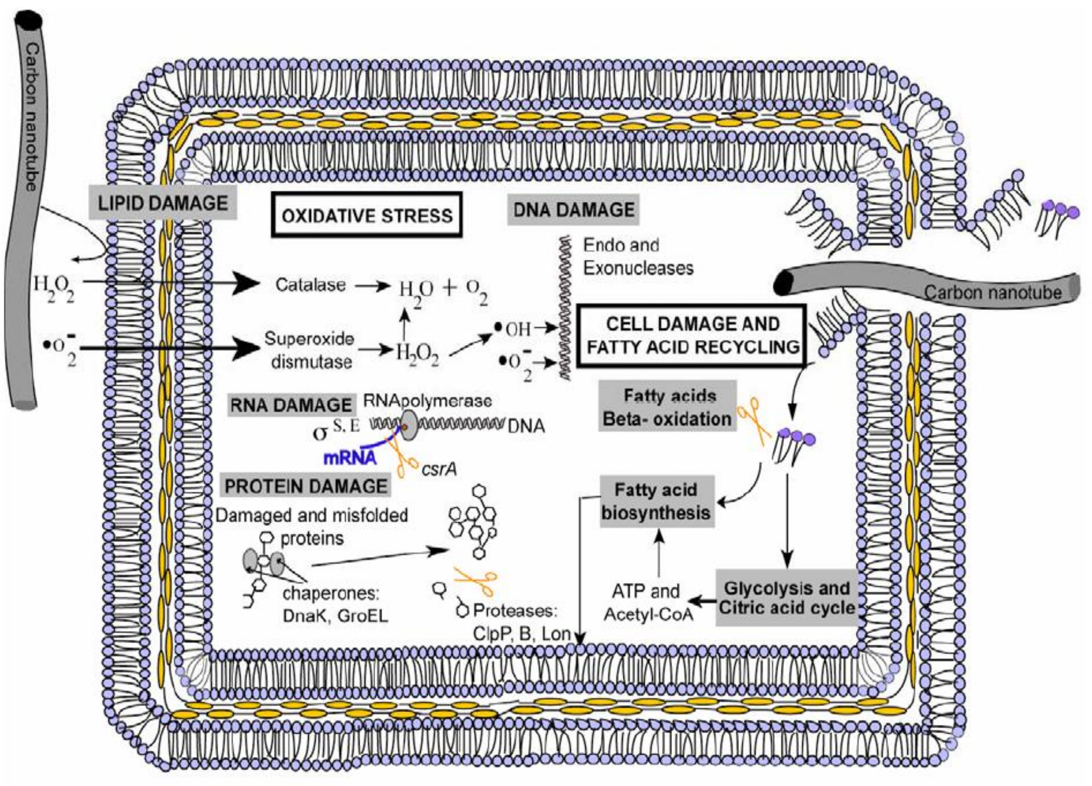
Nanotubes: „more toxic than quartz dust“ (NASA (3/2003)) – long term effects????

Leinss, 2007

Ecotoxicity - Role of NP shape und size



Concentrations of plasmid DNA and RNA in solution in the presence and absence of CNTs.



Schematic summary of *E. coli* K12 gene expression stress responses under exposure to SWNTs and MWNTs.

Kang, 2007

Ecotoxicity - Toxicity

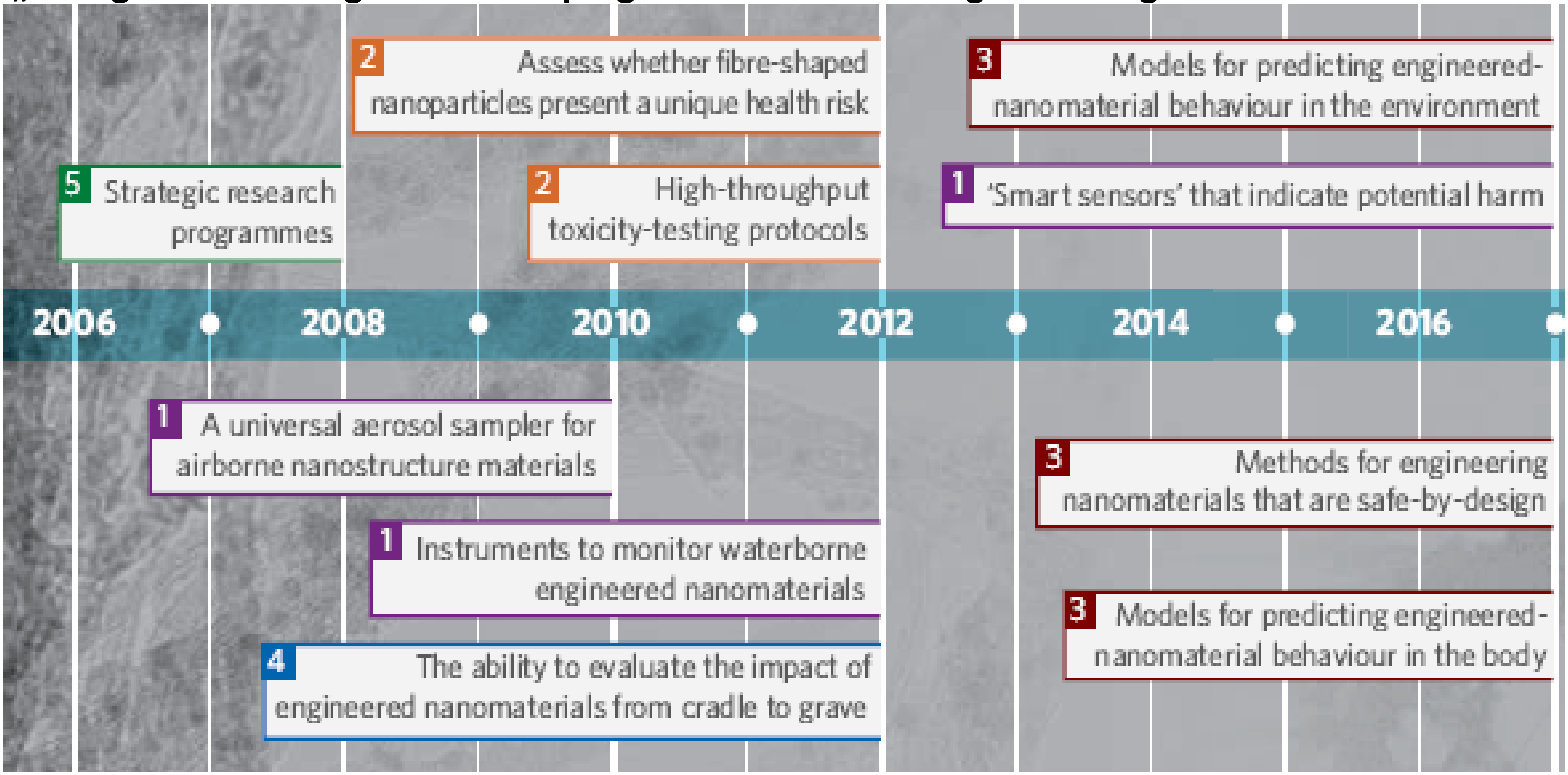
<u>Ecotoxicity</u>: practically unknown
<u>Toxicity</u>: hardly known, long term observation and investigation are needed

<u>Important factors of ´NP toxicity/ecotoxicity</u>:
Size
Composition
Shape
reactivity
Elektrical structure and properties
Catalytic activity
Bound species
Coating (passive/active)
Solubility(Dissolution)
Interactions with the surrounding (e.g. UV)
Aggregation behavior

Leinss, 2007

Research Needs- Nature, November 2006, Maynard et al.

„Five grand challenges – Developing safe nanotechnologies through sound science“



NP in the environment

Main focuses: natural and engineered nanoparticles (NPs) in water, soil, and atmosphere (80%); 2) Nanotechnologies in environmental protection (20%).

- Introduction, NP classification, application, and future application
- NP properties: morphology, specific surface area, colloidal stability and stabilization
- Natural NPs and colloids in waters and soils: inorganic and organic NMs/colloids and their stability, DLVO interaction forces, aggregation kinetics, NP fate and behavior in soils
- NPs in the air: formation, composition, behavior and determination methods
- Analysis and characterization of engineered NPs in waters: shape, size, concentration, composition; Scattering techniques, fractionation and separation methods, microscopy
- Ecotoxicology of NPs: mechanisms, interactions with cells, bioaccumulation, case studies
- Exposure and risk assessment
- Nanotechnologies in water purification and soil remediation: membrane-based techniques, adsorbents
- Case studies

VL „NP in the environment“ – literature sources

Lead, Smith (editors): Environmental and Human health impacts of Nanotechnogy, Wiley, 2009

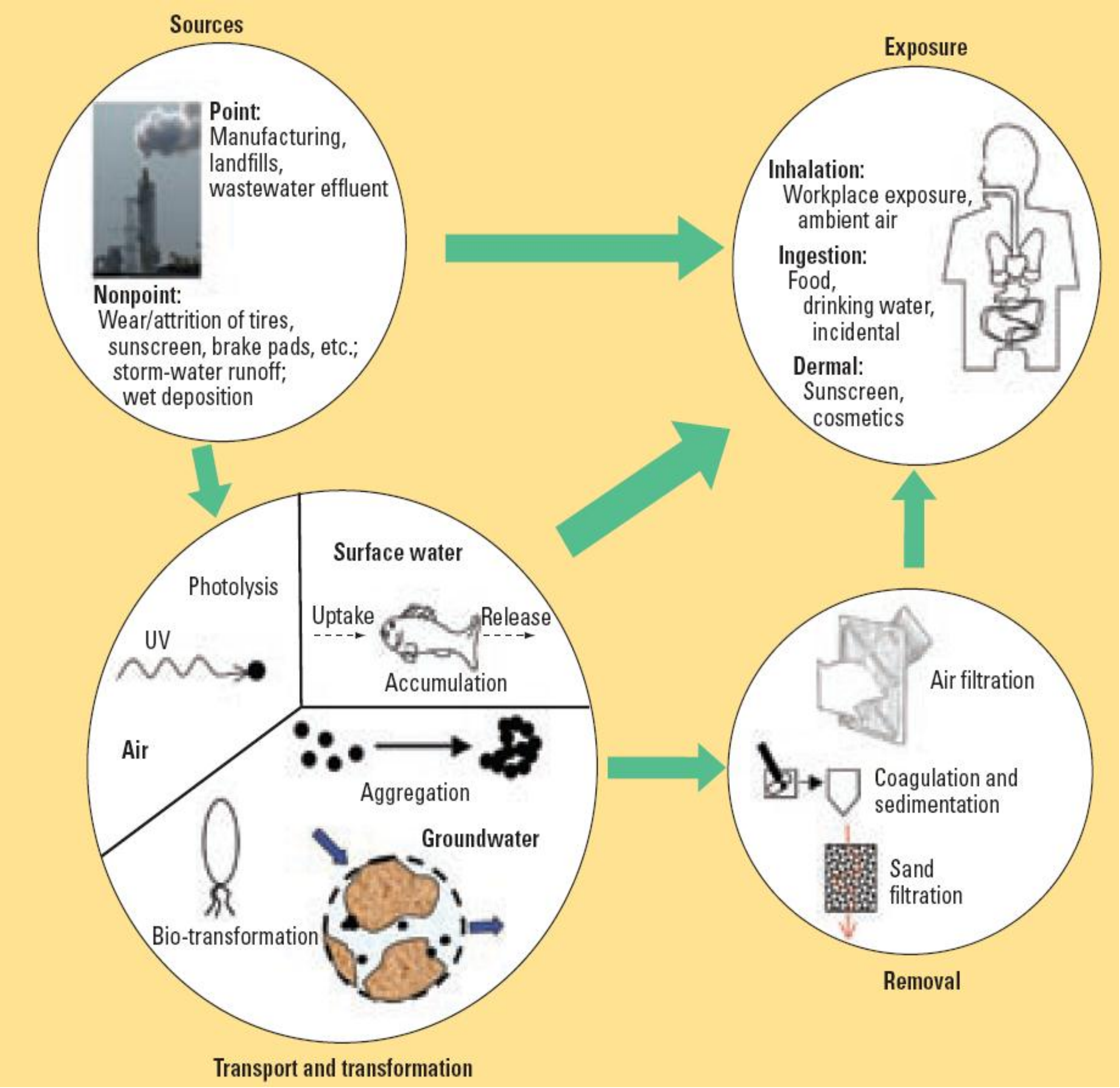
Frimmel, Niessner (editors): Nanoparticles in the water cycle, Springer, 2010

Cloete, de Kwaadsteniet, Botes, Lopez-Romero (editors): Nanotechnology in Water Treatment Applications, Caister Academic Press, 2010

Grassian, Wicki H., Nanoscience and Nanotechnology, Environmental and Health Impacts, Wiley, 2008

Wilkinson, Lead (editors): Environmental Colloids and Particles: Behaviour, Separation and Characterisation, Wiley, 2007

NP in the environment



Wiesner, ES&T 2006