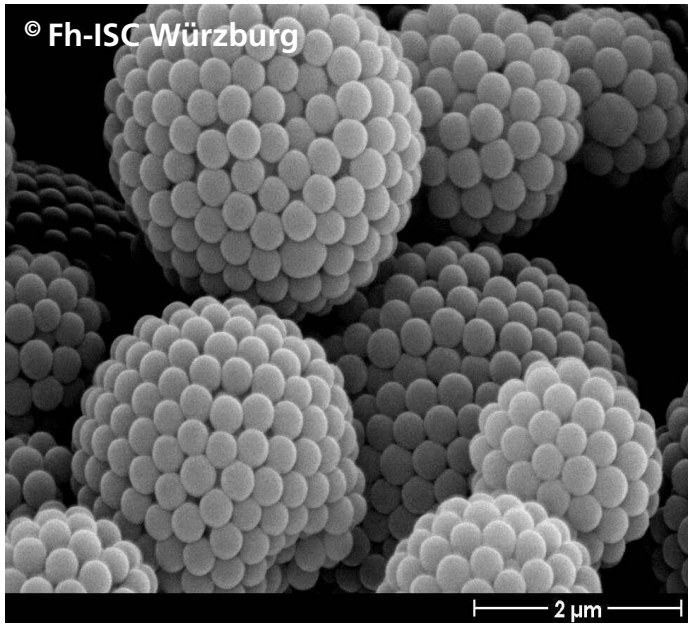
# Status of the industrial use of nanomaterials

## 1. Joint Symposium on Nanotechnology
## 05 and 06 March 2015 - Berlin

**Dr. Karl-Heinz Haas - FhI für Silicatforschung, Würzburg**

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BfR
Bundesinstitut für Risikobewertung





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# Short and simple: What is nanotechnology ?

## ISO/TS 80004-1 core terms

not nano
„by accident“

really small

„The purposeful engineering
of matter at scales of less than 100 nanometers (nm)
to achieve size-dependent properties and functions“

not just small:
small and different

source: \Lux research\





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# Technical Specification ISO/TS 80004-1 (Core terms)

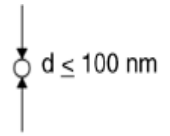
**nanoscale: size range from approximately 1 nm to 100 nm**

**nanotechnology: application of scientific knowledge to manipulate/control matter in the nanoscale in order to make use of size- and structure-dependent properties and phenomena, as distinct from those associated with individual atoms or molecules or with bulk materials. Manipulation and control includes material synthesis.**

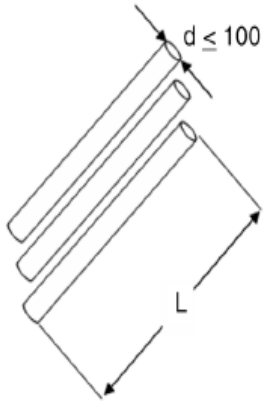
**nanomaterial: material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoregime.**

# Nanoobjects

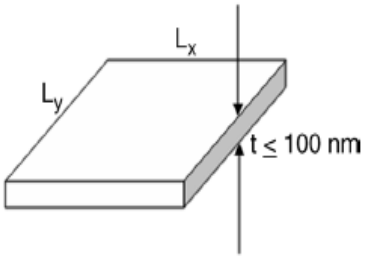
**0D:**
**All dimensions (x,y,z) at nano scale**
**example: Nanoparticle**



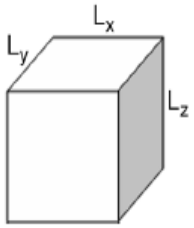

**1D:**
**Two dimensions (x,y) at nano scale;**
**L not**
**example: nanorod/-tube**




**2D:**
**One dimension (t) at nano scale;**
**two others not**
**example: nanofilm/ platelet**




**3D:**
**all external dimensions not nano scale**
**example: nanocomposite**




**Decreasing probability for crossing barriers**

**Decreasing risks**







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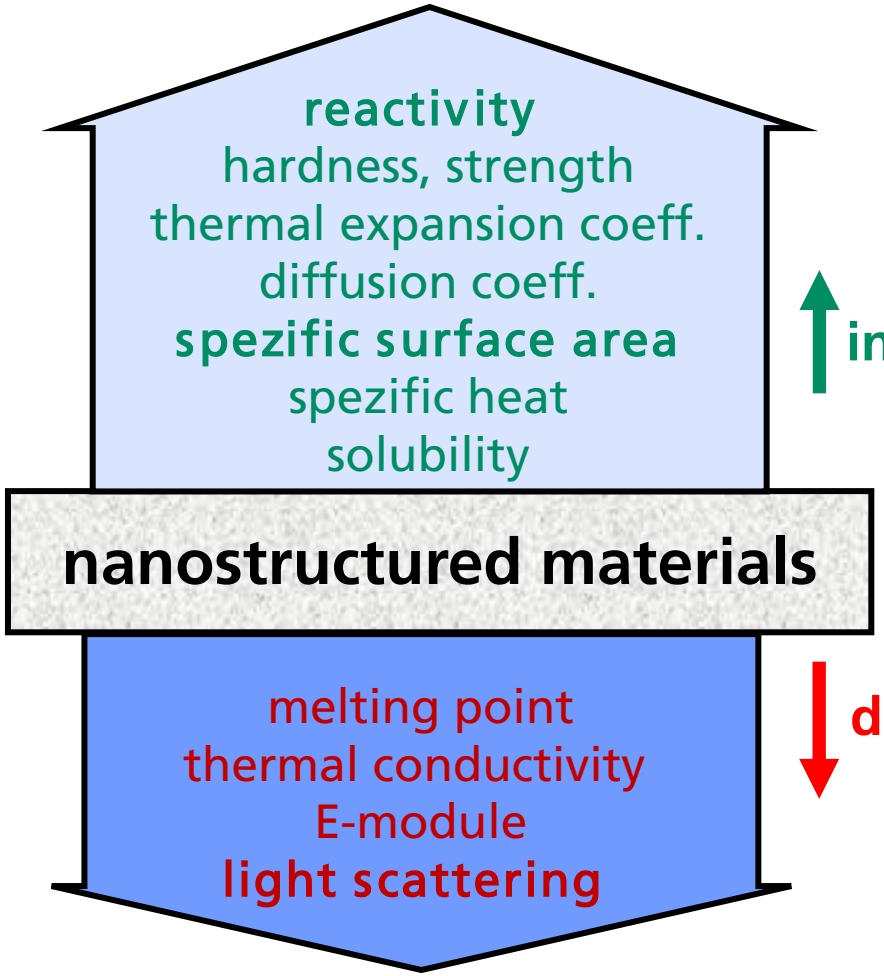
# Nanomaterials: what makes them so interesting ?




increasing

decreasing

**electronic, optical and magnetic properties are size dependent**





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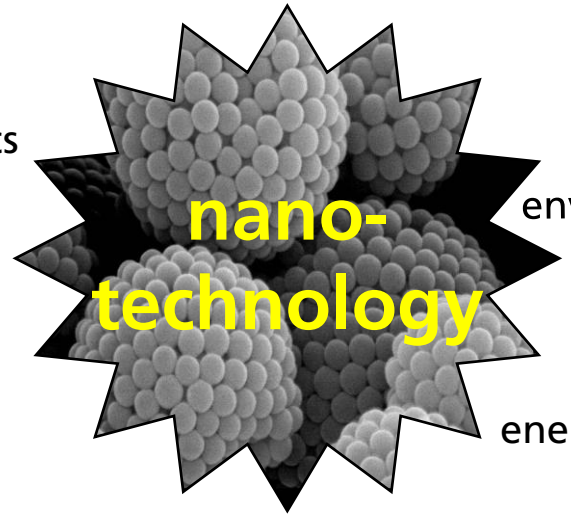
# Nanotechnology: world market around 150-200 Bill. €




**chemistry**
drug screening
synthesis/catalysts
sensors
process control

**medicine/health**
diagnostics
therapy
controlled drug release
tissue engineering

**consumer**
cosmetics
easy-to-clean surfaces
antimicrobial textiles
food packaging

**electronics I&C printing**
electronic paper
displays (OLED, FED)
polymer electronics
memory (GMR)
sensors
biochips
passivation

**environment**
sewage water treatment
photocatalysis
monitoring

**energy**
batteries, supercaps
fuel cells, solar cells
thermal power units
IR-reflection/glazing

**optics**
ophthalmics
photonics
wave guides
optical switches
optical memory
lighting

**automotive**
transparent hardcoats
weight saving (foams, polymers)
glazing
corrosion protection
sensors, tires
catalysis (combustion, exhaust gas)
fuel cells, supercaps
tribology

**construction**
clean surfaces
switchable glazing
heat insulators
corrosion protection

OLED: Organic Light Diode
FED: Field Emission Display
GMR: Giant Magnetic Resistance



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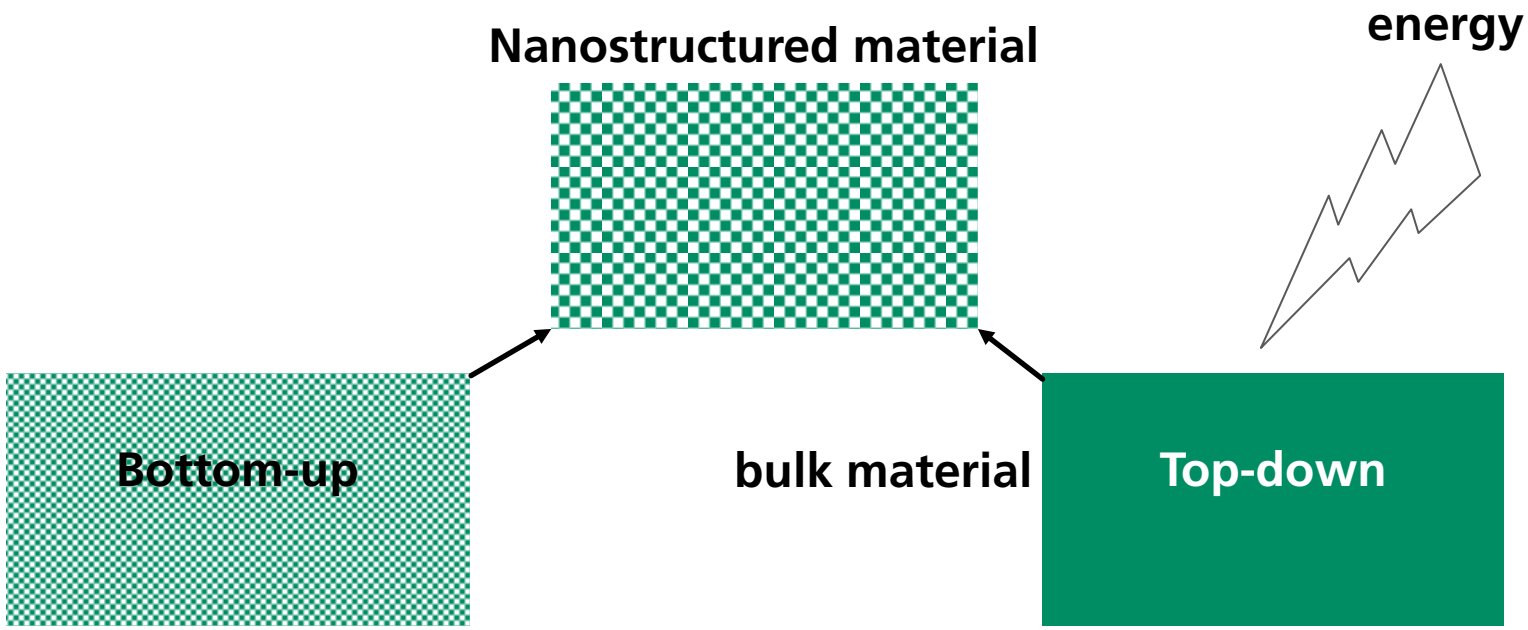
# Nanomaterials: Synthesis and structure formation




**Buildung from molecular units**

- powders, sols, colloids
- chemical synthesis

**Make big things smaller: classifying, selecting**

- milling
- lithography/etching





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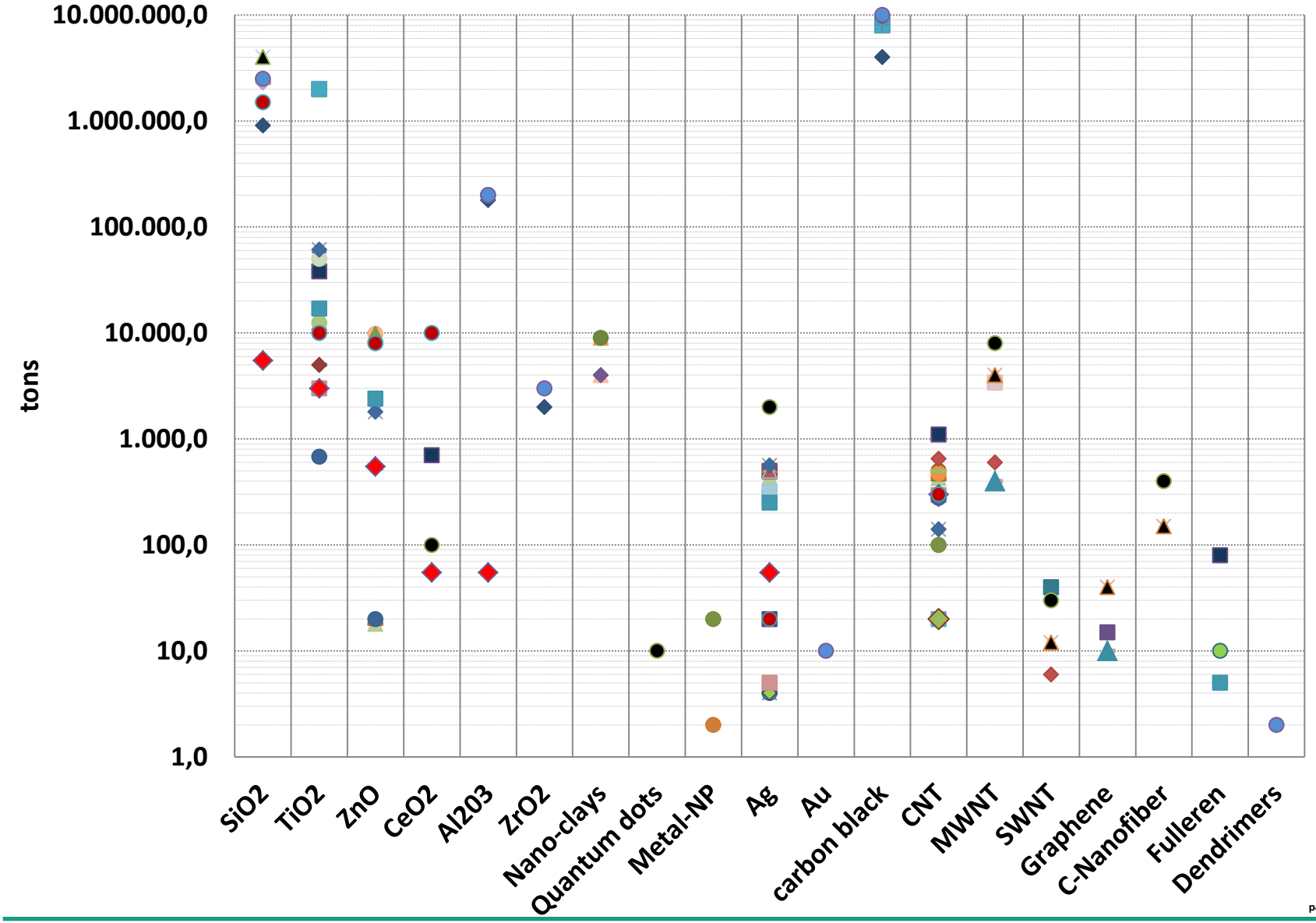
# Relevant production methods for nanoobjects

- milling
- electrospinning for nanofibres
- gas phase processes
  - evaporation
  - flame synthesis ⏩ pyrogenic silica
  - CVD
  - plasma
- liquid phase processing:
  - precipitation
  - solvo-/hydrothermal
  - sol-gel
  - ...

http://www.wacker.com/cms/media/publications/downloads/6174_EN.pdf

# production of nanomaterials (up to 2010)

Source: Haas 2013







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| Nanomaterial | Product group | % of total use |
|---|---|---|
| Nano-$TiO_2$ | Cosmetics (incl. sunscreens) | 70–80 |
| | Coatings & cleaning agents | <20 |
| | Plastics | <20 |
| | Paints | 10–30 |
| | Cement | 1 |
| | Others | <10 |
| Nano-ZnO | Cosmetics (incl. sunscreens) | 70 |
| | Paints | 30 |
| $CeO_x$ | Chemical mechanical planarization | 45–80 |
| | Fuel catalyst | 1–50 |
| | UV-coatings, paints | 5–10 |
| CNTs | Composites & polymer additives | 20 |
| | Materials | 80 |
| | Composites | 50 |
| | Batteries | 50 |
| Fullerenes | R&D | 80 |
| Nano-Ag | Paints, coatings & cleaning agents | 10–30 |
| | Textiles | 30–50 |
| | Consumer electronics & conductivity | 10–20 |
| | Cosmetics | 20 |
| | Medtech | 20 |
| | Anti-microbial coatings | 80–100 |
| Quantum dots | Light conversion for LED/OLED | 90 |
| | Lab use for imaging | 10 |

## Questionnaire: Usage of nanomaterials (Piccino et al 2012)

Each line represents different answers and therefore the percentages do not sum up to 100 %



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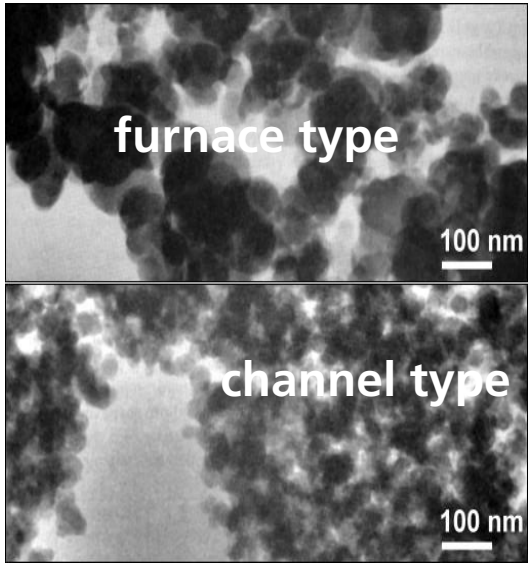
# Classical nanofillers

- **carbon black ⏩ produced by incomplete combustion of heavy petroleum products**




"Russvrp". Lizenziert unter CC BY-SA 2.5 über Wikimedia Commons - http://commons.wikimedia.org/wiki/File:Russvrp.jpg#mediaviewer/File:Russvrp.jpg

- **silica sols (e. g. Ludox) ⏩**
- **pyrogenic silica – hydrophilic/hydrophobic (e. g. Aerosil® - since 1943)**

https://grace.com/general-industrial/en-us/Documents/ludox_br_E_2012_f120504_web.pdf





source: Wikipedia

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# Classical nanofiller: Carbon black

http://en.wikipedia.org/wiki/Motorcycle_tyre

- nearly 70 % for tire industry ⏩
- of the remaining 30%
  - 70% as pigment black and of this
    - 40 % for the plastics industry and 40 % for printing inks

# Uses of classical nanofiller silica

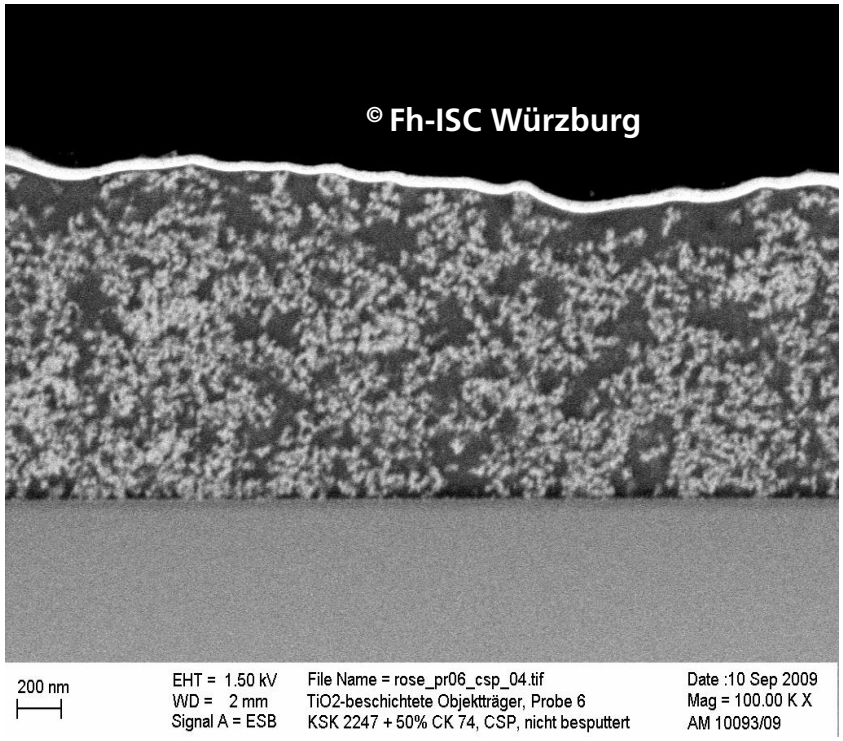
- **fumed/pyrogenic silica:**
  - **reinforcing filler**
  - **thickening/thixotropy**
  - **antisettling agent**
  - **dispersant**
  - **free flow agent**

⏩ https://www.uni-due.de/physik/fbphysik/Schuelerlabor/Skripte/freestyleph_winterer.pdf

https://www.aerosil.com/product/aerosil/Documents/TI-1279-Successful-use-of-AEROSIL-in-liquid-systems-EN.pdf

- **precipitated silica:**
  - **paper industry**
  - **CMP slurries**
  - **coatings, paints**
  - **metal casting**
  - **catalysis...**

# Example for the use of $TiO_2$-nanoparticles: Photocatalysis





**Transparent hybrid polymer coating with $TiO_2$ nanoparticles showing photocatalytic activity**

Source: Fraunhofer-ISC





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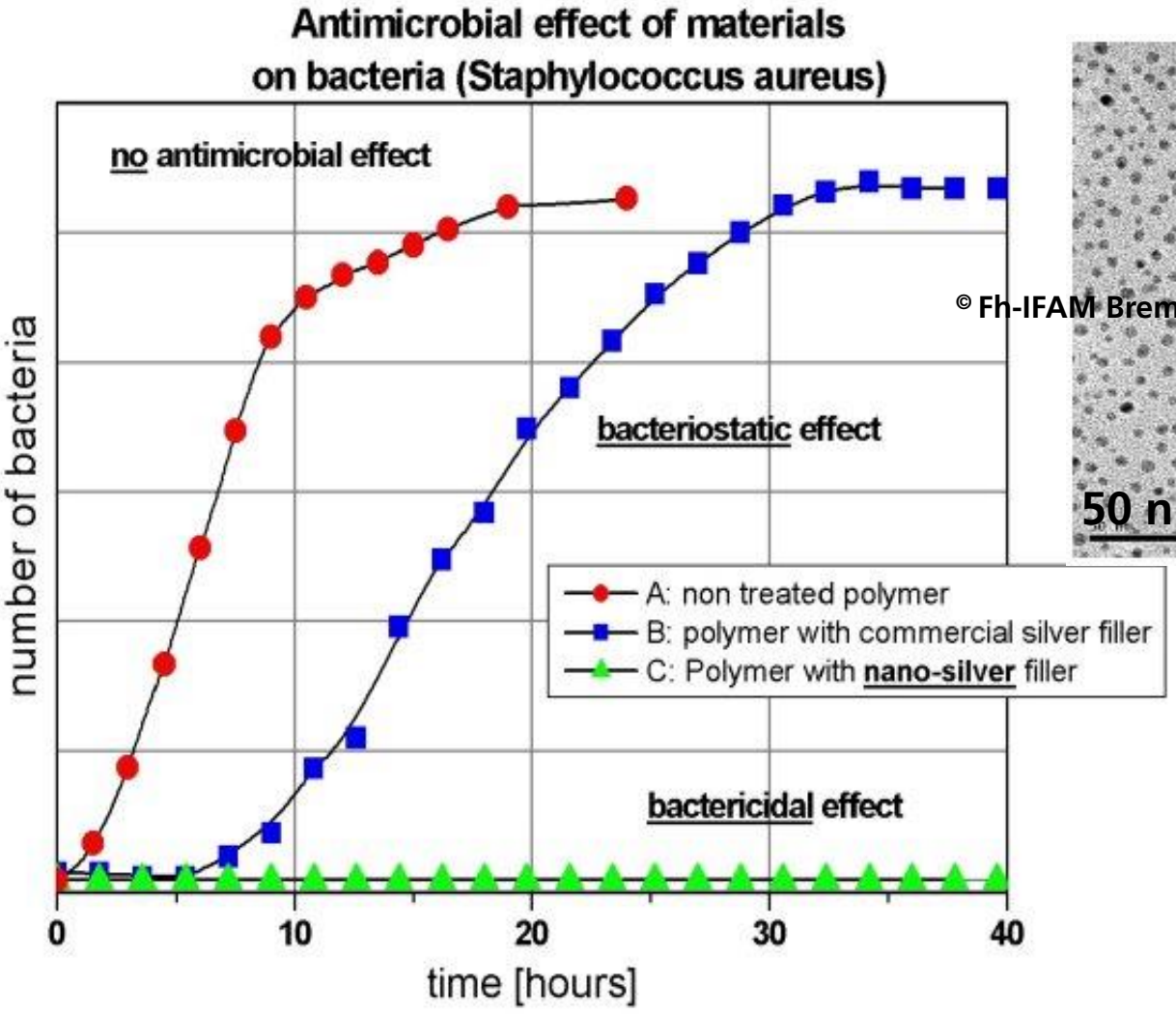
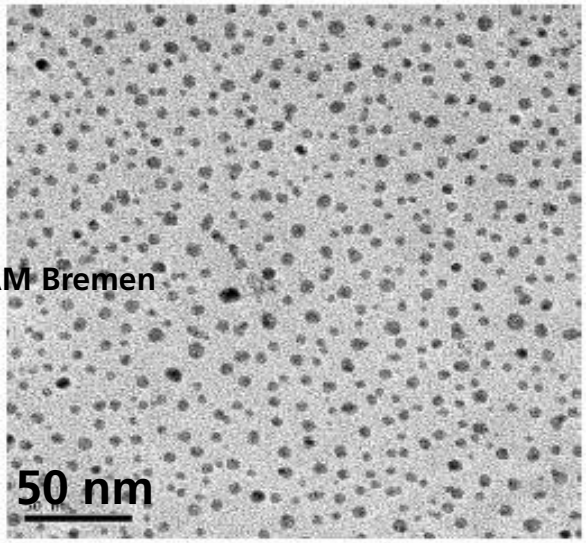
# Example for the use of Ag-Nanoparticles: Antimicrobial



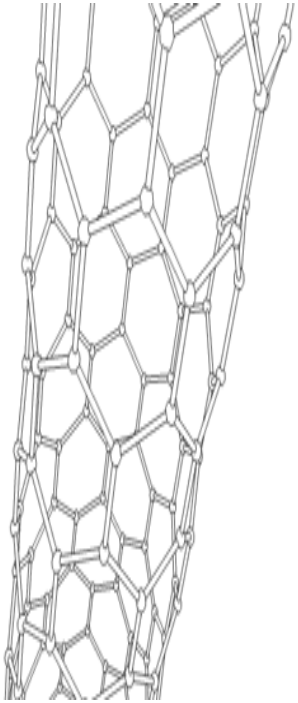



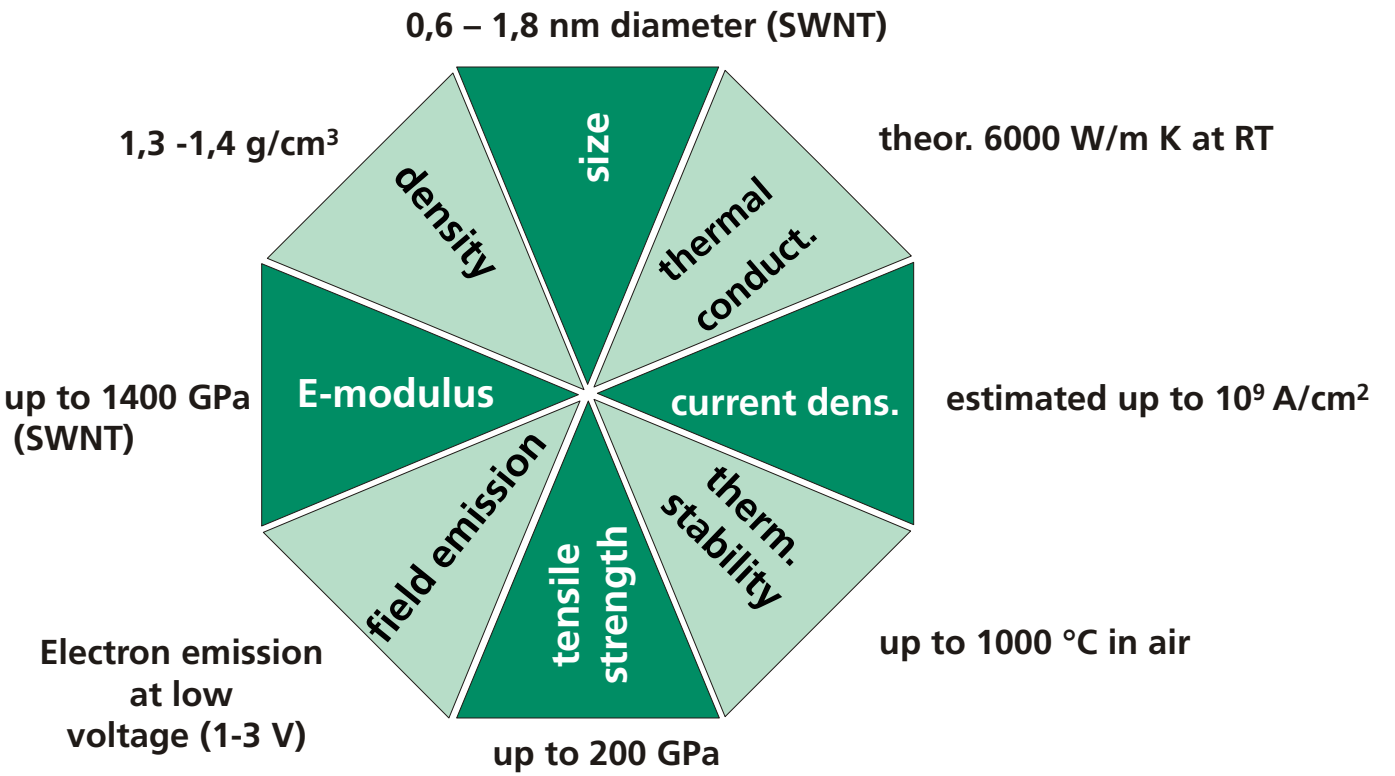

© Fh-IFAM Bremen

**antimicrobial surfaces: composition of polymer matrix determines release of $Ag^+$**
***WO 2005 /048708 A1***

Source: Fraunhofer-IFAM Bremen

# Carbon nanotubes: SWNT and MWNT






http://upload.wikimedia.org/wikipedia/commons/7/76/Kohlenstoffnanoroehre_Animation.gif

according to Vohrer et al 2007





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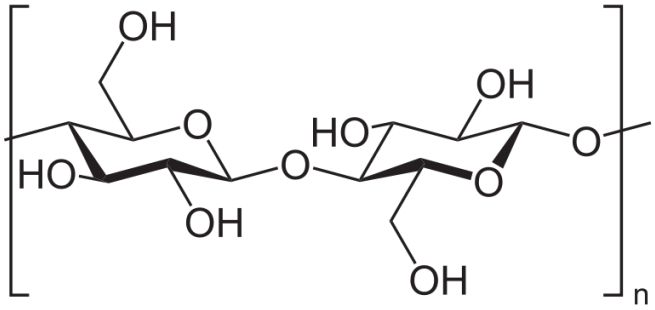
# Typical production methods for CNT

| method | types | purity | scalability | costs |
|---|---|---|---|---|
| Arc discharge | SWNT | post processing necessary | low | expensive |
| CVD (catalyst) | MWNT and SWNT | good | high | cost effective |
| Laser ablation | MWNT | high | low | expensive |
| | | | | |

# New nanomaterials

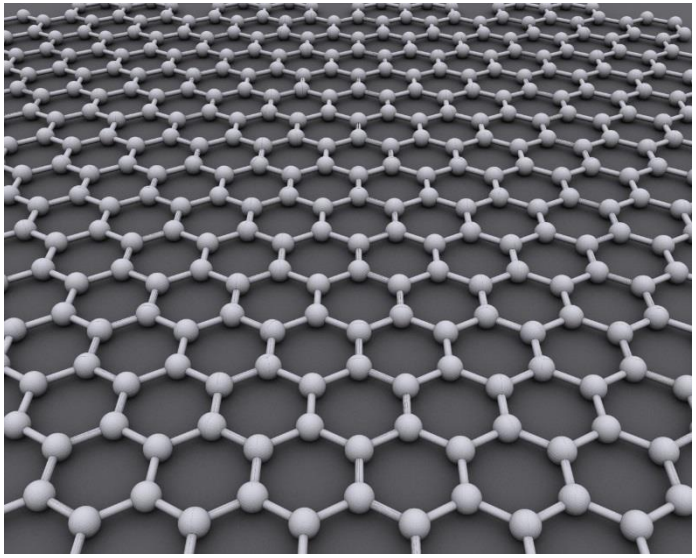
- **Nanocellulose:**

Source Wikipedia http://de.wikipedia.org/wiki/Cellulose




**intra- and intermolecular hydrogen bonding**

- **Graphene:**
  **2 dimensional carbon**



http://upload.wikimedia.org/wikipedia/commons/9/9e/Graphen.jpg





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# Nanocellulose production methods

**S. Rebouillat 2013**

- **Two steps:**
  - **Pretreatment of raw material to obtain individual cellulosic fibres**
  - **Fibrillation -> transformation of individual cellulose fibres into micro- and nanofibrils**

Cellulose nanomaterials from trees; www.tappinano.org/ppt/Nano-powerpoint.pptx

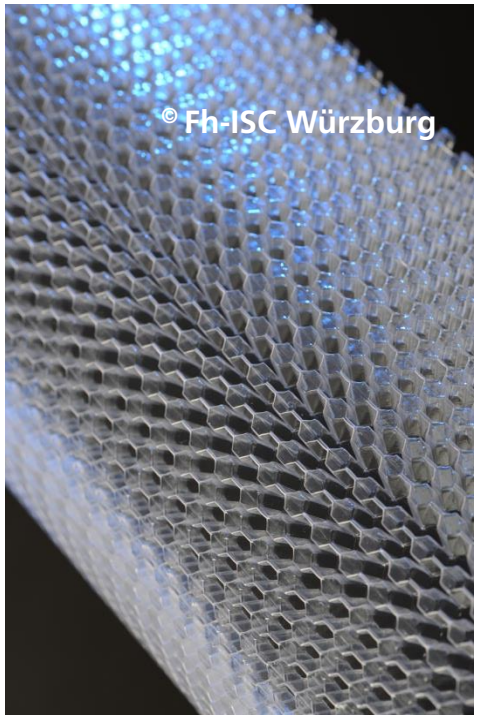
# Potential nanocellulose markets and applications

**(high-volume markets, worldwide, reasonable estimate) J. Cowie et al 2014**

| Selected markets/applications | Metric tons (thousend) |
|---|---|
| Packaging coatings | 5278 |
| Replacement plastic packaging | 4153 |
| Cement | 4130 |
| Automotive body | 3573 |
| Hygiene and adsorbents | 3241 |
| Textiles | 2543 |
| Paper filler | 2394 |
| Packaging filler | 2394 |
| Paper coatings | 2167 |
| Automotive interior | 587 |

# Example for nanocellulose as filler in coatings for light-weight structures

european project INCOM

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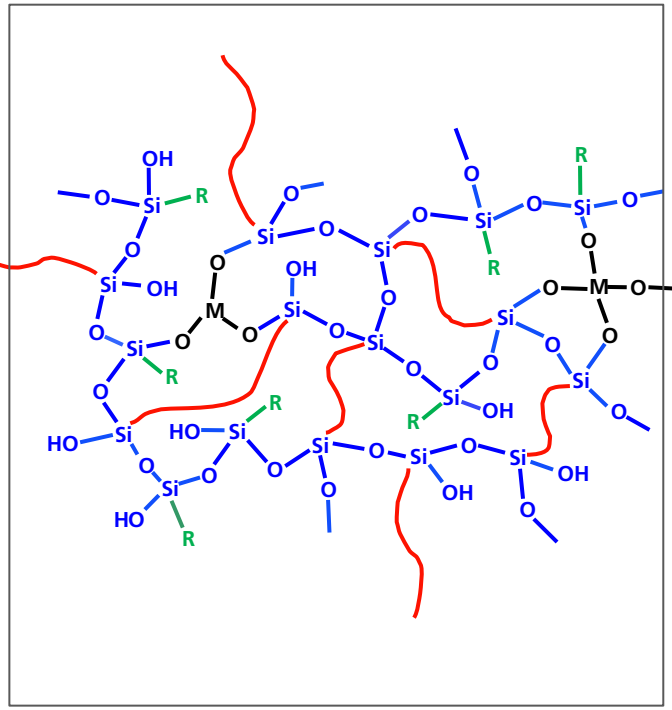

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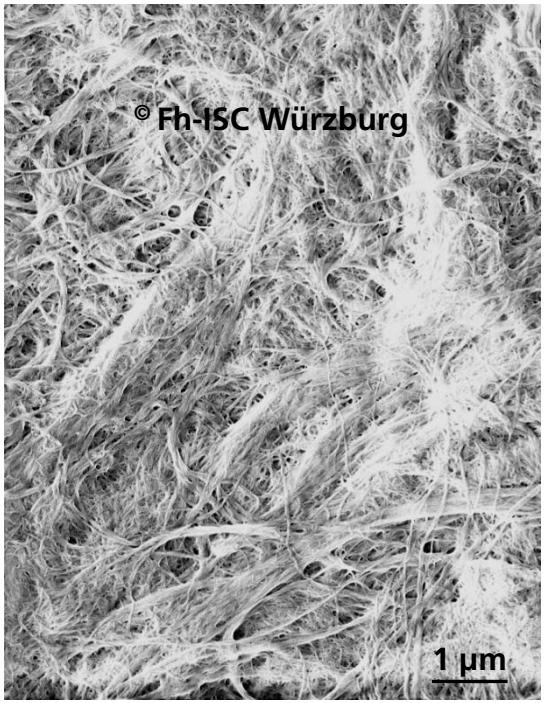


light weight structure | hybrid polymer matrix | nanocellulose

source: Fraunhofer ISC





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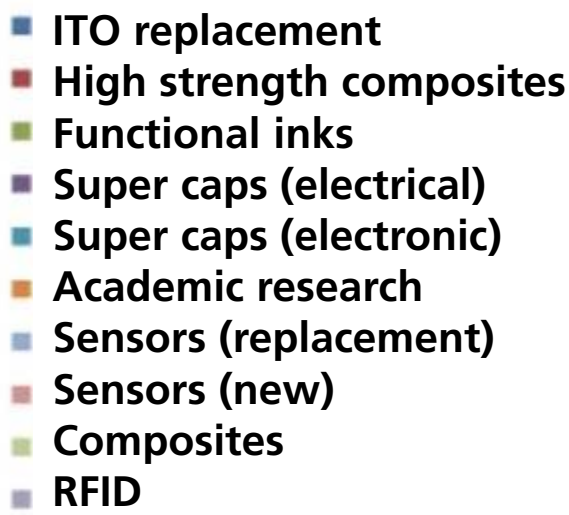
# Various synthesis methods for graphene

**(R. Garg et al 2014)**

| method | precursor | Electronic quality | Advantage | Disadvantage |
|---|---|---|---|---|
| Mechanical exfoliation | Graphite | high | inexpensive | poor yield, not scalable |
| Arc discharge | Graphite | high | doping possible (B, N) | not for pure graphene, not scalable |
| Wet chemical | Graphite | high | TCO, composites | Oxygen impurities, scalability unclear |
| CVD | Hydro-carbon | high | best method so far; scalability | film transfer complicated |
| Solvothermal | Ethanol | bad | cheap precursor, scalable | defects |
| Epitaxial growth | Ultrathin graphitic film | high | single and multilayer possible | complicated hight T-process, not scalable |

# Graphene: Application forecast up to 2018

http://www.idtechex.com/research/reports/graphene-markets-technologies-and-opportunities-2013-2018-000333.asp




IDTechEx, Graphene Analysis of Technology Markets and Players 2012 – 2018





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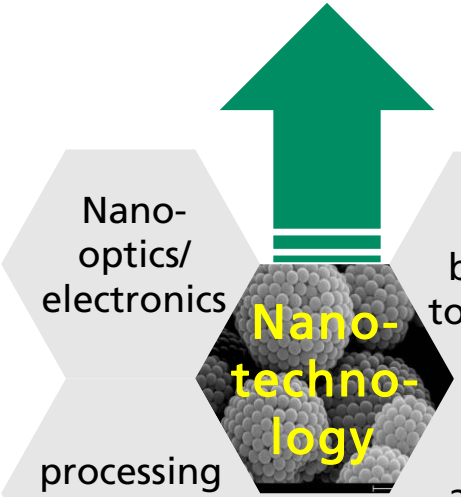
# Summary

- nanomaterials are interesting due to their size dependent properties, they are used in many industries and application areas
- classical nanomaterials cover more than 90 % of the market
- distinction between nanoobjects and nanostructured materials sometimes not easy due to agglomeration
- nanoobjects are often used as intermediate products e.g. for coatings
- new nanomaterials are slowly increasing in use
- new players: nanocellulose, graphene

# Fraunhofer Nanotechnology Alliance (19 Institutes)
# www.nano.fraunhofer.de

**New / improved products and processes**




IISB ISE ENAS EMFT

IGB ITEM

IAO IPA IFF ISI ILT

IKTS-MD IPA

IFAM ISC IKTS IWM IWS ICT IAP IVV





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