The 12th Geneva Association Annual Liability Regimes Conference

Session 4: Nanotechnology

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Nanotechnology

November 18 2016

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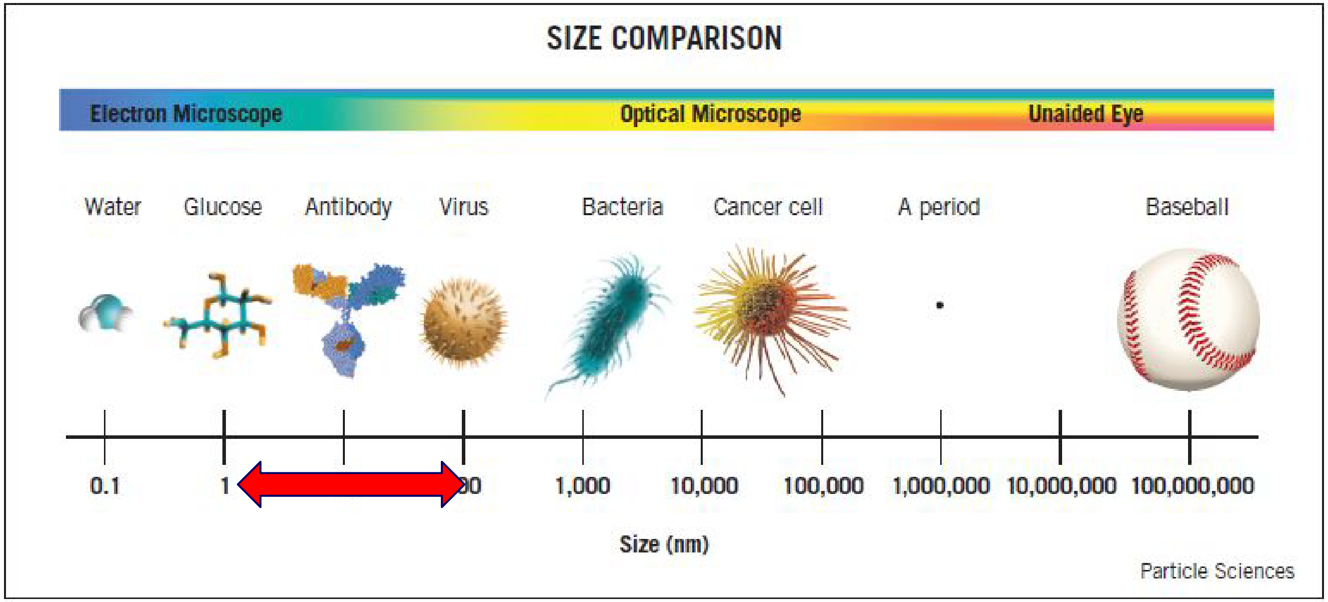
Geneva Association - Annual Liability Regimes Conference 2016

Nanotechnology

What are nanomaterials?



Materials containing particles with one or more dimensions in the size range of 1 nm – 100 nm.

Source: : http://ec.europa.eu/environment/chemicals/nanotech/faq/definition_en.htm

Nanotechnology

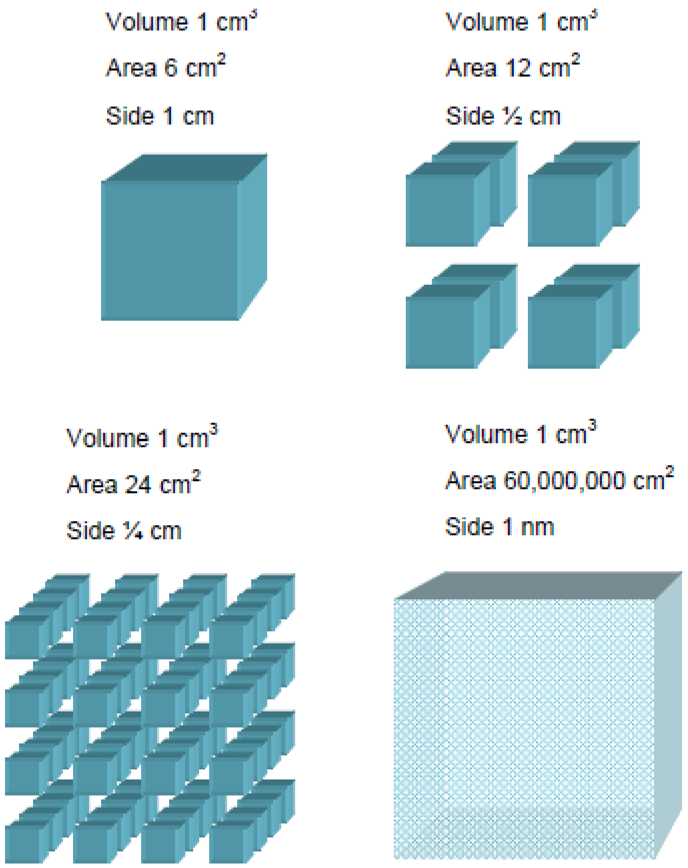
What makes nanomaterials so special?

By decreasing the size of a certain material, novel properties arise. As the result of particles getting smaller:

- mobility in the free stage increases
- specific surface area becomes enormous
- quantum effects can occur

Nano properties are simply different:

– electrical (conducting electricity),
– mechanical (stronger than steel),
– thermal (conducting heat),
– optical (color) etc.

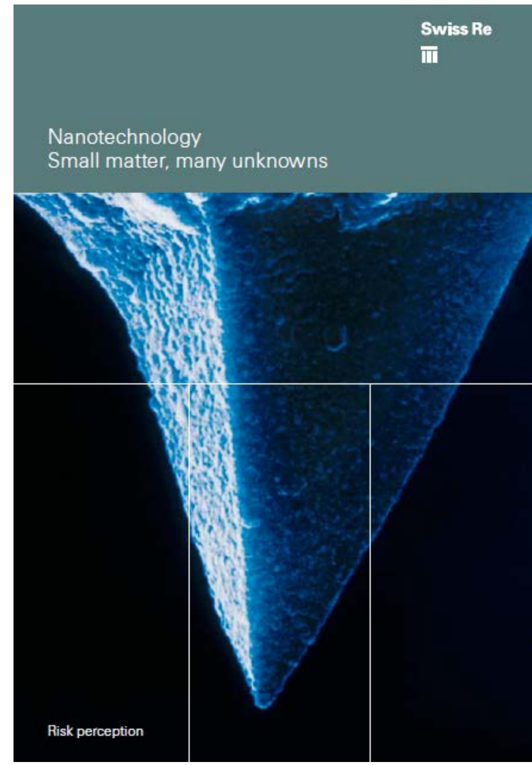


Source: http://www.lloyds.com/~/media/lloyds/reports/emerging%20risk%20reports/er_nanotechnology_report.pdf

Nanotechnology

What has changed since 2004?

- As nanotechnology is increasingly perceived more as a risk than a benefit, applications of nanoparticles have become less visible and integrated in other technology fields (e.g. energy)
- Applications for different particles are very distinct
  - commercial
  - potential
- Safety assessments
  - life cycle of NMs
  - regulatory environment
  - hazard identification
  - risk assessment approach (NanoTool)



Published 2004

Nanomaterials: Risk assessment tool (NanoTool)

November 18, 2016
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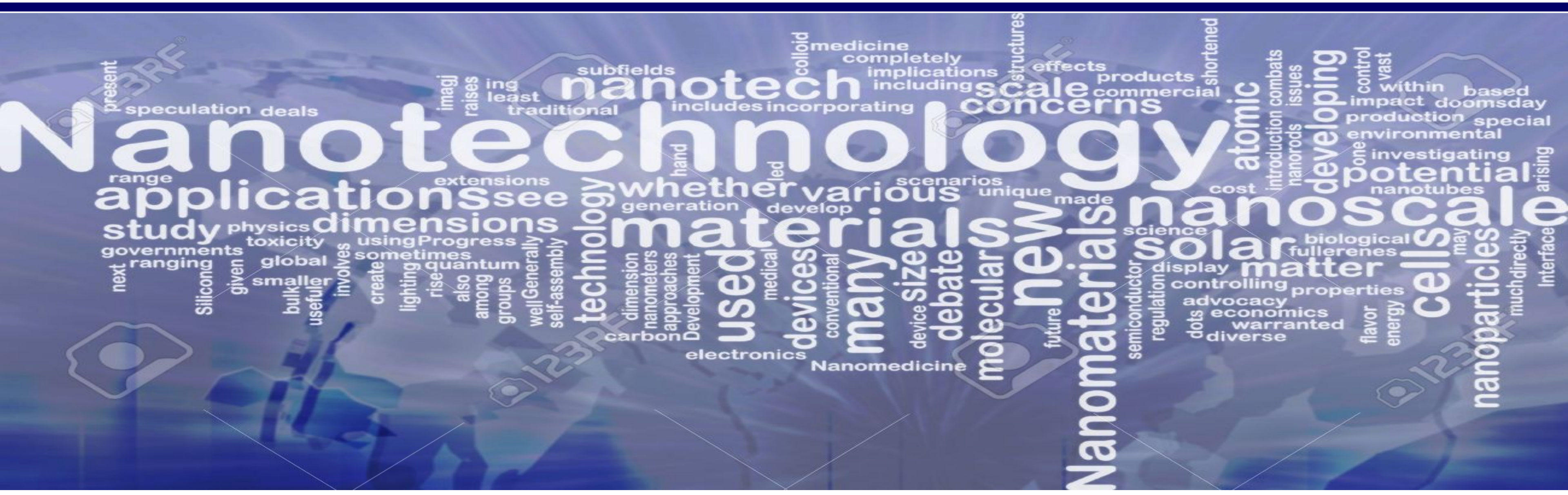


Nanomaterials

Why should we assess them?

- **Size matters**

A gold bar is not the same as nanogold particles

- **Impact**

Any incident in any industry, has an immediate effect on insurance companies

- **Emerging risk**

"Nano" is still on the emerging risk list of some insurance companies or associations for being potentially a "second asbestos" case

- **Knowledge gap**

Not many studies on human hazard / environmental hazard potentials available

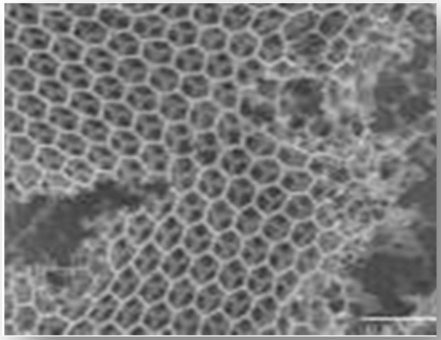
Nanomaterials

Laws and regulations

- **EPA** (Environmental Protection Agency): Toxic Substance Control Act (**TSCA**) and Comprehensive Environmental Response Compensation and Liability Act (**CERCLA**)

- **NIOSH** (National Institute for Occupational Safety), **OSHA** (Occupational Safety and Health Administration) and **NTP** (National Toxicological Program)

- **ECHA** (European Chemical Agency)**: REACH** (Registration, Evaluation, Authorization and Restriction of Chemicals)



Toxicological evaluation

Toxicological evaluation is substance-based

For a given substance, a corresponding classification / hazard class exists. LD50 (lethal dose) value corresponds to concentration of the substance which leads to a 50% probability of death.

Examples

Cyanide LD50= 140 mg (adult)

Carbon monoxide LD50= 1.500 ppm (adult, more than 60 min)

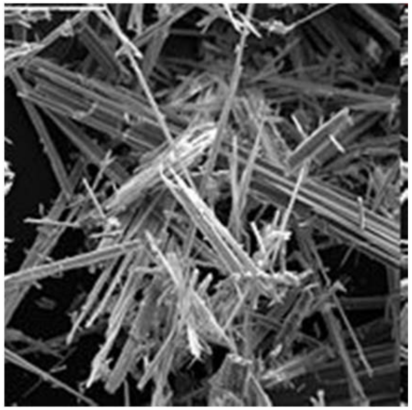
Chloroform LD50= 695 mg/kg (rat, oral)

Ethanol LD50= 7.060 mg/kg (rat, oral; human being 3-4 ‰)

$BaCO_3$ LD50= 418 mg/kg (rat, oral)

Toxicological evaluation

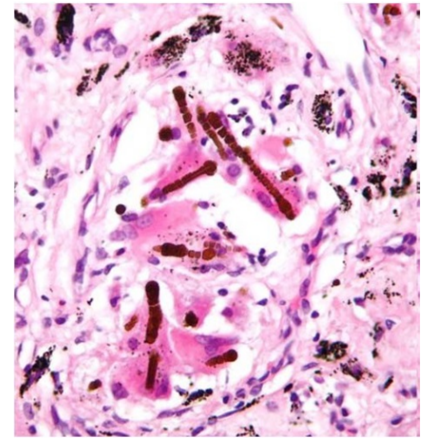
This solely substance-based evaluation **has already failed once** ...



- Asbestos was used from 1900 as a "miracle fibre" for a multitude of applications - especially as a building material
- Composition: various silicates, particularly chrysotile: $Mg_3(Si_2O_5)(OH)_4$ which possess a fibrous structure
- For a long time, the general assumption existed that asbestos is completely safe as these silicates showed no toxicity

Toxicological evaluation

This solely substance-based evaluation **has already failed once** ...



Problem:

- µm-sized fibers enter the lungs easily where they cause severe damage to the lung tissue (called asbestosis);
- After 10-15 years: fibrosis stage (formation of scar-like structures: shortness of breath, chronic cough);
- After a long latency period: Often lung cancer or pleural cancer

→ General ban of asbestos in the 1990s

Can the same happen with Nanomaterials?

Toxicology of Nanomaterials

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Possible additional hazards through nano-properties:

- Potential **asbestos-like behavior** (some materials)
- Nanomaterials **diversity** (nanoparticles, nanorods, nanotubes etc.)
- Finer particles favor the absorption into the body (NMs are **small enough** to enter the pulmonary **alveoli → bloodstream → brain**)

Important considerations:

✓ NMs synthesized in liquid phase are **usually agglomerated →** after drying their size is >500 nm → do not enter the bloodstream

✓ **Main source**: gas phase based pyrolysis or physical processes

✓ **Main exposure:** workplace and non-embedded products

Nanomaterials: Risk assessment tool (NanoTool)

Motivation and Goals

- Providing detailed hazard and exposure assessment for number of nanomaterials

- Identifying:
  - general information and hazard values for each NM of interest (based on scientific literature and publicly available data)
  - industries dealing with specific NM
  - workers / consumers exposure values
  - gradual / accidental environmental pollution exposure values

- Main contributors: Zurich, Swiss Re, XL-Catlin and SIA

- Out of scope: risk appetite, UW guidelines, exclusions etc.

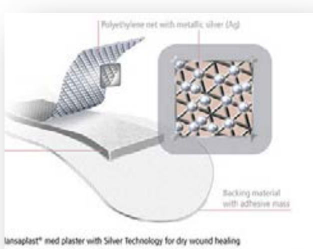
NanoTool: NMs (to be) assessed

1st priority NMs used widely with potential EHS concerns (NanoTool evaluation)	2nd priority NMs used widely with potential EHS concerns	3rd priority NMs not yet widely used or no apparent EHS concerns
• **Silver nanoparticles (Nanosilver)** • **Carbon nanotubes (CNTs)** • **Titanium dioxide (Titania)**	• **Silicium dioxide nanoparticles (Silica)** • **Zinc oxide** • **Carbon black** • Copper • Iron oxide • Cerium oxide	• Quantum dots • Graphene • Gold nanoparticles • Fullerenes • Nanoclay

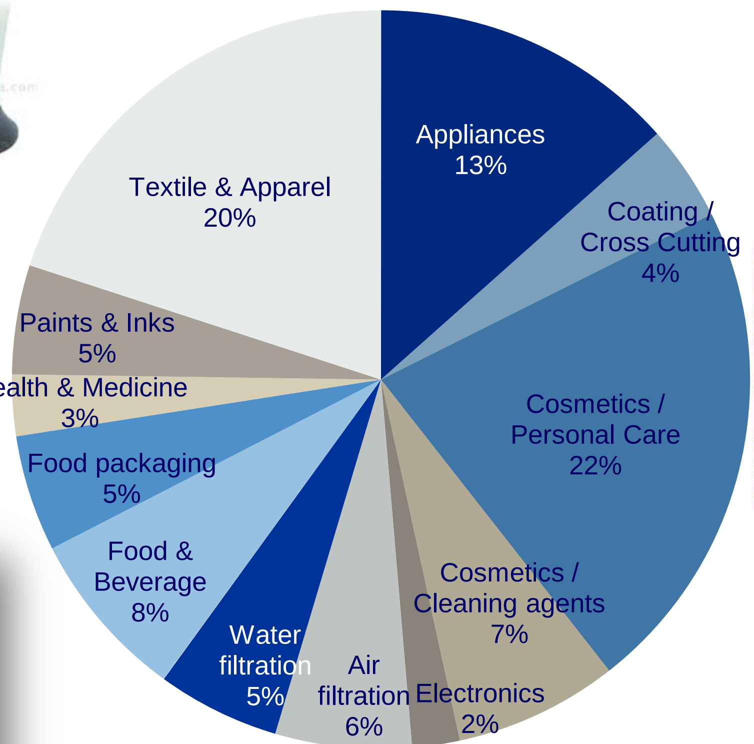
Silver nanoparticles (nano Ag)

Identification of industries / existing applications

- 335 end products/product types
- produced by 301 companies worldwide
- 12 categories of applications identified



Application split*



This information is gathered form online sources. It is not meant to be a comprehensive list of all activities in this area.

NanoTool: General information

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- General information on production processes and existing / potential applications are summarized (based on publicly available sources)
- For each of the assessed NMs, general production volume and spread are presented for informative purpose
- Overview for all assessed NMs is shown below

Nanomaterial	Global production volume in tpa					Spread in No of products		
	1	2	3	4	5	1	2	3
	100-1'000	1'000-10'000	10'000-100'000	100'000-1'000'000	>1'000'000	<100	100-1'000	>1'000
silver		2					2	
CNTs	1						2	
titanium dioxide		2					2	
carbon black					5		2	
zinc oxide			3			1		
silica					5		2	

NanoTool: Risk assessment methodology

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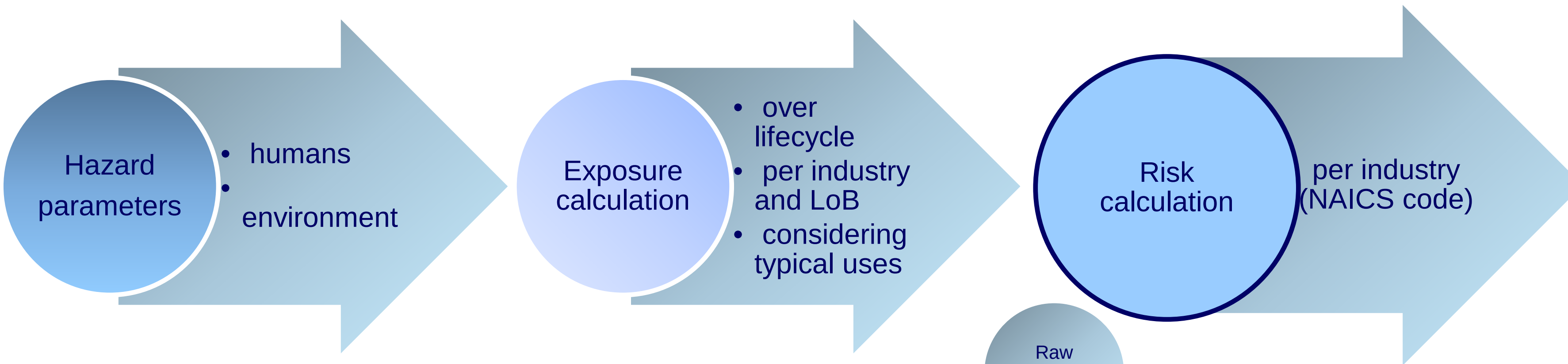
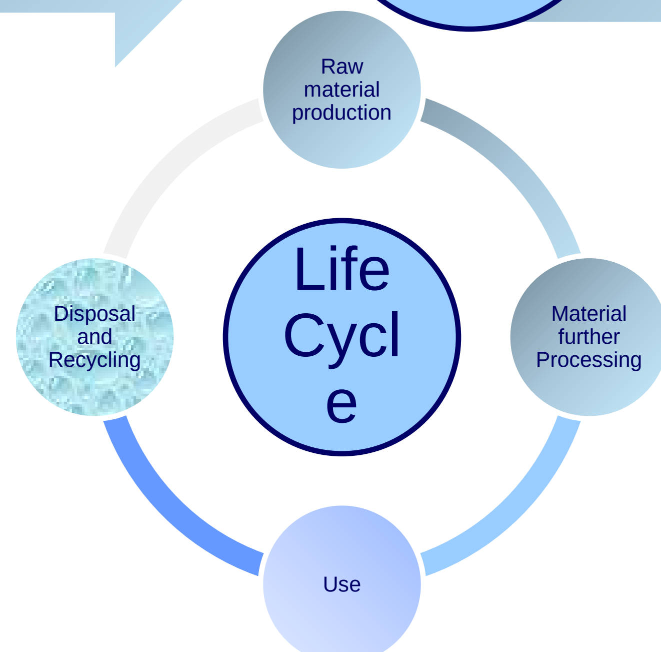


Additional information:
- Most relevant applications
- Wide spread use
- Production volumes
- Information sources



NanoTool: Hazard parameters

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Human Hazard

- toxicity (path: oral, inhalation, dermal ; value: LD 50, PEL, MAK)
- carcinogenicity (value IARC)
- mutagenicity (value IARC)
- reproductive toxicity (value IARC)

Hazard category	Value (LD 50)
>2000	1
>200-2000	2
>25-200	3
<=25	4

Hazard category	Value (IARC)
probably not CMR	0
not classifiable	2
possibly or probably CMR	3
CMR to humans	4

Environmental Hazard

- persistence / bioaccumulation
- aquatic toxicity (value LC 50)
- other (e.g. microbial resistance)

Hazard category	Value (LC 50 fish)
>1000	1
>100-1000	2
>10-100	3
<10	4

Hazard category (PB)	Hazard category (AT)	Value
no	-	0
equivocal	1,2,3	0
	4	2
yes	1,2	2
	3,4	4

IARC – International Association on Research for Cancer; LD50 – Lethal Dose; LC50 – Lethal concentration; PEL - permissible exposure limits; MAK – Maximale Arbeitsplatz-Konz.

NanoTool: Human hazard for nano Ag

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- Carcinogenicity is a killer criteria → sum up goes to the maximum value
- Additional penalty points may apply (carbon nanotubes for asbestos like behavior)
- If LC 50 value does not exist, PEL value is taken instead (e.g. TiO_2 nanoparticles)

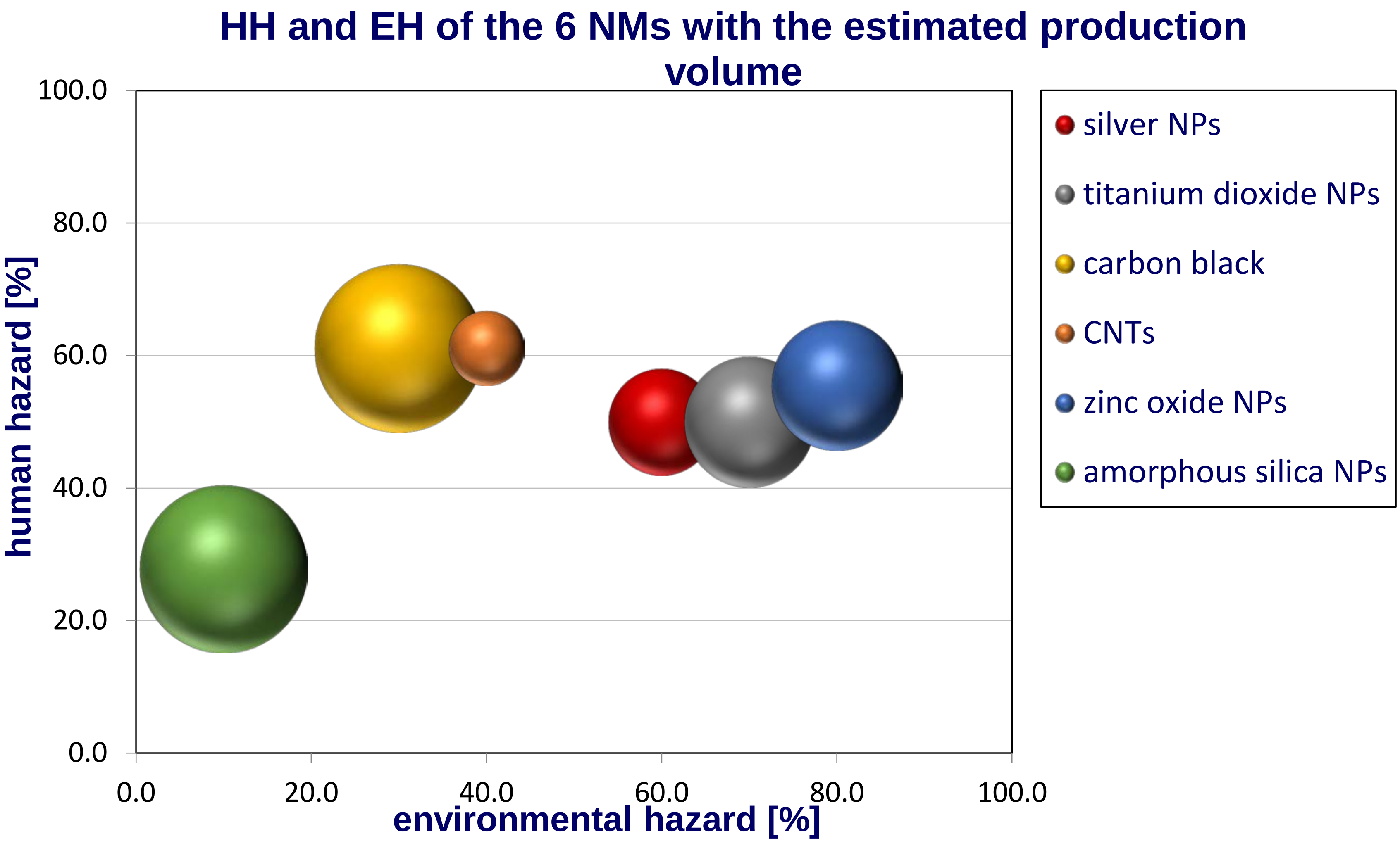
		input	CATEGORY	COMMENT	REFERENCES
HUMAN HAZARD	**TOTAL**	**18**	**9**	**The range of the categories is 1-4. The final value for the human hazard is calculated by summing up all categories and penalty points. Therefore, the maximum value (without penalty points) is 18.**	
	toxicity (LD50 [ppm]) ORAL	>200-2000	2	The main uptake path for humans is via the skin or by ingestion (drinking/eating). Therefore, the oral LD50 was chosen to represent the specific toxicity of these nanoparticles: The oral LD50 was 169/213/354/391.5 mg/kg in Elkhawass et al. (2015) (single dose administrations, observation for 14 days, 2 NPs sizes and two calculation methods). The oral administration of 5000mg/kg (Maneewattanapinyo et al., 2011) produced neither mortality nor acute toxic signs throughout the observation period of 24h. Additionally, the oral LD50 in Amin et al. (2015) is 268 mg/kg (oral administration for 28 days to mice). This value goes in line with Elkhawass et al. (2015).	Amin Y.M., Hawas A.M., El-Batal A.I., Hassan H.M., and Elsayed M. E. 2015. 'Evaluation of Acute and Subchronic Toxicity of Silver Nanoparticles in Normal and Irradiated Animals'. British Journal of Pharmacology a Nd Toxicology. http://www.maxwellsci.com/print/bjpt/v6-22-38.pdf. Elkhawass, E.A., M.E. Mohallal, and M.F. Soliman. 2014. 'Acute Toxicity of Different Sizes of Silver Nanoparticles Intraperitonally Injected in BALB/C Mice Using Two Toxicological Methods'. International Journal of Pharmacy and Pharmaceutical Sciences 7 (2). http://innovareacademics.in/journals/index.php/ijpps/article/view/3776. Maneewattanapinyo, P., W. Banlunara, Chuchaat Thammacharoen, S. Ekgasit, and T. Kaewamatawong. 2011. 'An Evaluation of Acute Toxicity of Colloidal Silver Nanoparticles'. Journal of Veterinary Medical Science 73 (11):
	carcinogenicity	ot classifiable (GROUP	2	No scientific information was found. It is mentioned in Gressler et al. (2010) that tumours can be promoted. However, no more information is given. On the other hand, nanosilver is used in cancer therapy by naturopaths (Welt im Wandel (2014) is a very unscientific source!).	Greßler, S., and R. Fries. 2010. Nanosilber in Kosmetika, Hygieneartikeln und Lebensmittelkontaktmaterialien Produkte, gesundheitliche und regulatorische Aspekte. Wien: Bundesmininsterium für Gesundheit, Sekt. II. Welt im Wandel. 2014. 'Borrelioseheilung Mit Kolloidalem Silber'.
	mutagenicity	not classifiable	2	There are several ways described in EPA (2012) how silver nanoparticles affect the DNA or the repair mechanisms of the latter. On the other hand, no mutagenicity was seen in Kim et al. (2010) in a cell experiment. More studies have to be done to make an assessment possible.	EPA. 2012. 'Nanomaterial Case Study: Nanoscale Silver in Disinfectant Spray'. http://ofmpub.epa.gov/eims/eimscomm.getfile?p_download_id=507239. Kim, Y-J., S.I. Yang, and J.-C. Ryu. 2010. 'Cytotoxicity and Genotoxicity of Nano-Silver in Mammalian Cell Lines'. Molecular & Cellular Toxicology 6 (2):
	reproductive toxicity	obably toxic for reprod	3	Abnormal fetal development in human correlates with silver concentration (not	Asharani, P.V., Y. Lian Wu, Z. Gong, and S. Valiyaveettil. 2008. 'Toxicity of
	penalty points	no	0	no comment	
comments	The main uptake path for humans is via the skin or by ingestion (drinking/eating). Therefore, the oral LD50 was chosen to represent the specific toxicity of these nanoparticles.				

NanoTool: Environmental hazard for nano Ag

- No killer criteria
- Additional penalty points may apply (e.g. nano Ag for bacterial resistance)
- Persistence/Bioaccumulation effect calculated in respect to aquatic toxicity

		input	CATEGORY	COMMENT	REFERENCES
ENVIRONMENTAL HAZARD	**TOTAL**	**10**	**6**	**The range of the categories is 1-4. The final value for the environmental hazard is calculated by summing up all categories and penalty points. Therefore, the maximum value (without penalty**	
	persistence/bioaccumulation	no	0	Generally, naturally occuring silver is accumulated in the human body. Therefore, there are maximum concentrations for drinking water recommended by the EPA (Gressler et al., 2010). However, nanosilver does not have to accumulate in the environment. It can dissolve, diassemble, sorb to soil or sediment, undergo oxysulfidation, form complexes with organic matter or reform from ionic silver in the presence of humic and fulmic acids. Therefore, the persistence depends on the surface coating, the pH, the temperature and the presence of organic matter (EPA, 2012).	EPA. 2012. 'Nanomaterial Case Study: Nanoscale Silver in Disinfectant Spray'. http://ofmpub.epa.gov/eims/eimscomm.getfile?p_download_id=507239. Greßler, S., and R. Fries. 2010. Nanosilber in Kosmetika, Hygieneartikeln und Lebensmittelkontaktmaterialien Produkte, gesundheitliche und regulatorische Aspekte. Wien: Bundesmininsterium für Gesundheit, Sekt. II.
	aquatic toxicity (LC50 for fish [ppm]=[mg/l])	<10	4	LC50 values (48h) for fish of 7mg/l and 84 µg/l were found in two different studies by Griffitt et al. (2008) and Bilberg et al. (2012) mentioned in the paper of the European Commission (2014) and the Danish Protection Agency (2015).	Bilberg, K., M.B. Hovgaards, F. Besenbacher, and E. Baatrup. 2012. 'In Vivo Toxicity of Silver Nanoparticles and Silver Ions in Zebrafish (Danio Rerio)'. doi:10.1155/2012/293784. European Commission, and Directorate General for Health & Consumers. 2014. Opininon on Nanosilver Safety, Health and Environmental Effects and Role in Antimicrobial Resistance. Luxembourg: [European Commission]. http://dx.publications.europa.eu/10.2772/76851. Griffitt, R. J., J. Luo, J. Gao, J.-C. Bonzongo, and D. S. Barber. 2008. 'Effects of Particle Composition and Species on Toxicity of Metallic Nanomaterials in Aquatic Organisms'. doi:10.1897/08-002.1.
	penalty points	yes	2	Research shows that bacterial resistences can develop when silver is used in small concentrations (European Commission, 2014; Friends of the Earth Australia, 2011; Gressler et al., 2010).	European Commission, and Directorate General for Health & Consumers. 2014. Opininon on Nanosilver Safety, Health and Environmental Effects and Role in Antimicrobial Resistance. Luxembourg: [European Commission]. http://dx.publications.europa.eu/10.2772/76851. Friends of the Earth Australia. 2011. 'Nano-Silver: Policy Failure Puts Public Health at Risk'. http://www.foe.org/system/storage/877/e2/8/549/NanoSilverUS.pdf.
comments	no comment				

NanoTool: Human hazard, Environmental hazard and production volume



NanoTool: Exposure assessment methodology

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PRODUCTION SITE

- **Workers** (Probability for employee to be exposed to the nanomaterials)
- **Accidental release** (Probability for NMs to be released to the third party property in case of an accident) and **Gradual release** (Probability that NMs are gradually released to the environment)

FINAL PRODUCT

- **Product** (Probability that consumers are exposed to NMs)
- **Gradual release** (Probability that NMs are released to the environment during the product use)

Hazard category	Value
no exposure / no application	0
low	1
medium	2
high	3

NanoTool: Exposure assessment for nano Ag

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Nanosilver		production site related (raw material producing and further processing companies)		final product related		
NAICS	INDUSTRY	workers exposure	gradual and accidental environmental exposure	consumer exposure	gradual environmental exposure	products
11	Agriculture, Forestry, Fishing and Hunting	0	0	0	0	
21	Mining, Quarrying, and Oil and Gas Extraction	0	0	x	x	
22	Utilities	0	0	0	0	
236	Construction of Buildings	0	0	0	0	
311	Food Manufacturing	1	1	3	1	influence of plastic packaging containing silver NPs
312	Beverage and Tobacco Product Manufacturing	1	1	3	2	colloidal silver; influence of beverage containers (plastic beer bottles)
313/314/315	Textiles & Apparels	2	3	2	3	yarns, threads; textile mills
316	Leather and Allied Product Manufacturing	2	3	2	1	leather treated with silver
321	Wood Product Manufacturing	0	0	0	0	
322	Paper Manufacturing/Packaging	2	2	3	1	filters, masks, packaging material
323	Printing and Related Support Activities	0	0	0	0	
324	Petroleum and Coal Products Manufacturing	0	0	0	0	
325/3251	Chemical Manufacturing (inlcuding Base Chemical Man	3	3	x	x	raw material manufacturing (powder, solution/dispersion)
3252	Resin, Synthetic Rubber, and Artificial Synthetic Fibers	2	2	x	x	raw materials for food packaging etc.
3253	Pesticide, Fertilizer, and Other Agricultural Chemical Ma	2	2	2	3	algaecide ("NSPW-L30SS"/"Nanosilva"),
3254	Pharmaceutical and Medicine Manufacturing	1	1	3	2	acne cream
3255	Paint, Coating, and Adhesive Manufacturing	2	2	2	2	coating sprays, antibacterial paints, inks for electronic boards
3256	Soap, Cleaning Compound, and Toilet Preparation Manu	2	2	3	3	body lotions, toothpaste, deodorants, creams, brushes, soap, shampoo, hair
32591	Printing Ink Manufacturing	0	0	0	0	
326	Plastics and Rubber Products Manufacturing	2	1	3	1	food preparation equipment, condoms, baby toys, food containers, milk stora
327	Nonmetallic Mineral Product Manufacturing	0	0	0	0	
331	Primary Metal Manufacturing	0	0	x	x	
332	Fabricated Metal Product Manufacturing	0	0	0	0	
333	Machinery Manufacturing	2	1	1	1	filtration (air), AC, humidifiers etc.
334	Computer and Electronic Product Manufacturing	2	1	2	1	mouse, keyboard, mobile phone, notebook; medical equipment and control ins
335	Electrical Equipment, Appliance, and Component Manu	2	1	2	2	washing machine, vacuum cleaner, refrigerator, curling iron, air filtration devi
336	Transportation Equipment Manufacturing	0	0	0	0	
337	Furniture and Related Product Manufacturing	2	1	2	1	garden furniture, matraces
339	Miscellaneous Manufacturing	2	1	2	1	jewelry, silverware; toys
3391	Medical Equipment and Supplies Manufacturing	1	1	3	1	wound dressings, catheters; medical devices coated
622	Hospitals	1	1	3	1	wound dressings, catheters
562	Administrative and Support and Waste Management ar	2	2	x	x	recycling processes

comments
> The categories were first set individually by every member of the working group and then discussed in a group meeting.
> As there are no end products but intermediate products only in chemical manufacturing, resin production, primary metal production and the waste management these fields cannot be filled (x).
> The waste management part is neglected in all rows except the last one (waste water treatment plants, landfills, incineration).
> As silver NPs are mainly produced in wet chemistry processes without dust production the exposure for workers was assessed to be "medium" except in the chemical manufacturing.
> It is assumed that in the pharmaceutical sector the securitiy guidelines are high, leading to a "low" exposure. However, drugs with nanosilver were found to be in research but without current appliance except for the acne cream.
> For plastic products it was assumed that silver is added in resins production and not later as a coating.
> In hospitals the production part is related to the employees that (hopefully) don't get in contact with the equipment containing nanosilver. Therefore, the exposure there is negligible. The product

NanoTool: Risk calculation for nano Ag

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$$risk = \frac{hazard * exposure}{max\ hazard * max\ exposure} * 100$$

Nanosilver		production site related (raw material producing and further processing companies)		final product related	
NAICS	INDUSTRY	workers exposure	gradual and accidental environmental exposure	consumer exposure	gradual environmental exposure
11	Agriculture, Forestry, Fishing and Hunting	0	0	0	0
21	Mining, Quarrying, and Oil and Gas Extraction	0	0	x	x
22	Utilities	0	0	0	0
236	Construction of Buildings	0	0	0	0
311	Food Manufacturing	17	20	50	20
312	Beverage and Tobacco Product Manufacturing	17	20	50	40
313/314/315	Textiles & Apparels	33	60	33	60
316	Leather and Allied Product Manufacturing	33	60	33	20
321	Wood Product Manufacturing	0	0	0	0
322	Paper Manufacturing	33	40	50	20
323	Printing and Related Support Activities	0	0	0	0
324	Petroleum and Coal Products Manufacturing	0	0	0	0
325/3251	Chemical Manufacturing (inlcuding Base Chemical Man	50	60	x	x
3252	Resin, Synthetic Rubber, and Artificial Synthetic Fibers	33	40	x	x
3253	Pesticide, Fertilizer, and Other Agricultural Chemical M	33	40	33	60
3254	Pharmaceutical and Medicine Manufacturing	17	20	50	40
3255	Paint, Coating, and Adhesive Manufacturing	33	40	33	40
3256	Soap, Cleaning Compound, and Toilet Preparation Man	33	40	50	60
32591	Printing Ink Manufacturing	0	0	0	0
326	Plastics and Rubber Products Manufacturing	33	20	50	20
327	Nonmetallic Mineral Product Manufacturing	0	0	0	0
331	Primary Metal Manufacturing	0	0	x	x
332	Fabricated Metal Product Manufacturing	0	0	0	0
333	Machinery Manufacturing	33	20	17	20
334	Computer and Electronic Product Manufacturing	33	20	33	20
335	Electrical Equipment, Appliance, and Component Manu	33	20	33	40
336	Transportation Equipment Manufacturing	0	0	0	0
337	Furniture and Related Product Manufacturing	33	20	33	20
339	Miscellaneous Manufacturing	33	20	33	20
3391	Medical Equipment and Supplies Manufacturing	17	20	50	20
622	Hospitals	17	20	50	20
562	Administrative and Support and Waste Management ar	33	40	x	x

NanoTool: Outcome

Industries with highest risk potentials for nano Ag

silver NPs			
PRODUCTION		**PRODUCT**	
workers risk		**consumers risk**	
50%	Chemical manufacturing (325)	50%	Food manufacturing (311)
			Beverage product manufacturing (312)
			Paper manufacturing (322)
			Pharmaceutical manufacturing (3254)
			Soap, cleaning compound and toilet preparation manufacturing (3256)
			Plastics and rubber product manufacturing (326)
			Medical equipment (3391)
			Hospitals (622)
environmental risk		**environmental risk**	
60%	Textiles & apparels (313/314/315)	60%	Textiles & apparels (313/314/315)
	Leather product manufacturing (316)		Pesticide & fertilizer (3253)
	Chemical manufacturing (325)		Soap, cleaning compound and toilet preparation manufacturing (3256)

NanoTool: Outcome

Risk score overview per nanomaterial

	PRODUCTION (average risk)	
	workers risk	environmental risk
silver NPs	30.0	32.0
CNTs	39.6	16.0
titanium dioxide NPs	31.9	29.2
carbon black	39.4	15.0
zinc oxide NPs	35.0	41.5
amorphous silica NPs	17.6	4.0

	PRODUCT (average risk)	
	consumers risk	environmental risk
silver NPs	40.2	31.8
CNTs	25.1	13.3
titanium dioxide NPs	27.8	36.3
carbon black	31.5	14.5
zinc oxide NPs	42.3	53.3
amorphous silica NPs	16.3	6.1

NanoTool: Outcome

Industries with highest risk potentials overall

general			
PRODUCTION		PRODUCT	
workers risk		**consumers risk**	
1.	Chemical manufacturing (325)	1.	Food manufacturing (311)
2.	Plastics and rubber product manufacturing (326)	2.	Soap, cleaning compound and toilet preparation manufacturing (3256)
3.	Paint, coating and adhesive manufacturing (3255)	3.	Pharmaceutical manufacturing (3254)
environmental risk		**environmental risk**	
1.	Chemical manufacturing (325)	1.	Soap, cleaning compound and toilet preparation manufacturing (3256)
2.	Waste management services (562)	2.	Plastics and rubber product manufacturing (326)
3.	Soap, cleaning compound and toilet preparation manufacturing (3256)	3.	Paint, coating and adhesive manufacturing (3255)

Can Nanomaterials become a "second asbestos"?

ZURICH

1. **NMs** are very **diverse** → there are no simple answers (it depends on the size, surface properties, aggregation state, type of application, handling procedure etc.)
2. The transition to NMs is “fluent” → many **products are not regulated** by law and are on the market without any risk assessment or labeling requirements
3. **Traditional toxicological methods** (LD50 values) **are suitable** for the risk evaluation of NMs but have **to be extended**!

   Two main factors are IMPORTANT:

   - Effects due to small particle sizes
   - Novel features (different applications → different risks)
4. **Long-term** and **direct effects** of NMs have not be sufficiently studied → subject to change → regular assessment necessary

Can Nanomaterials become a "second asbestos"?

ZURICH

5. **No acute toxicity** in humans has been observed **so far**. Toxicity was found in animal studies, but the doses used were unrealistic (↑)
6. NMs **deposit** at different locations of the respiratory tract and are **not removed** by the usual processes (via macrophages) from the body
7. **Complete evaluation of all the risks is almost impossible**
   - **Production processes information limited** (often patented, workers protection level unknown etc.)
   - **Scientific support incomplete** (HH, EH)
   - **Products that contain "nano" are difficult to track** (same products - various brand names; nano labeling: advertising or requirement; no unique products inventory etc.)

NMs are difficult to assess → keep tracking is the only way!

Thank you for your attention!

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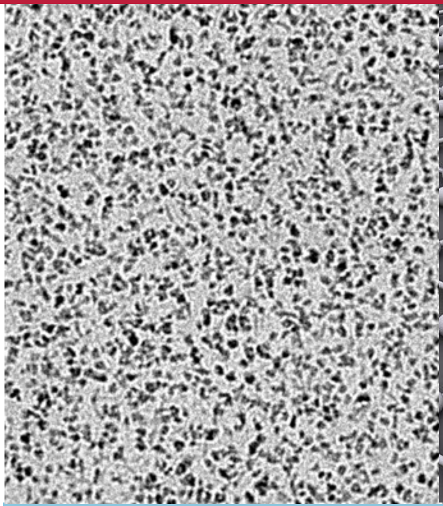
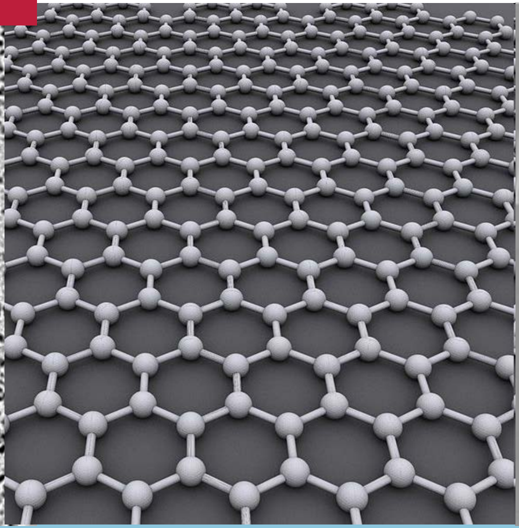
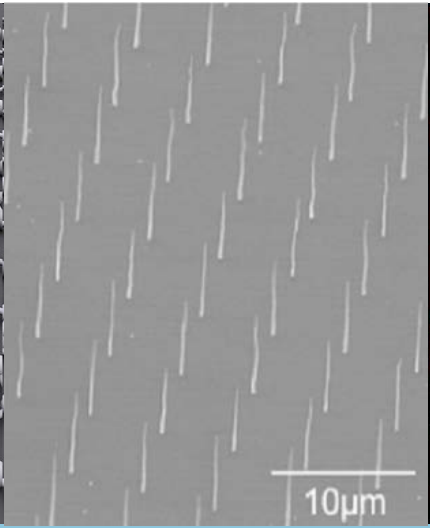
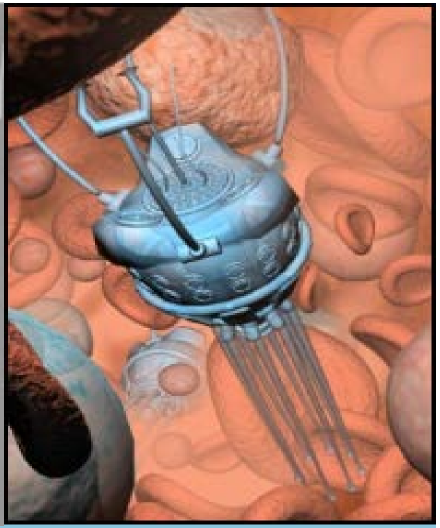








Nanoparticles and Nanotechnology – Classification, Properties and Applications

Prof. Dr. Georg Garnweitner

Geneva Association Summit 2016

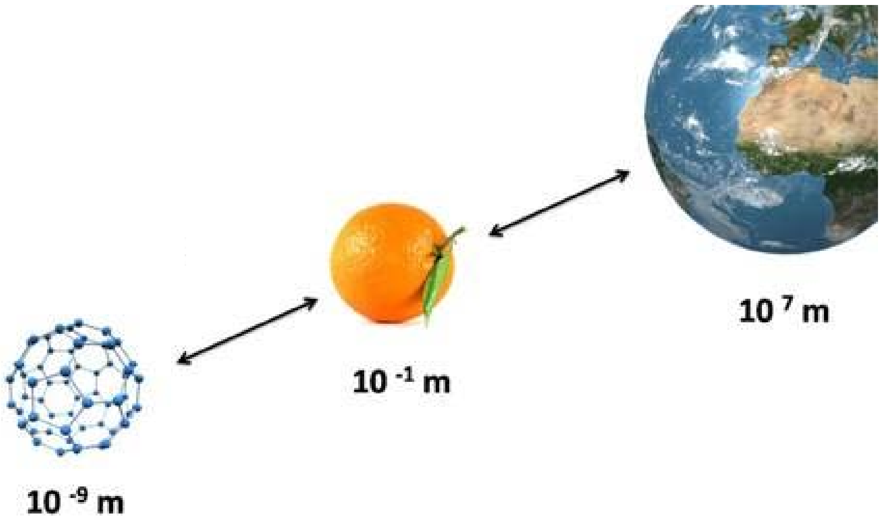
Outline

- Introduction and Classification of Nanomaterials
- Properties of Nanoparticles
- Applications of Nanoparticles
  - Generations of Nanotechnology
  - Established Applications of Nanoparticles
  - Novel Applications
  - Nanostructures
- Future Developments

Definition of Nanomaterials

Nanomaterials are materials that at least in one dimension show a size range of 1-100 nm and are deliberately produced because of advantageous or novel properties due to their small size.

Nanomaterials are incredibly small…



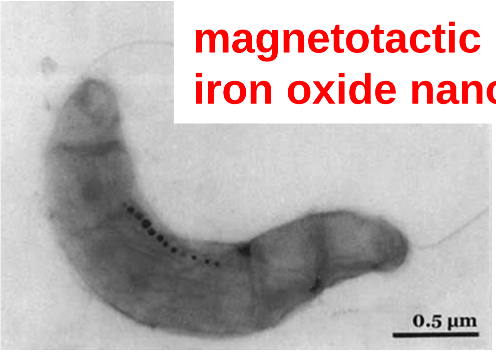
Source: Die Innovationsgesellschaft mbH

Introduction: Nanomaterials

…but are not exclusively a product of modern technology!

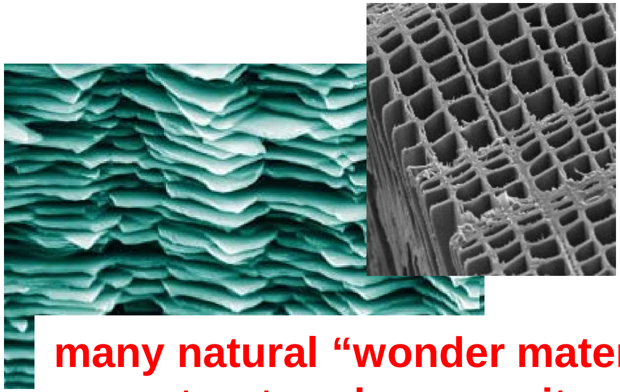
- Natural nanomaterials:

salt nanoparticles are part of the marine air



magnetotactic bacteria with iron oxide nanoparticles

large amounts of nanoparticles are released during vulcanic eruptions, in addition to larger particles



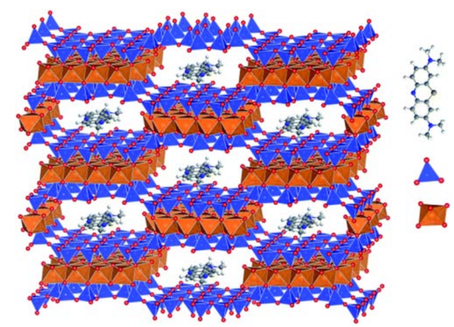
many natural “wonder materials” like wood or nacre are nanostructured composites

Introduction: Nanomaterials

…and have been produced unintentionally by mankind for thousands of years, mainly as pigments.

Lycurgus cup (5th century AD) containing gold nanoparticles.

Maya blue is a nanocomposite of indigo and clays



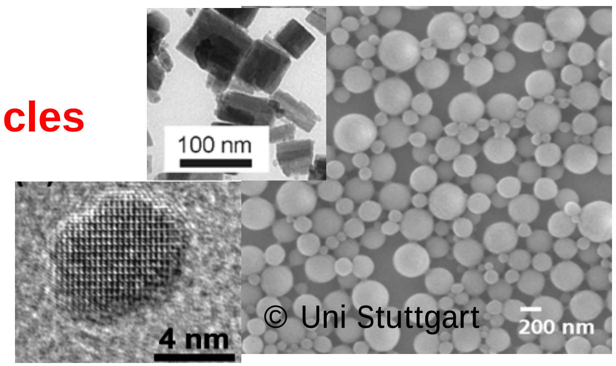
metal nanoparticles have been used to color church windows since the 17th century

Types of Nanomaterials

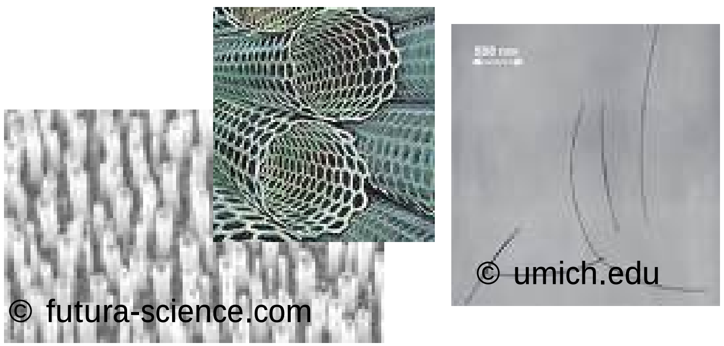
Nanomaterials show a high diversity –
in principle, any material can be brought into the “nano form”!

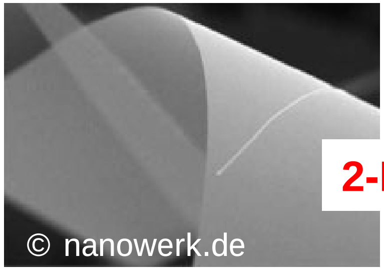
Distinction by geometry:

0-D: nanoparticles



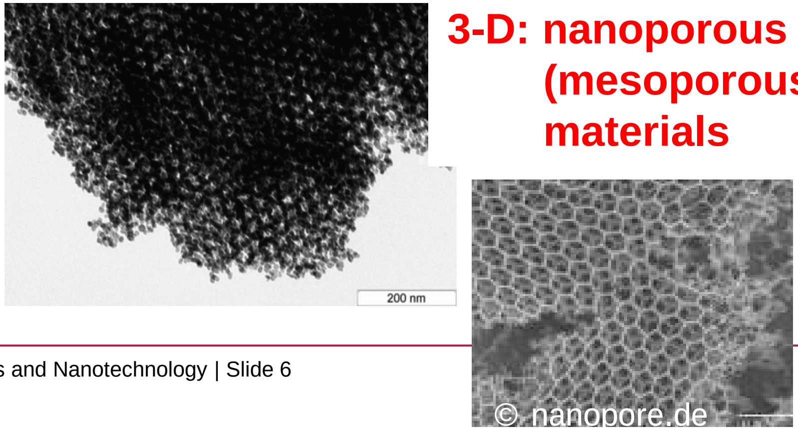
1-D: nanorods and -tubes





2-D: nanosheets

3-D: nanoporous (mesoporous) materials

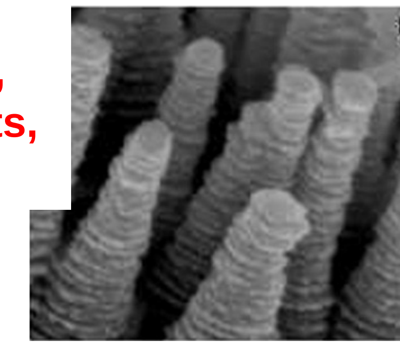


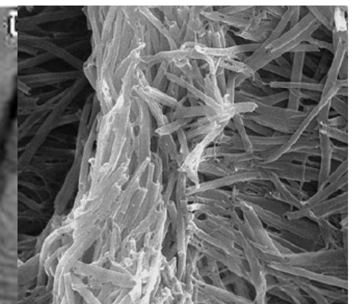
Types of Nanomaterials

Nanomaterials show a high diversity –
in principle, any material can be brought into the “nano form”!

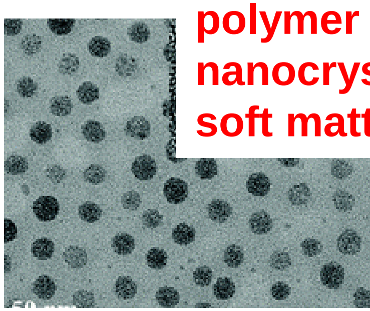
Distinction by type of material:

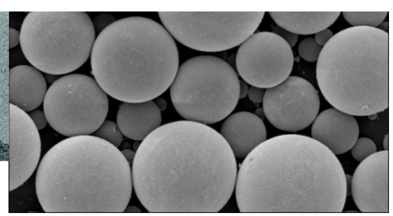
inorganic materials: metals, metal oxides, semiconductors, salts, carbon



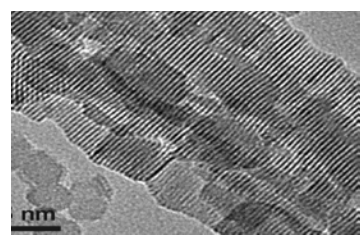


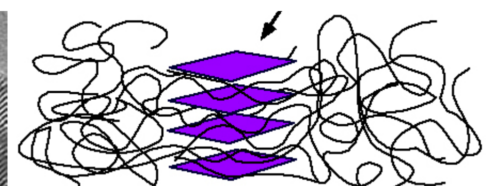
organic nanomaterials: polymer particles, organic nanocrystals (e.g. APIs), soft matter





hybrid materials, nanocomposites



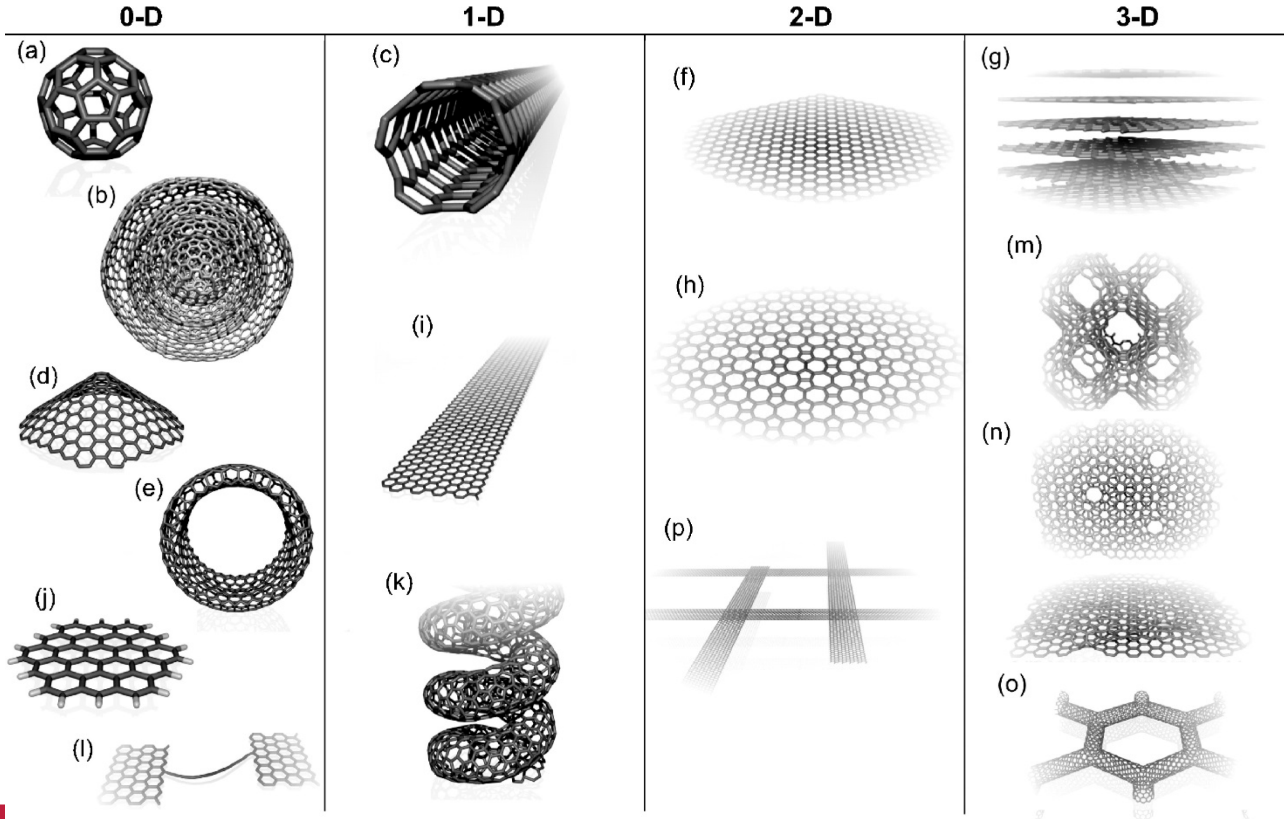


Types of Nanomaterials

Carbon-based Nanomaterials

- multitude of structures possible, molecule-like materials

Very high stability, diversity of structures and properties



a) Buckminster fullerene
b) giant fullerene
c) nanotube
d) nano-cone
e) nano-ring
f) graphene surface
g) graphite crystal
h) Haeckelite nanotubes
i) graphene ribbon
j) graphene cluster
k) helical nanotube
l) carbon chains
m) Schwarzite crystal
n) nanofoam
o) nanotube network
p) nanotape network

Types of Nanomaterials

Stable nanomaterials are important for applications!

- Metals: simple construction (cluster of atoms), simple synthesis under good control, smallest structures possible

  Problems of chemical stability (oxidation!), mostly only noble metals suitable
- Metal salts (chlorides, carboxylates, phosphates etc.): simple synthesis

  Problems of stability against liquids – solubility?
- “*Compound semiconductors*” e.g. sulfides, selenides, arsenides: “Quantum Dots” size-dependent properties; synthesis by more complex reactive precipitation

  Problems: material toxicity! Partial solubility and/or chemical reaction
- Organics: large variety and diversity between macromolecules and organic crystals

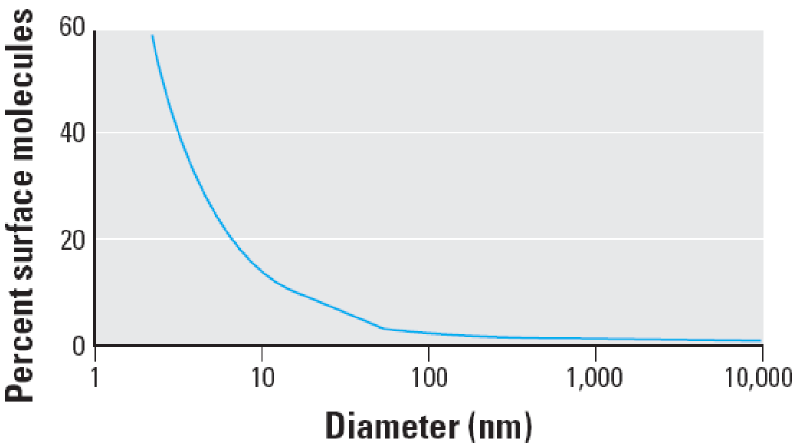
  Problems: Solubility, mechanical, thermal stability
- Metal oxides: high stability, diverse properties

  Hardly any problems for applications

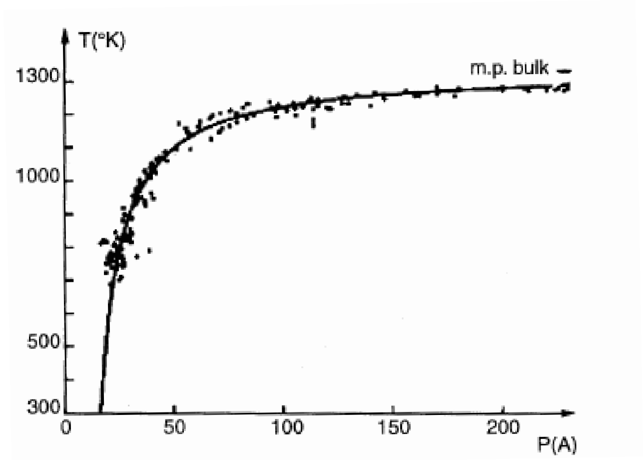
Properties of Nanomaterials: Surface Effect

When approaching the low-nm regime:

- Ratio of surface atoms to internal atoms increases
- Lower influence of inertial forces, higher influence of surface forces (Van der Waals)
- Reactivity increases
- Change in chemical and physical properties



Percentage of the surface atoms of inorganic particles in dependence of particle size



Sharp drop of the melting temperature of small gold nanoparticles (depending on the particle size, here in Å)

Properties of Nanomaterials: Quantum Size Effect

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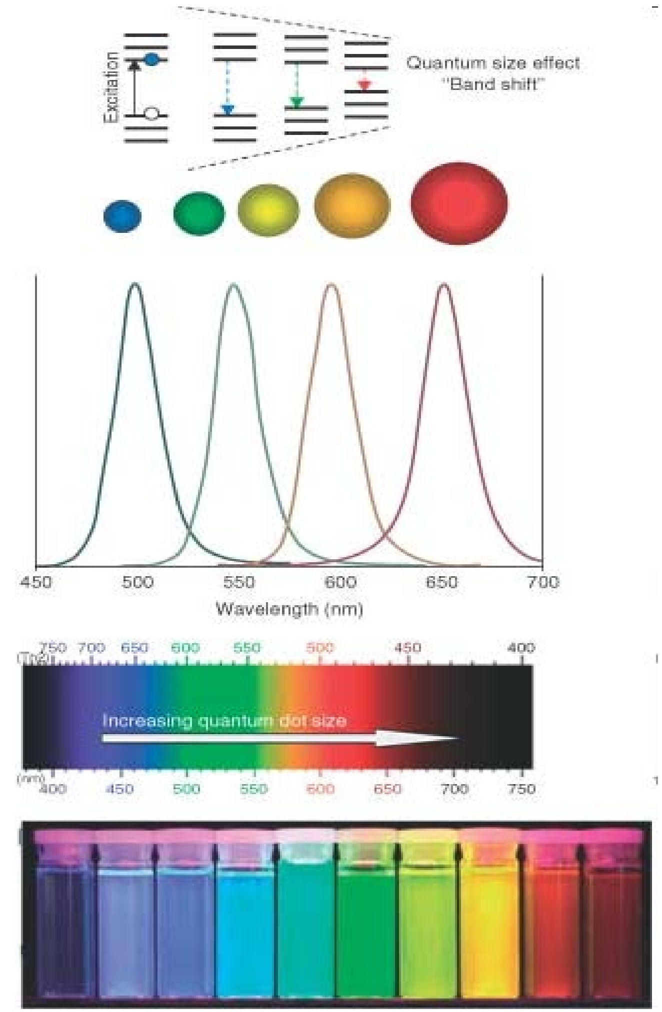
In nanomaterials, electronic (and optical) properties are coupled to size – the quantum size effect.

As a consequence, quantum dots show a size-dependent color:

- The band gap decreases with increasing size of the quantum dots (due to additional electronic states) being in the VIS-light range for sizes <10 nm
- Interaction with visible light as a function of the band gap (wider than in bulk material)

  → correlation $\Delta E = h \cdot \nu$
- Different fluorescent colors depending on the size of the quantum dots

  → The same material shines in different colors!



source: Wiley Interdisciplinary Reviews

Properties of Nanomaterials: Quantum Size Effect

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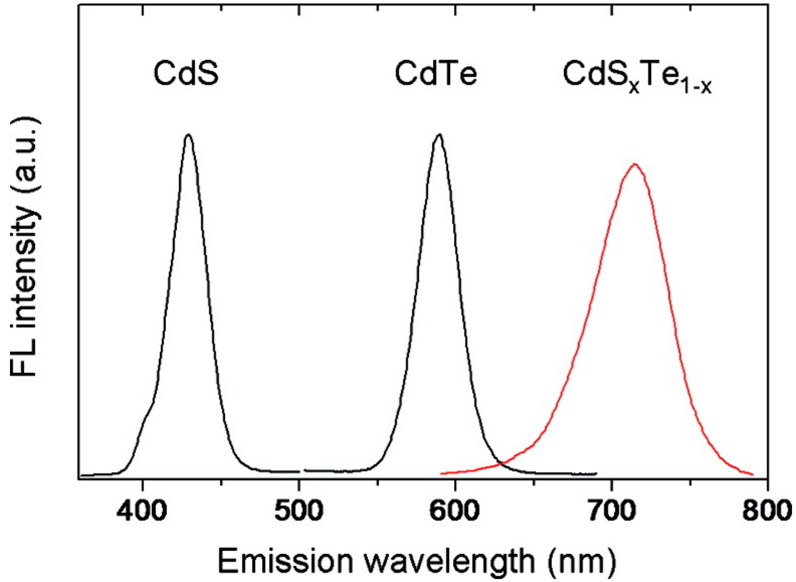
In nanomaterials, electronic (and optical) properties are coupled to size – the quantum size effect.

- In addition to particle size the particle composition is crucial for the fluorescence
- There are also quite stunning effects when an exchange of elements (doping) is performed

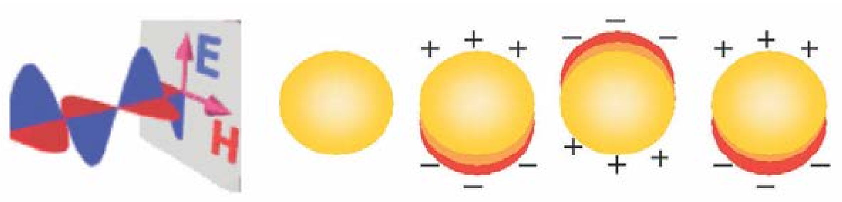


Published in: Nilanka P. Gurusinghe; Nishshanka N. Hewa-Kasakarage; Mikhail Zamkov; *J. Phys. Chem. C* **2008,** 112, 12795-12800.
DOI: 10.1021/jp804045p

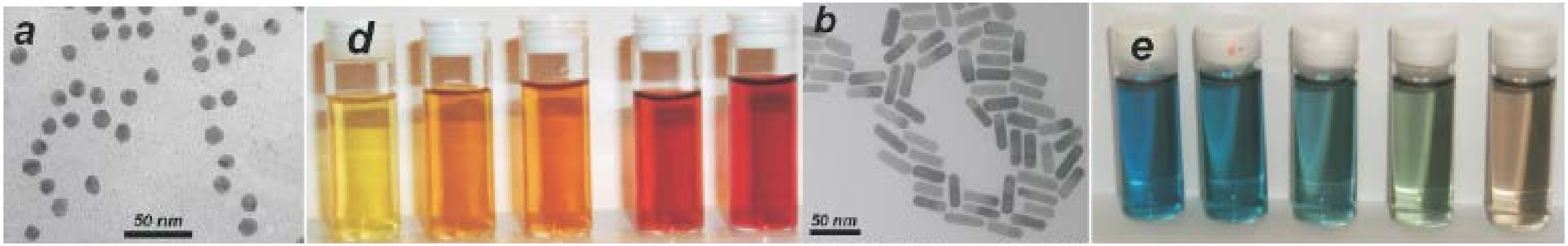
Properties of Nanomaterials: Plasmonic Effect

Plasmonic nanomaterials

- In the case of metal nanoparticles there is yet another strong effect: the **surface plasmon resonance**.
- Through interaction of the free conduction electrons and electromagnetic radiation, dipoles in the near-surface metal layers are induced, which oscillate in phase with the electric field and can propagate along the metal surface. Such coupled oscillations of electrons are called plasmons → plasmonic nanomaterials.



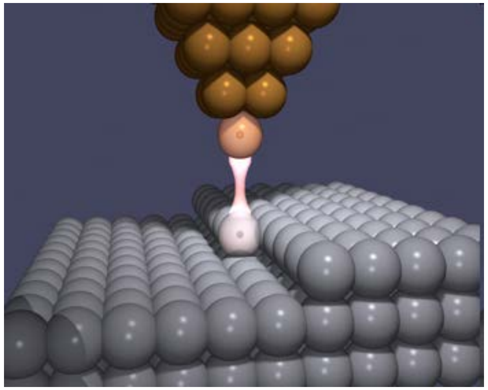
Example: Gold nanoparticles strongly absorb light and thus appear in different colors depending on size and shape

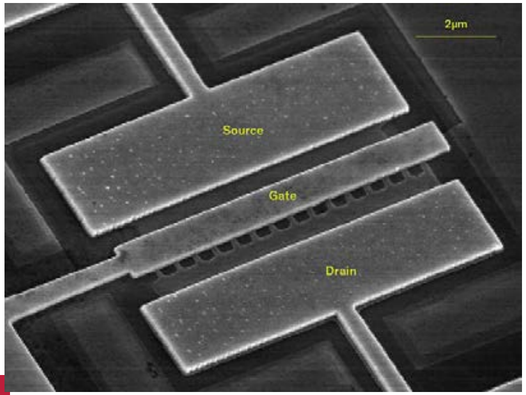


Quantum tunneling

- For nanostructures, the quantum tunneling effect can be exploited
- Thus, in nanoelectronics, components need not be always contacted directly, but a gap (a few nm) can be utilized, allowing to increase the resistance of the contact → quantum tunneling devices

Example: tunneling effect in scanning tunneling microscope





Example: TFET transistor,
R. Li, University of Notre Dame, USA

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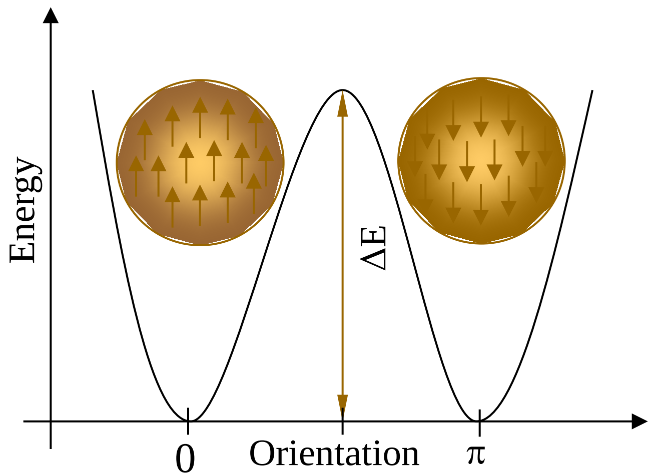
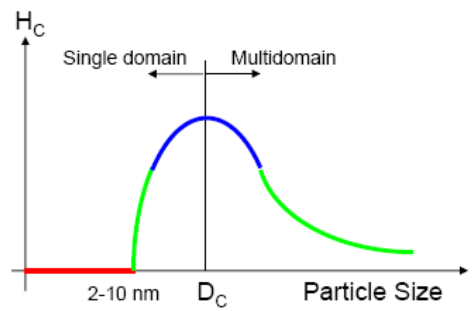
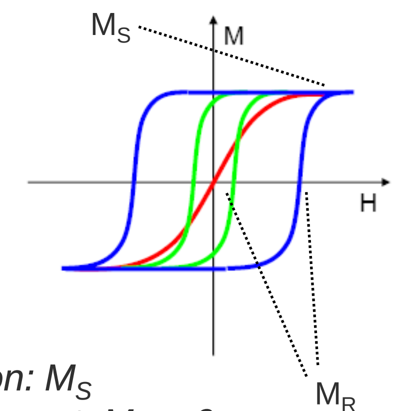
Superparamagnetism

Nanoparticles are significantly smaller than the typical domain size in a magnet. Therefore, the the magnetization can easily be "switched", i.e. a reversal of the magnetization can be achieved, by an external magnetic field or by thermal energy.





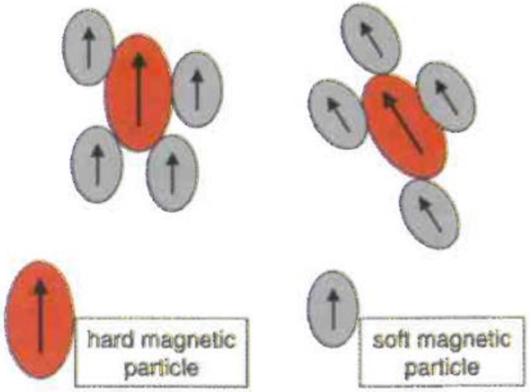


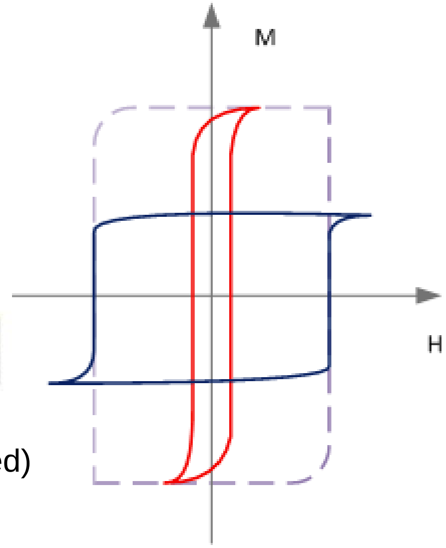
- *High saturation magnetization: M_S*
- *No magnetic remanence moment: $M_R = 0$*

- This results in a "fluctuating" magnetic moment for small nanoparticles – they do not magnetically attract themselves.
- However, in an external magnetic field the magnetic moment aligns (→ superparamagnetism).

Superparamagnetism

- This allows the preparation of “magnetic fluids” from nanoparticles, or stable magnetic suspensions, where the nanoparticles can be manipulated by a magnet.

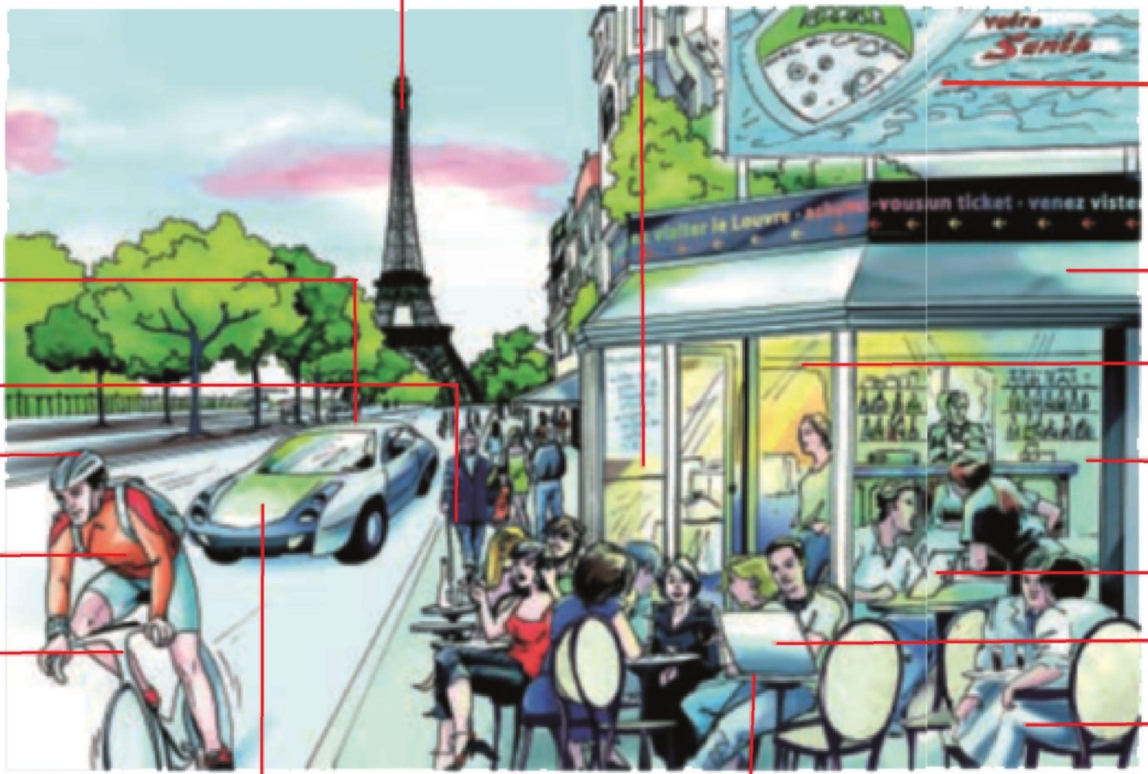




exchange coupled magnet (Dashed)
hard component (Blue)
soft component (Red)

- Additionally, magnetic nanocomposites can be prepared that show novel magnetic properties – e.g. exchange coupled magnets resulting in ultra-strong magnetic materials.

Applications of Nanotechnology



Applications of Nanotechnology

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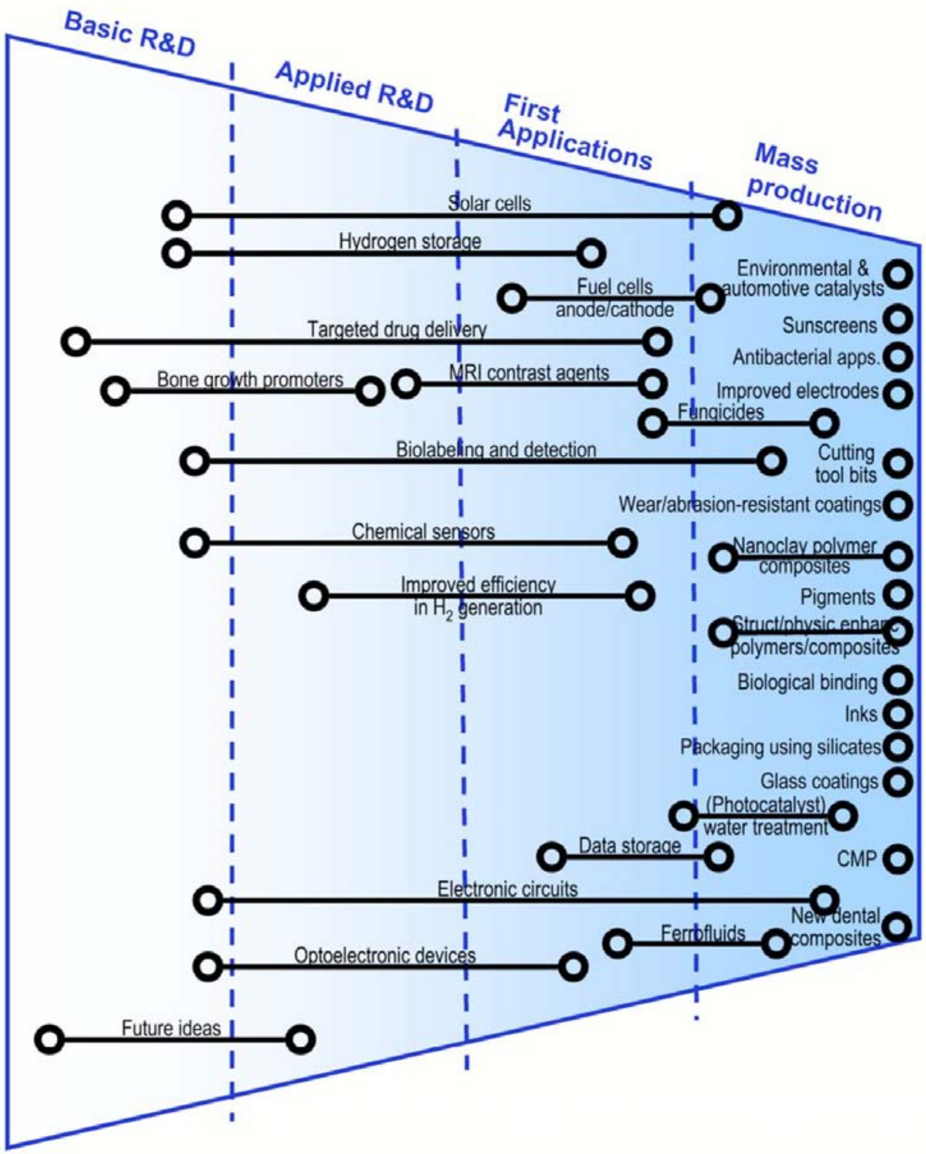

Willems & van der Wildenberg, NanoRoadMap report, projection for 2015.

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The Generations of Nanotechnology

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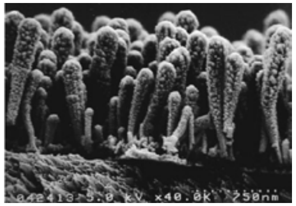
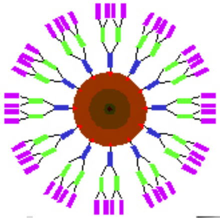
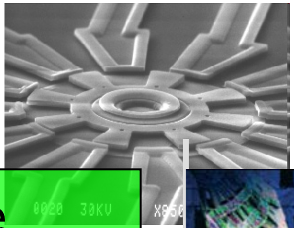
There are different "generations" of nanotechnology:

Level 1: passive nanomaterials

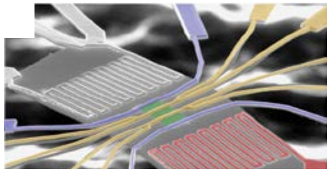


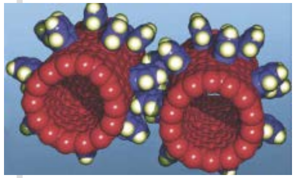
Level 2: active nanomaterials: nanoelectronics, drug targeting

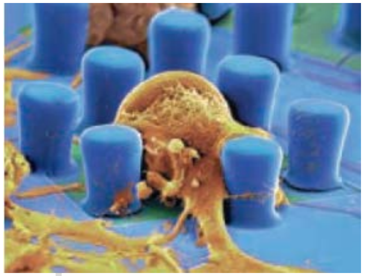


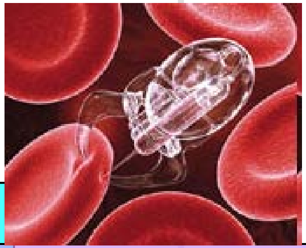


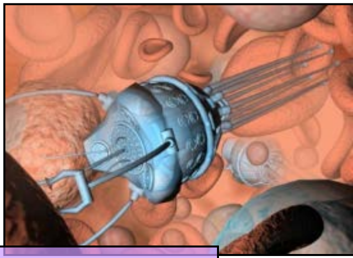
Level 3: nanosystems, supramolecules, 3D nanonetworks











Level 4: intelligent nanosystems, nanorobots, hierarchical functions, evolutionary structures

today | 5 years | 10-15 years | 15+ years

Established Applications of Nanoparticles

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- Degussa: Production of pyrogenic nanoparticle powders since 1940

Flow agents

Control 2 % AEROSIL R 972

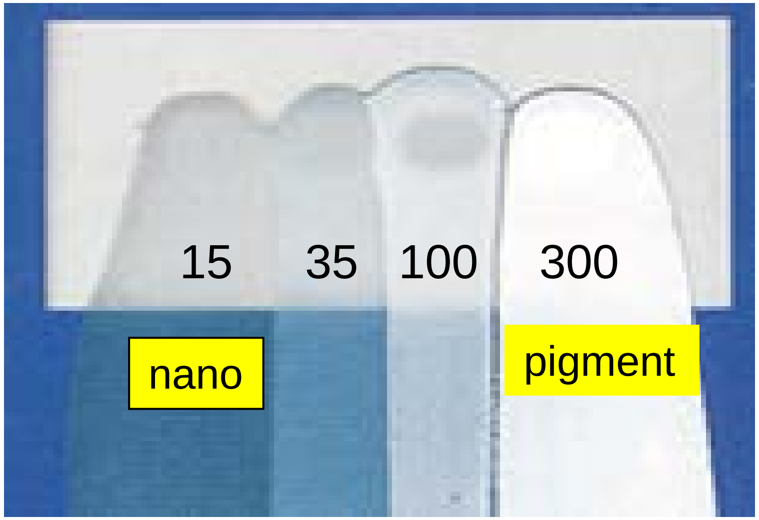
Stabilization of suspensions:

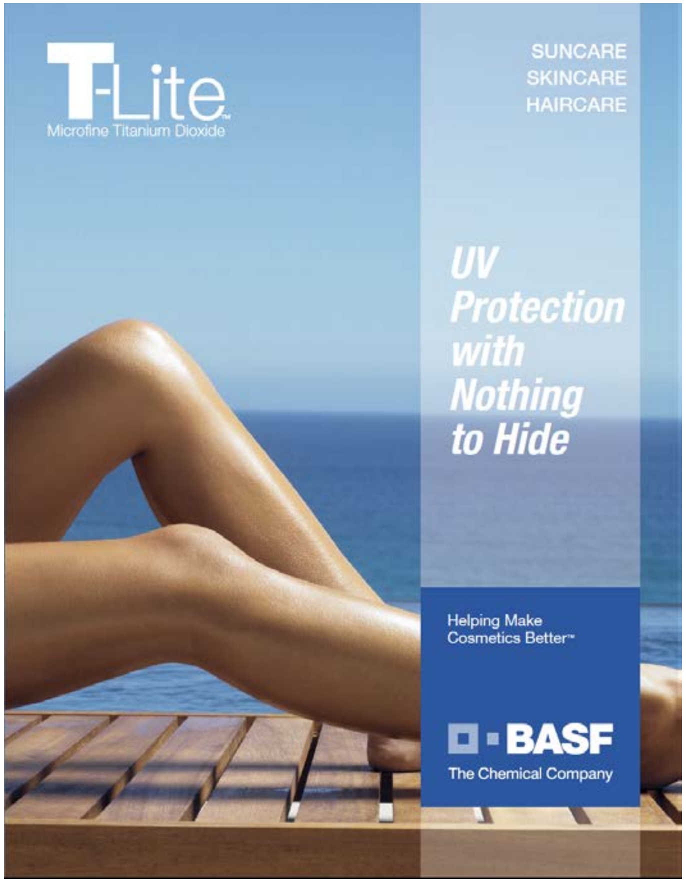
Established Applications of Nanoparticles

- Degussa: Applications of nanoparticle sized powders

Example: Titania nanoparticles

- Used as pigments and in sunscreens for UV protection





Established Applications of Nanoparticles
Example: Sunscreens

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Sunscreens with high protection factors can only be transparent through the use of nanoparticles!

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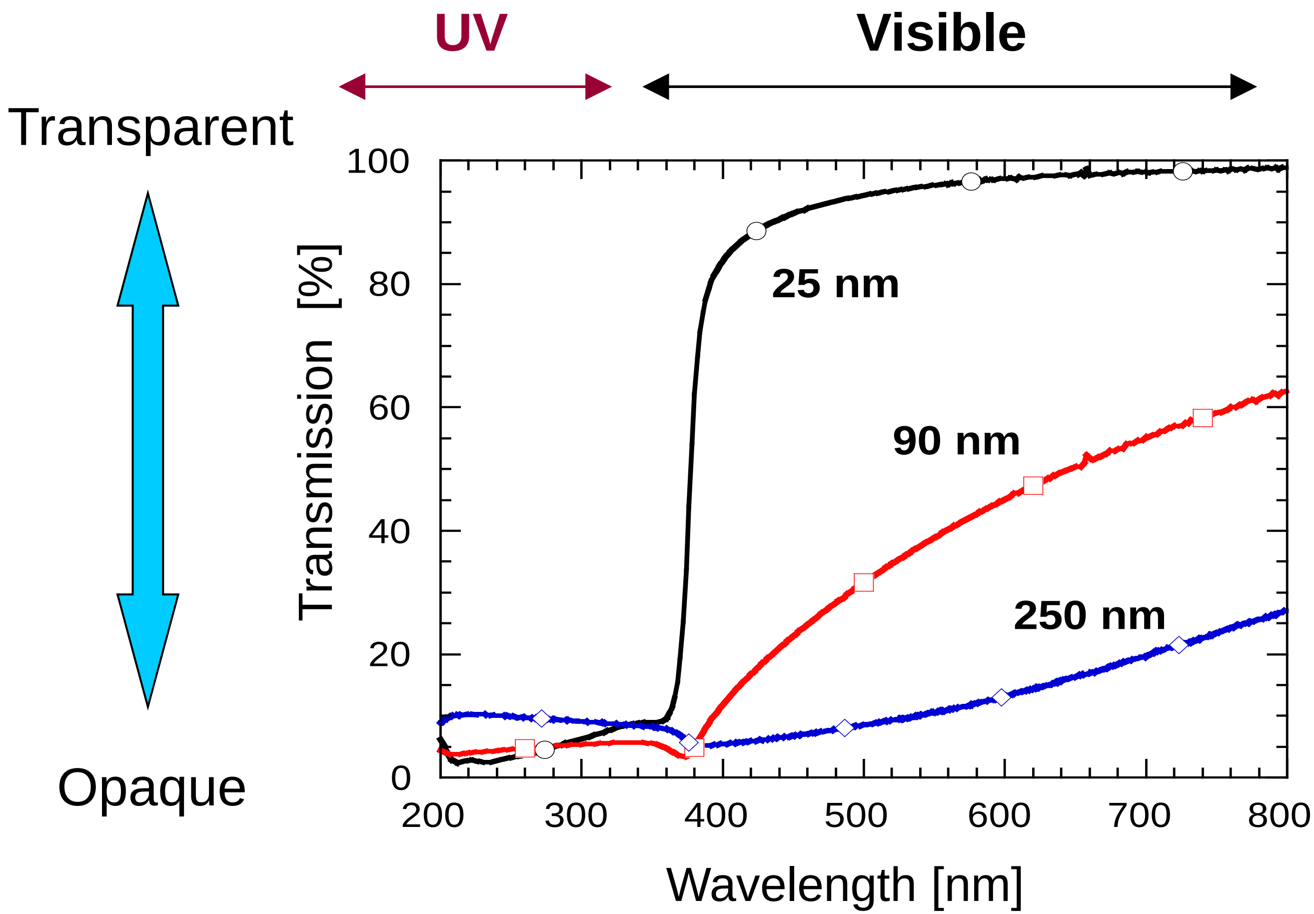
Established Applications of Nanoparticles
Example: Sunscreens



For many materials: ZnO, TiO_2 …

Established Applications of Nanoparticles

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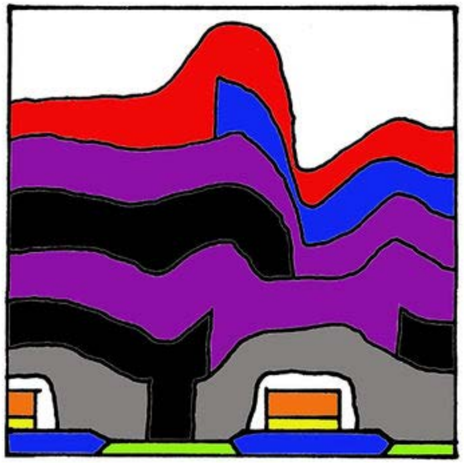
- Nanoscale adjuvants and APIs are used in the pharmaceutical industry

Important for precise dosing!

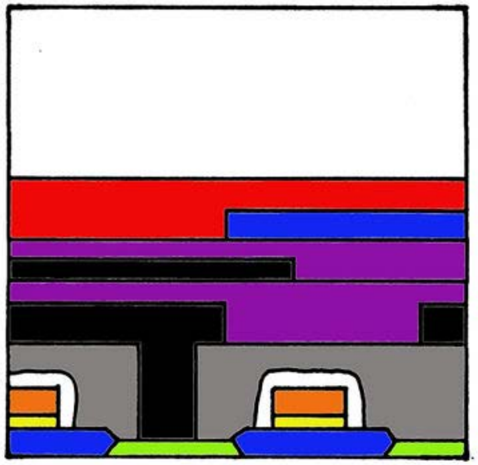
Established Applications of Nanoparticles

- Today, main application of hard ceramic nanoparticle dispersions (CeO_2, Al_2O_3): CMP (Chemical-Mechanical Polishing/Planarization)

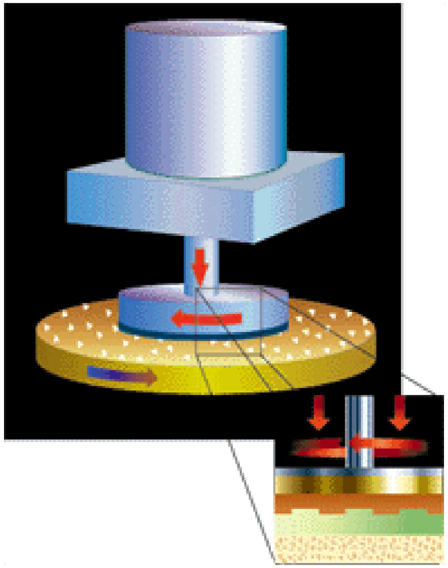
Circuit fabrication by lithography requires perfectly flat substrates to prevent shadow effects – roughness at 10^{-1} nm scale can only be achieved by use of nanoparticle dispersions in combination with chemical etching treatment.



Conventional lithography without polishing



Lithography with CMP treatment



Novel Applications

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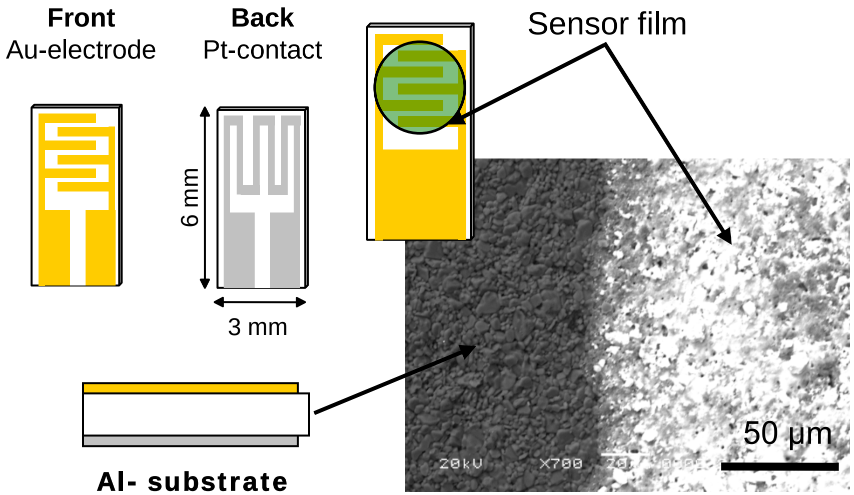
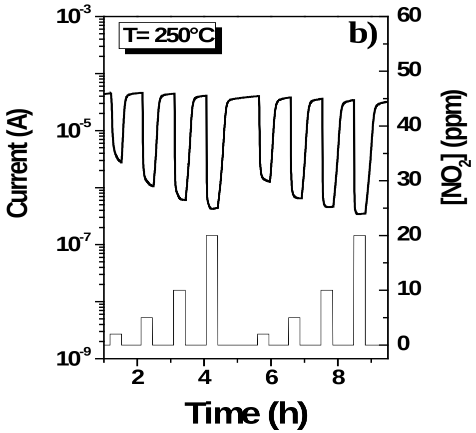
The use of nanomaterials for devices with new/improved features is heavily investigated and partially implemented in first applications.

Example: Sensors made from nanoparticle-based thin films

- very promising due to high sensitivity for low material quantities

SnO_2 for gas sensors





Conductivity of many oxides is given only through adsorption of certain gases → good gas sensors

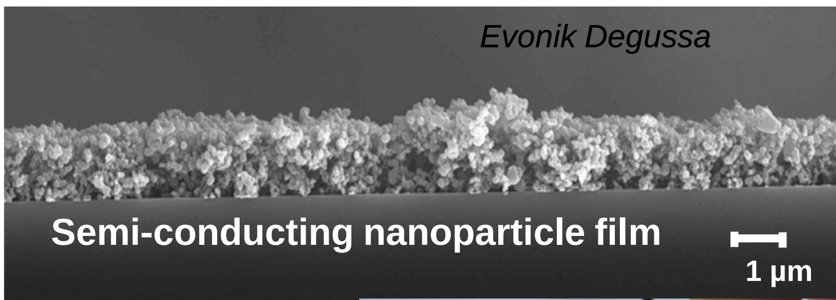
→ Nanostructuring provides high surfaces and therefore high sensitivities with the low required amount of material

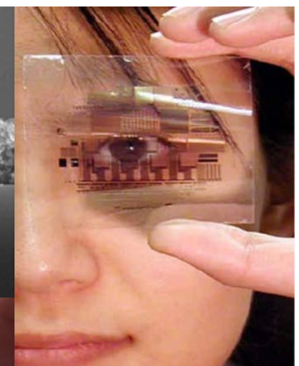
Novel Applications

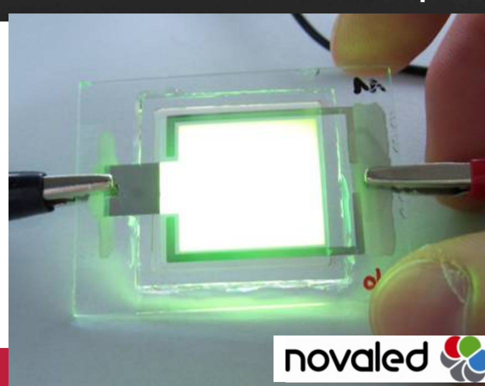
The use of nanomaterials for devices with new/improved features is heavily investigated and partially implemented in first applications.

Example: Printable Electronics

- more and more functional components (TCO layers, resistors, capacitors) will be printable with decreasing layer thickness / feature size due to tailored nanoparticle inks







- Flexible electronic devices
- (Semi-) transparent electronics
- Ubiquitous electronics
- New integrated functionalities (e.g. chemical sensor, defined surface chemistry)

Nokia Morph, Nokia 2008

Novel Applications

Example for a failed application of nanoparticles in catalysis:

e.g. Oxonica (GB): **Envirox™ Fuel Additive**

CeO_2 nanoparticles were promoted as fuel additives and added into diesel fuels in low amounts – they were shown to act catalytically in the engine during the fuel combustion

+ Efficiency

– Harmful emissions

about 10% fuel saving reported

→ But the release of the nanoparticles is problematic. Nevertheless, it was already used in field tests in communal buses, -vehicles, etc. in UK & Hong Kong

→ Did not reach large-scale application due to low support from official agencies – Oxonica discontinued this business

Novel Applications

Nanocomposites / hybrid materials:

- Rising field with established and many prospective applications

Improvement of polymeric materials:

- Mechanical properties (strength, stiffness)
- Thermal characteristics
- Chemical stability
- Electrical / electrochemical functionality
- Gas impermeability, low flammability, ...

Novel Applications

iPAT Institut für Partikeltechnik

Especially in the form of **coatings**:

Abrasion resistant coatings

Scratch-resistant coatings

Antistatic, anti-fingerprint coatings

UV protective coatings

Thermal conductive coatings

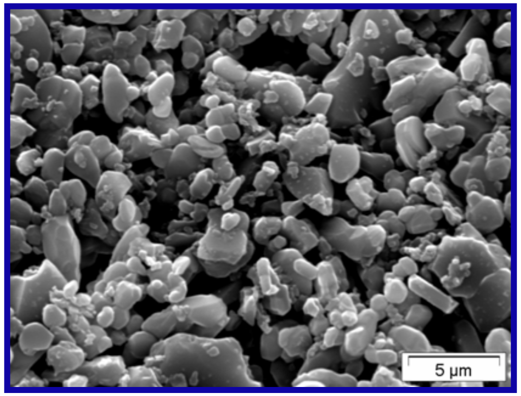
Self-cleaning coatings

→ **Nanocomposite thin films**

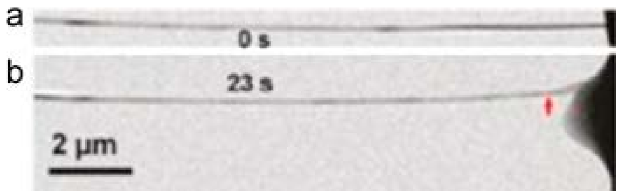
Novel Applications

“Hidden nano-applications” – especially in the energy sector

- Examples in batteries: SEPARION® separator contains ceramic nanoparticles



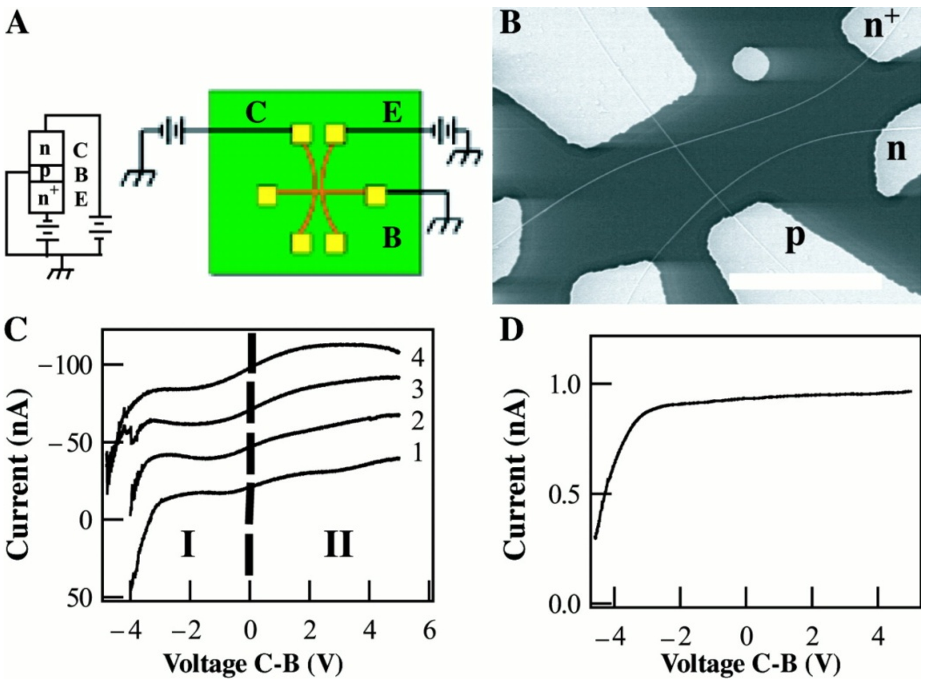
- Active cathode / anode materials: increasingly nanomaterials (nano-Si) or nanostructures are utilized

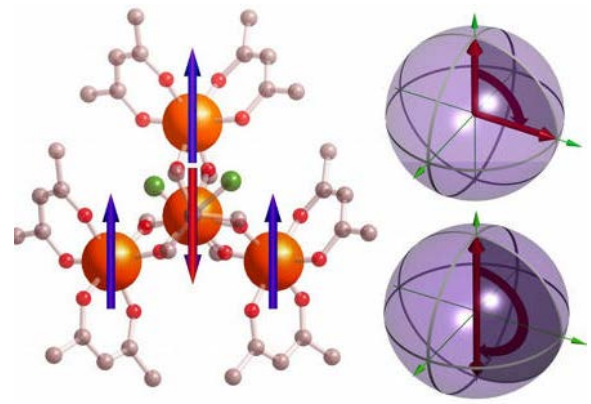


X.H. Liu et al., *Nano Lett.* 11 (**2011**), 2251–2258

Nanostructures: Nanoelectronics

"Real" nanoelectronics: use of single nanomaterials
with defined orientation
→ further size reduction of electronics





Molecular computing (top); Transistors made of carbon nanotubes (left)

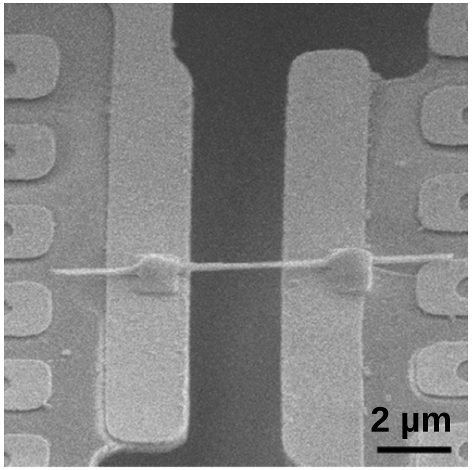
Soon, entire circuits made of nanomaterials?

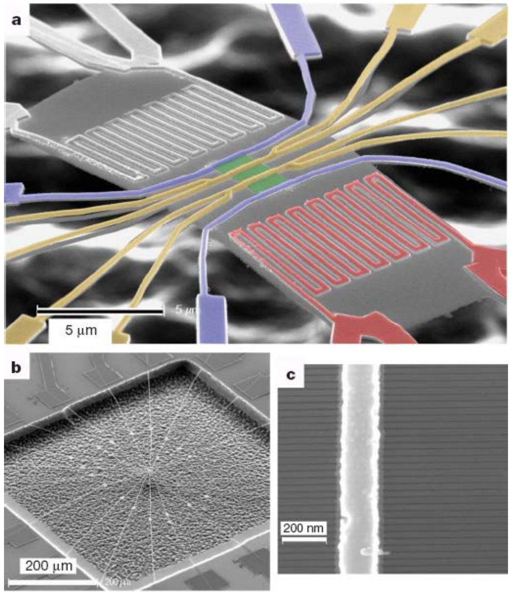
Problem: coupling to the macroscopic world, mass fabrication

Nanostructures: Nanoelectronics

- New characteristics of nanomaterials:

  E. g.: Thermoelectric activity of Si nanowires (normal Si shows no thermoelectric effect, due to good heat conductivity)





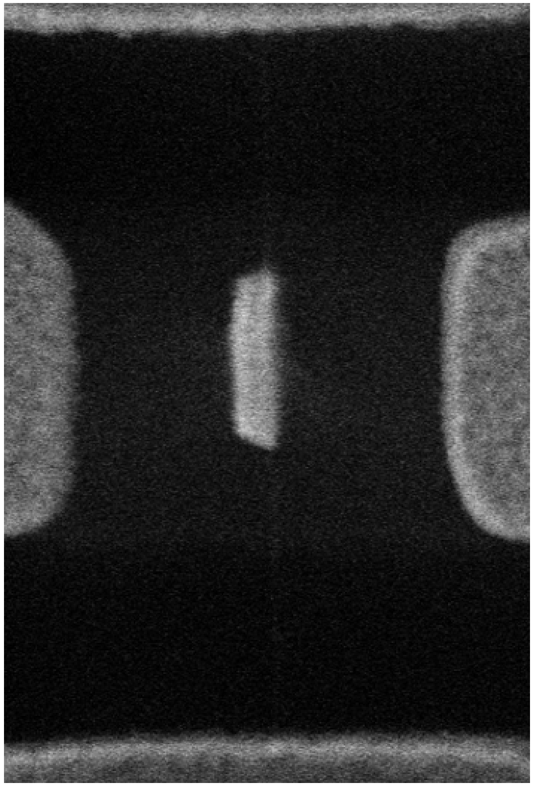
Will thermoelectronics soon be cheap and widely available?

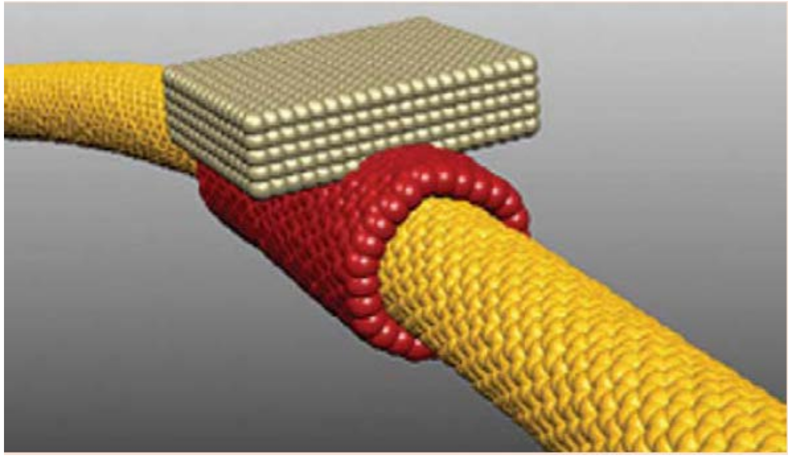
Use of exhaust heat in power stations (currently only 30-40% efficiency); power generation from processor heat in laptops? (Nature 2008)

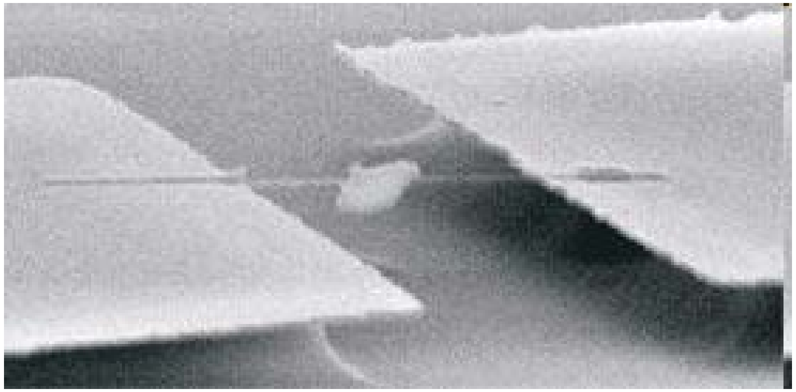
Nanostructures: Nanomachines

Nanomotors: NEMS

Nano-electromechanical systems
Nanomotors: 500 nm-Skala realized





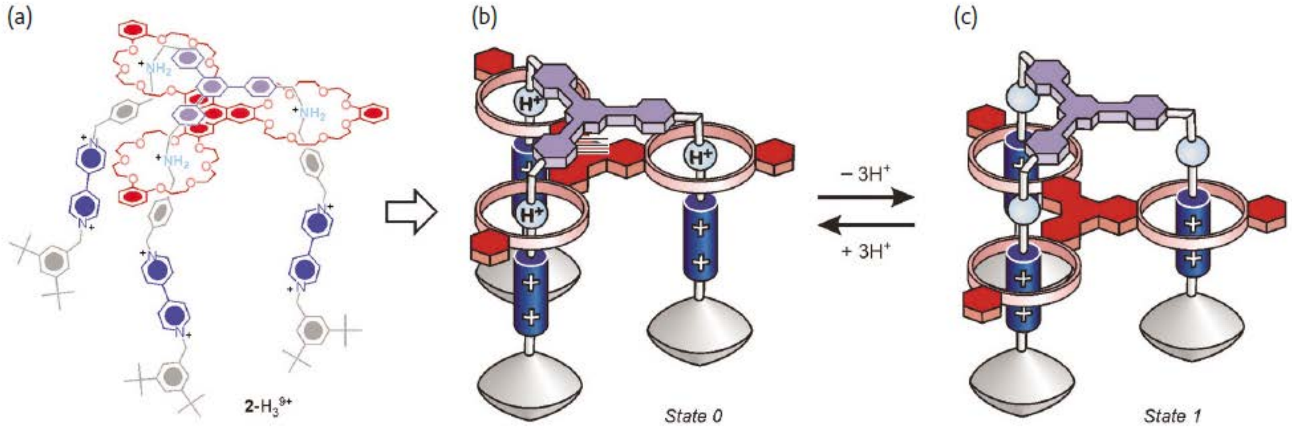


Au-nanoplatelet bound to multiwalled CNTs

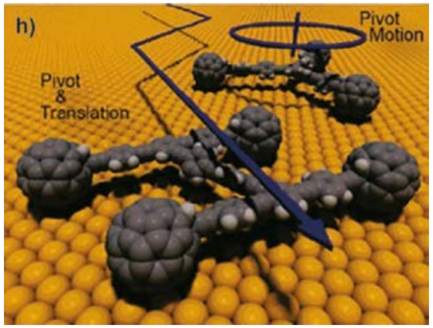
Barreiro et al., Science 2008

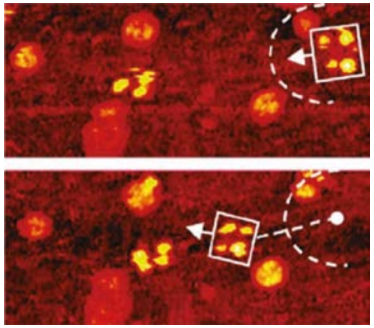
Nanostructures: Nanomachines

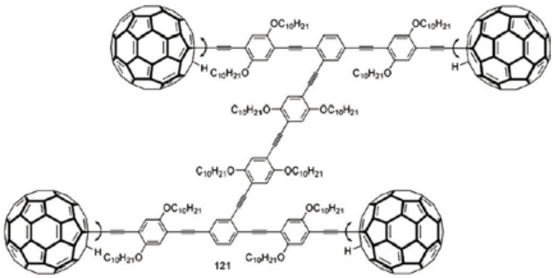
Molecular motors – Molecule as active machine elements



Balzani et al., Nano Today 2007







Shiray et al., Nano Lett. 2005, 5, 2330

Future Development

What the future may bring…

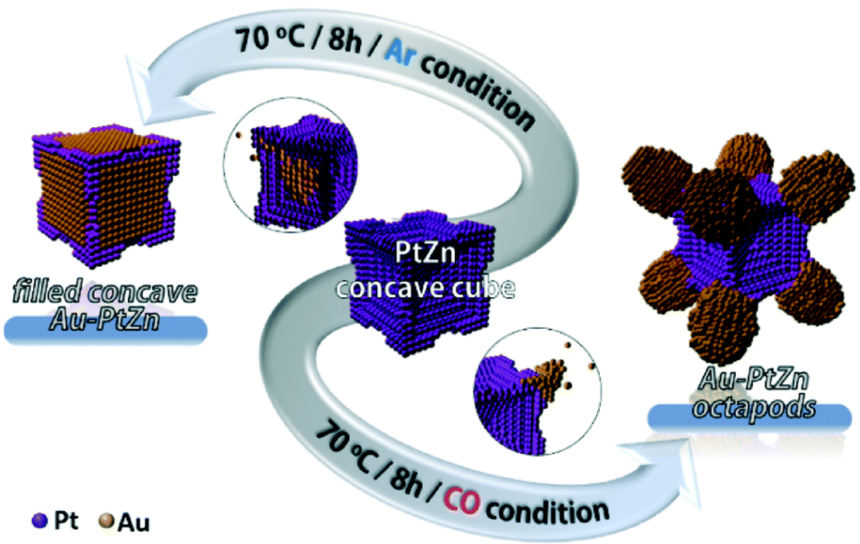
Expectations by Delphi panel, NanoRoadMap project:

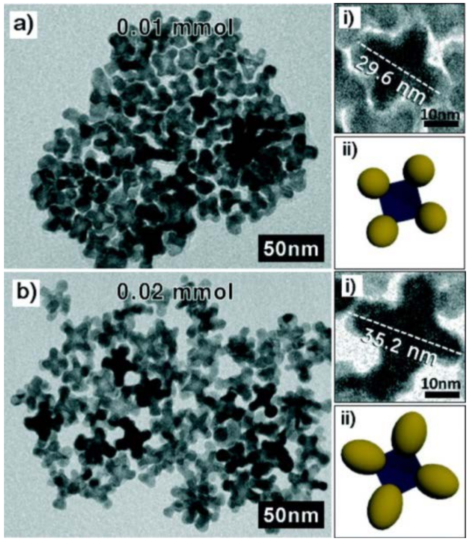
- Manufacture of small nanoparticles with extremely precise size and crystal orientation
- Self-assembly of complex hybrid inorganic nanoparticles / organic materials with novel properties
- Design of novel bulk materials through computer modelling of nanocomposite elements
- Direct biological control / treatment through intracellular delivery of interference RNA
- Physical nanosensors based on precise control of nanomaterials/nanostructures

Willems & van der Wildenberg, NanoRoadMap report, 2005.

Optimization of nanoparticles e. g. for catalytic applications

Nanoparticles increase in complexity:





Example: Selective growth of a second metal (Au) on the surface of nanoparticles of a metal alloy (PtZn) – Goal: optimum nanoparticles for catalytic applications

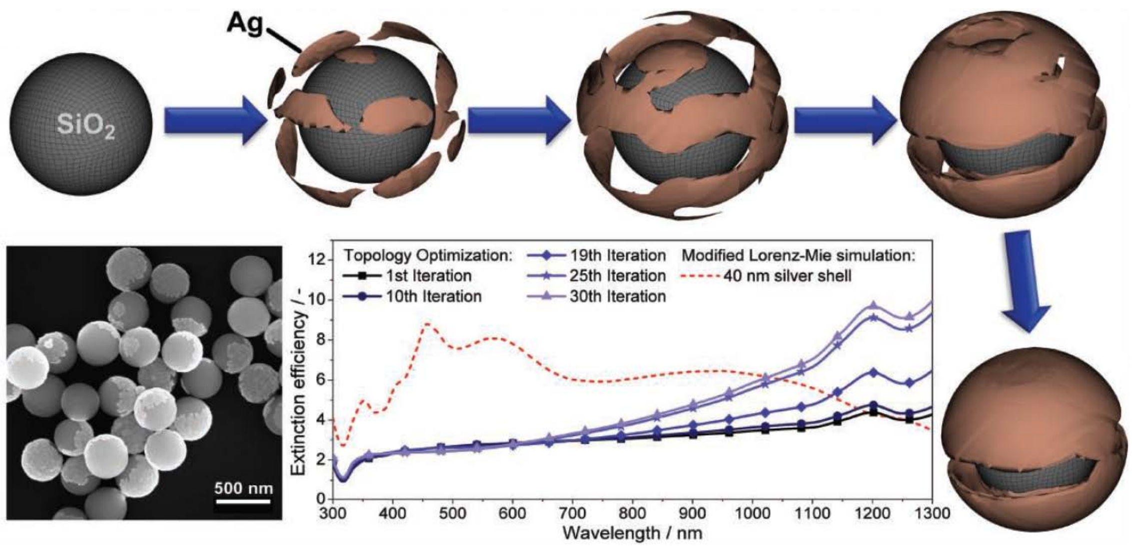
K.W. Lee et al., *CrystEngComm* **2015**, 17, 6838-6842.

Future Developments

Example for the complexity of current nanoparticle systems:

In the future, the targeted design and engineering of nanoparticles will become more and more important

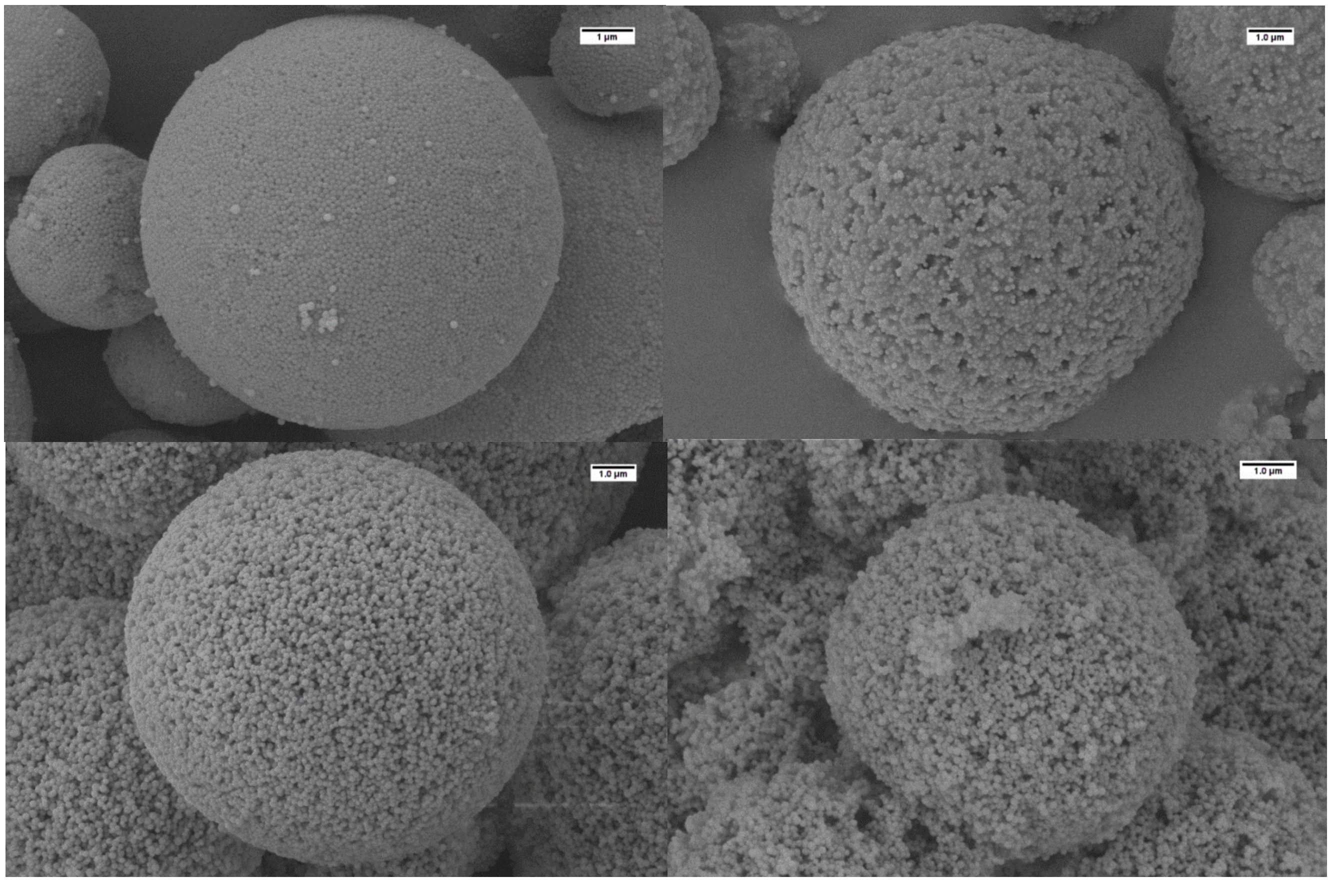
- Design of nanoparticles with ideal properties



Example: Design of SiO_2@Ag core-shell nanoparticles with optimized absorption in the VIS- und IR-ranges

Klupp Taylor et al., *Adv. Mater.* **2011**, 23, 2554

Rational and defined fabrication of porous aggregate with tailored properties

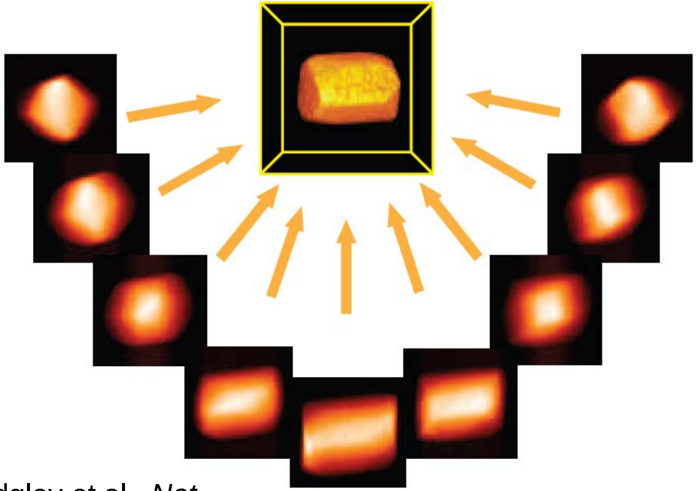


S. Zellmer, G. Garnweitner, T. Breinlinger, T. Kraft, C. Schilde, *ACS Nano* **2015**, 9, 10749.

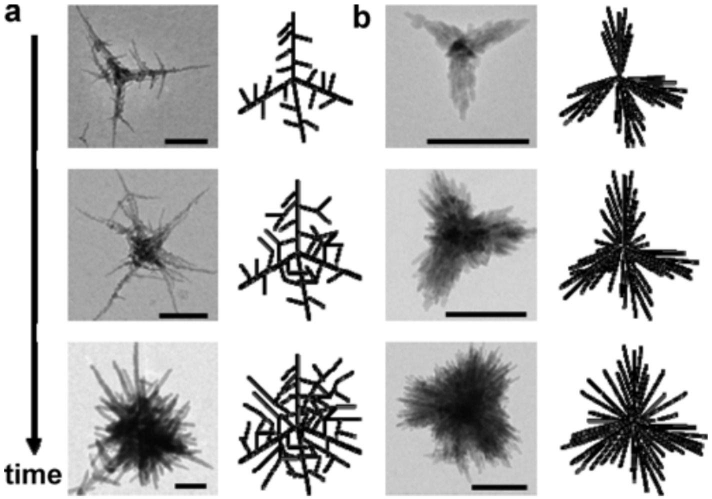
Future Developments

… characterization of these structures already is a big problem and will be an even greater challenge in the future!

- In particular the 3D-charakterization of complex structures is a big problem



Midgley et al., *Nat. Mater.* **2009**, 8, 271



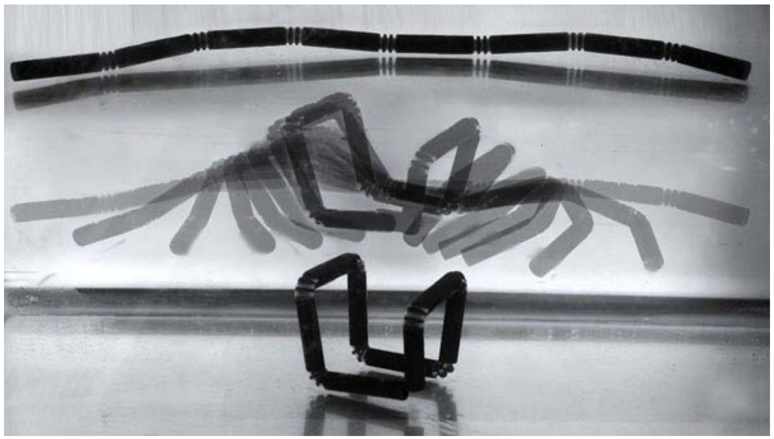
Kanaras et al., *Nano Lett.* **2005**, 2164;

Xu et al., *Cryst.Eng. Comm.* **2014**

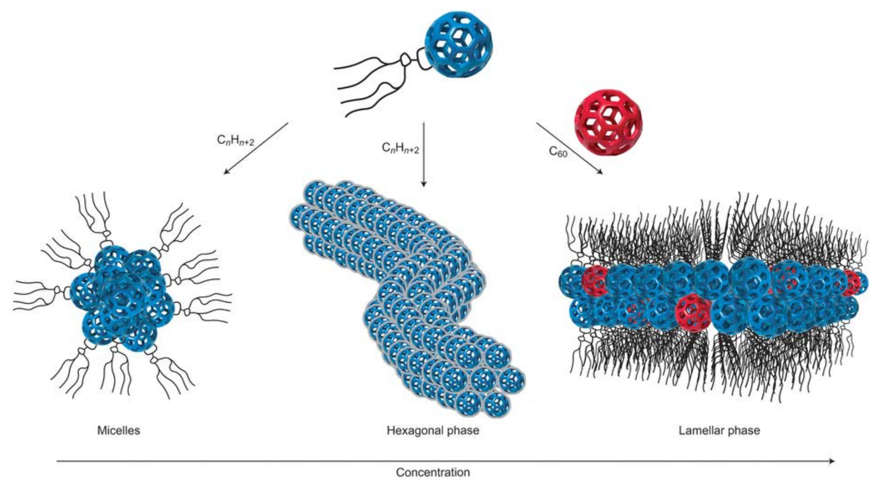
Hardly any universal standards are available – different methods of analysis need to be combined

→ problematic for industrial application!

Production concepts of the future: Self-assembly instead of top-down fabrication



Macroscale: Folding of individual intelligent segments
MIT SelfAssembly Lab, 2015



Nanoscale: Self-assembly of fullerene building blocks
Schenning et al., Nature Chem. 2014, 6, 658

Summary

- **Diversity of nanoparticles and nanomaterials**
  - Many different geometries of nanomaterials are possible
  - Variety of materials is utilized as nanoparticles

- **Properties of nanomaterials**
  - Surface effect leads to different physical properties
  - Fascinating optical, electronic and magnetic properties

- **Application of nanomaterials**
  - Different generations of nanotechnology
  - Many established applications in consumer products
  - Novel applications in electronics, nanomachines, functional composites, …
  - Future trends