OPCW **Scientific Advisory Board**

Thirteenth Session
30 March – 1 April 2009

SAB-13/1
1 April 2009
Original: ENGLISH

REPORT OF THE THIRTEENTH SESSION OF THE SCIENTIFIC ADVISORY BOARD

1. AGENDA ITEM ONE – Opening of the session

The Scientific Advisory Board (SAB) met for its Thirteenth Session from 30 March to 1 April 2009 at the OPCW Headquarters in The Hague, the Netherlands. The session was opened by the Chairperson of the SAB, Philip Coleman of South Africa. Mahdi Balali-Mood of the Islamic Republic of Iran served as Vice-Chairperson. A list of participants appears as Annex 1 to this report.

2. AGENDA ITEM TWO – Adoption of the agenda

The SAB adopted the following agenda for its Thirteenth Session:

1. Opening of the session
2. Adoption of the agenda
3. Welcome address by the Director-General
4. Overview of developments at the OPCW since the last session of the Scientific Advisory Board
5. Introduction to nanoscience:
    (a) Presentation on the basics of nanotechnology (definitions, physico-chemical properties, and applications)
    (b) Presentation on the toxicology of nanomaterials
    (c) Discussion
    (d) Scientific Advisory Board recommendations
6. Scheduled chemicals, including ricin and saxitoxin:
    (a) Discussion
    (b) Scientific Advisory Board recommendations

7. Review of operational requirements and technical specifications for inspection equipment:

   (a) Discussion

   (b) Scientific Advisory Board recommendations

8. Consideration of the report of the meeting of governmental experts

9. Future work of the Scientific Advisory Board:

   (a) Agenda for the Fourteenth Session of the Scientific Advisory Board

10. Any other business

11. Adoption of the report

12. Closure of the session

3. AGENDA ITEM THREE – Welcome address by the Director-General

3.1 The Director-General expressed his deep appreciation to Rolando Spanevello of Argentina, Detlef Männig of Germany, Bjørn-Arne Johnsen of Norway, Young-chul Lee of the Republic of Korea, Miguel A. Sierra of Spain, and Robert Gibson of the United States of America—SAB members completing their second term on the Board—for their dedicated commitment to the important work of the SAB.

3.2 The Director-General highlighted the fact that the governmental experts who had been consulted concurred with the SAB that science and technology were advancing in areas relevant to the Chemical Weapons Convention (hereinafter "the Convention") at a significant pace. These experts thus provided confirmation of the importance of the work of the SAB. The Director-General also pointed out that matters the SAB will be considering and working on in the future fall into various categories. These include issues that should be kept under SAB review, where additional information and advice should be sought from the SAB, that should be reviewed by the Technical Secretariat (hereinafter "the Secretariat"), and that are pending decisions by the Executive Council (EC-56/2/Rev.1, dated 16 April 2009).

3.3 The Director-General thanked Harald Krug from Switzerland and Markus Pridöhl from Germany for sharing their knowledge on the basics and the toxicology of nanomaterials, and for their support to the work of the SAB.

4. AGENDA ITEM FOUR – Overview of developments at the OPCW since the last session of the Scientific Advisory Board

4.1 The Secretary gave a presentation to the SAB on developments at the OPCW since the SAB's Twelfth Session (which was held from 23 to 26 November 2008). The members were informed about the status of the destruction of Category 1 chemical weapons as at 28 February 2009. They were also briefed on the status of chemical

weapons abandoned by Japan on the territory of China, information about which is contained in "The Report of the Current Status of the ACW Projects in China (Reporting Period: From 1 July to 30 September 2008)" (EC-55/NAT.1, dated 20 October 2008).

4.2 The SAB was informed of the progress made on universality and of the fact that, as at 30 March 2009, there were 186 States Parties to the Convention. The Secretary also briefed the SAB on what the follow-up had been in relation to the Second Special Session of the Conference of the States Parties to Review the Operation of the Chemical Weapons Convention (hereinafter "the Second Review Conference"). In addition, the SAB was briefed on the financial status of its trust fund.

5. AGENDA ITEM FIVE – Introduction to nanoscience

Subitem 5(a): Presentation on the basics of nanotechnology (definitions, physico-chemical properties, and applications)

5.1 The joint IUPAC[1]/OPCW meeting on the impact of scientific developments on the Convention, held in 2007 in Zagreb, Croatia, considered nanotechnology to be one of the most important emerging technologies that may have an impact on the Convention. The members of the SAB were highly appreciative of a presentation by Markus Pridöhl on nanomaterials and nanotechnology. He provided a general overview, emphasising the differences in properties of nano-sized materials compared to micro- and macro-sized materials, and described numerous applications of this technology. His presentation is attached in Annex 2.

Subitem 5(b): Presentation on the toxicology of nanomaterials

5.2 A general concern about nanomaterials among the scientific community is their potential toxicity or their ability to enhance the toxicity of chemical substances. The SAB was highly appreciative of a presentation by Harald Krug on some of the characteristics of nanomaterials that might influence their toxicity. He briefed the SAB members on the specific transport, material, and surface principles of nanotechnology. It was suggested that, currently, there is a limited potential for this technology to be applied to the production of chemical weapons. A lively and detailed discussion ensued as to the possible threat that nanotechnology posed to the Convention. His presentation is attached in Annex 3.

Subitem 5(c): Discussion

5.3 No nanomaterials are currently known to have an intrinsic toxicity that might make them attractive for use in chemical weapons. The risk posed by nanomaterials to the Convention is, therefore, currently regarded as low. However, there is undoubted potential for nanotechnology to be misused—for example by providing enhanced delivery of toxic materials to their biological target or by protecting, by means of encapsulation, dispersed chemical agents from degradation (or weathering). The prevailing view of the SAB was that nanotechnology is unlikely to provide a dramatic improvement in the military utility of existing chemical agents, but it is possible that

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1 IUPAC = International Union of Pure and Applied Chemistry

this technology could be utilised in the development of new agents. Considerable potential exists, however, for nanotechnology to be used to improve defensive countermeasures—for example, in detection devices, protective equipment, and medical countermeasures. This potential is attracting increasing attention.

Subitem 5(d): Scientific Advisory Board recommendations

5.4 The SAB recommended that developments in nanoscience and nanotechnology continued to be carefully monitored. The SAB further recommended that potential applications for protective purposes be addressed in greater detail in a future session.

5.5 The SAB noted the overwhelming benefits of inviting experts in developing technologies to address the SAB and participate in the ensuing discussions, as an alternative to convening temporary working groups (TWGs).

6. AGENDA ITEM SIX – Scheduled chemicals, including ricin and saxitoxin

Subitem 6(a): Discussion

Ricin

6.1 As part of its continuing oversight of ricin, the SAB discussed a specific form of recombinant ricin (TTR-114) that is used for diagnostic purposes, and which, it was claimed, could be rendered inactive by the presence of an additional peptide linkage that may prevent separation of the A and B chains. This structure falls within the definition of ricin recommended by the SAB in a previous report (paragraph 3 of SAB-8/1, dated 10 February 2006 and Corr.1, dated 15 March 2006). The majority view was that such modifications should still be regarded as falling within the definition of ricin, but further information would be required before a modification to the SAB recommendation could be considered.

Saxitoxin

6.2 During this session, the SAB revived a previous discussion on the Chemical Abstract Service (CAS) number of saxitoxin (included in Schedule 1 as "saxitoxin dihydrate") in contrast to the different CAS number for the dihydrochloride salt, which is the form of saxitoxin that was previously weaponised (as TZ) on a small scale (paragraph 4.4 of SAB-8/1 and Corr.1).

6.3 Robert Mathews of Australia gave a briefing on the evolution of the nomenclature of saxitoxin, an issue that was relevant during negotiations at the Geneva Conference on Disarmament in the 1980s. A survey of the literature on the matter shows how the nomenclature of saxitoxin has changed since the 1960s. In particular, since the elucidation of the structure, the term "saxitoxin" has been used variously to describe the dihydrochloride salt of the molecule, or the free base, or its cation. More recently (and since the negotiations on the Convention were concluded in 1992), the nomenclature of saxitoxin has become more specific—distinctions are made between saxitoxin dihydrochloride and saxitoxin dihydrate. From the record of the negotiations, it appears that what negotiators had wanted to include in the schedules was the form of saxitoxin that had been weaponised in the past (the agent TZ, which

is the dihydrochloride salt), and other forms of weaponisable saxitoxin. During the negotiations held in Geneva, there were also discussions about whether saxitoxin should be included as a Schedule 1 or a Schedule 2 chemical; it was finally agreed to include it in Schedule 1. The presentation on saxitoxin is attached in Annex 4.

Subitem 6(b): Scientific Advisory Board recommendations

6.4 The SAB agreed to prepare a fact sheet on ricin in the intersessional period to facilitate further consideration of this matter when it meets for its Fourteenth Session.

6.5 The SAB agreed to prepare a fact sheet on saxitoxin in the intersessional period to facilitate further consideration during its Fourteenth Session of what constitutes saxitoxin, and whether it should be listed as a Schedule 1 or a Schedule 2 chemical.

7. AGENDA ITEM SEVEN – Review of operational requirements and technical specifications for inspection equipment

Subitem 7(a): Discussion

7.1 The SAB, at its Twelfth Session, was briefed by the Secretariat on the review of operational requirements and technical specifications for inspection equipment, as specified in C-I/DEC.71 and Corr.1, both dated 23 May 1997. The Secretariat was requested by the Second Review Conference (paragraph 9.147 of RC-2/4, dated 18 April 2008) to seek the advice of the SAB when reviewing these requirements and specifications. Accordingly, in order to facilitate the SAB's discussions on this matter, the Secretariat (by means of the SAB's Port@l website), provided a draft decision to it four weeks in advance, thus enabling it to consider various proposed revisions before discussions on this issue with relevant members of the Secretariat during its Thirteenth Session.

7.2 There was a preliminary discussion of the draft decision by SAB members, who were generally in agreement with the approach being adopted by the Secretariat and supportive of many of the proposed revisions. However, SAB members raised some questions in relation to this draft decision, especially in regard to advances in analytical instrumentation. These queries could not be addressed by the Secretariat, because the substantive officer concerned was not available.

7.3 In order not to unnecessarily delay the finalisation and adoption of this draft decision, the SAB members offered, during the intersessional period, to provide questions, comments, and any recommendations through an internet discussion group that would include appropriate members of the Secretariat, interested members of the SAB, and the TWG on sampling and analysis (S&A).

Subitem 7(b): Scientific Advisory Board recommendations

7.4 It was agreed that the internet discussion group would aim to finish its deliberations and provide any recommendations for changes to the draft decision by the end of June of this year.

8. AGENDA ITEM EIGHT – Consideration of the report of the meeting of governmental experts

The SAB took note of the summary of discussions of the meeting of governmental experts, which was held at OPCW Headquarters from 11 to 13 February 2009 (EC-56/2/Rev.1).

9. AGENDA ITEM NINE – Future work of the Scientific Advisory Board

Subitem 9(a): Agenda for the Fourteenth Session of the Scientific Advisory Board

9.1 The SAB discussed the agenda for its Fourteenth Session, currently planned to take place from 9 to 11 November 2009.

9.2 During its Fourteenth Session, the SAB will conclude its discussions on the issue of saxitoxin; a summary fact sheet will be prepared during the intersessional period and will be presented during this session.

9.3 The SAB will continue its discussions on ricin; a summary fact sheet will be prepared during the intersessional period and will be presented during this session.

9.4 The SAB will consider the report of the Fourth Meeting of the TWG on S&A; this meeting is currently scheduled to take place on 5 and 6 November 2009.

10. AGENDA ITEM TEN – ANY OTHER BUSINESS

Possible OPCW involvement in the proposed International Year of Chemistry

10.1 Robert Mathews brought the proposed International Year of Chemistry (to take place in 2011) to the attention of the SAB and suggested consideration of the possible involvement of the OPCW.

Joint meeting of the OPCW Scientific Advisory Board and the National Academy of Science/National Research Council Committee on Chemical Demilitarisation

10.2 Robert Gibson presented a proposal for a joint meeting of the SAB and the National Academy of Science/National Research Council Committee on Chemical Demilitarisation (NAS/NRC CCD), which could be held in Atlanta, Georgia, and which could be followed by a visit to Anniston, Alabama, in the United States of America. He indicated that such a meeting would be an opportunity for the members of the SAB to receive analyses and updates on the United States of America's chemical weapons destruction programme. It would also provide an occasion for the members of the SAB to visit the Anniston Chemical Agent Disposal Facility in Alabama. During the meeting, both groups would make presentations on their respective roles, functions, and future activities. The SAB requested the Secretary to take this matter up with the Director-General.

Terms of office of Scientific Advisory Board Members

10.3 The Secretary briefed the SAB on the follow-up on its recommendation to the Director-General to consider implementing a succession plan that would reduce the impact of the replacement of a large number of SAB members at once.

Departure of some members of the Scientific Advisory Board

10.4 The Chairperson of the SAB bade farewell to the six members who have completed their second term on the Board. He thanked them for their invaluable contribution to the work of the SAB.

11. AGENDA ITEM ELEVEN – Adoption of the report

The SAB considered and adopted the report of its Thirteenth Session.

12. AGENDA ITEM TWELVE – Closure of the Session

The Chairperson closed the Session at 17.20 on 1 April 2009.

Annexes:

Annex 1: List of Participants in the Thirteenth Session of the Scientific Advisory Board

Annex 2 (English only, unedited): Presentation by Dr Markus Pridöhl: Nanotechnology: An Introduction

Annex 3 (English only, unedited): Presentation by Professor Harald Krug: Nanomaterials and Health-Related Effects: Possible Use as Chemical Weapons?

Annex 4 (English only, unedited): Presentation by Dr Robert Mathews on Saxitoxin

Annex 1

LIST OF PARTICIPANTS IN THE THIRTEENTH SESSION OF THE SCIENTIFIC ADVISORY BOARD

	Participant	State Party
1.	Rolando A. Spanevello	Argentina
2.	Robert Mathews	Australia
3.	Herbert de Bisschop	Belgium
4.	Zhiqiang Xia	China
5.	Danko Škare	Croatia
6.	Jean-Claude Tabet	France
7.	Detlef Männig	Germany
8.	László Halász	Hungary
9.	Mahdi Balali-Mood	Iran (Islamic Republic of)
10.	Alberto Breccia Fratadocchi	Italy
11.	Shuzo Fujiwara	Japan
12.	Abdool Kader Jackaria	Mauritius
13.	José González Chávez	Mexico
14.	Godwin Ogbadu	Nigeria
15	Bjørn-Arne Johnsen	Norway
16.	Titos Quibuyen	Philippines
17	Young-chul Lee	Republic of Korea
18.	Igor V. Rybalchenko	Russian Federation
19.	Philip Coleman	South Africa
20.	Miguel A. Sierra	Spain
21.	Stefan Mogl	Switzerland
22.	Valery Kukhar	Ukraine
23.	Robin Black	United Kingdom of Great Britain and Northern Ireland
24.	James Robert Gibson	United States of America

Annex 2

PRESENTATION BY DR MARKUS PRIDÖHL
NANOTECHNOLOGY: AN INTRODUCTION

OPCW

Nanotechnology
An introduction

Dr. Markus Pridöhl
March, 2009

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Agenda Nanotechnology

- Company policy
- Market data and definitions
- Nanomaterials
- Technical applications
- Medical applications

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Evonik policy for sustainable nanotechnology

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Excerpt

- Degussa regards nanotechnology as an **opportunity** to develop new products and efficient scientific and technological solutions, and so make essential contributions towards **environmental protection, health and product quality**.
- Degussa produces and markets nanomaterials only if, according to the latest available research, they can be manufactured and applied in a **safe and environmentally** compatible manner.
- Our research, production and application of nanomaterials are guided by the findings of **scientific investigation** into hazard and risk assessment.
- Nanoscale materials are not fundamentally new, and have been examined in epidemiological and toxicological studies. To enable the risk assessment to be refined we **support** the establishment of **new investigation methods**.
- We develop tailor-made nanomaterials for our customers in line with the chemical industry's '**Responsible Care**' initiative.
- We encourage **open discussion** on the opportunities and the risks of nanotechnology. We therefore support all measures that serve to provide **consumers with comprehensive and proper information**.

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Market data and definitions

Nanotechnology

Definitions 1

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ISO TC 229 – Current draft of PG 5 Core Terms

nanotechnology
the application of scientific knowledge to control and utilize matter at the **nanoscale**, where size-related properties and phenomena can emerge.

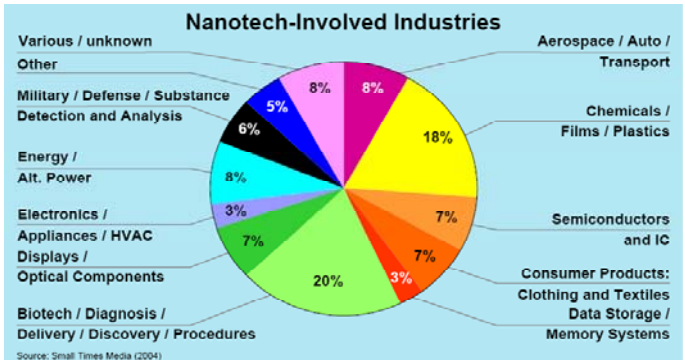
ISO TS 27687

nanoscale:
size range from approximately 1 nm and 100 nm

How small is the nanoscale?

Diameter of the earth = 13.765,3 km

Segmentation of nanotechnolgy by industry



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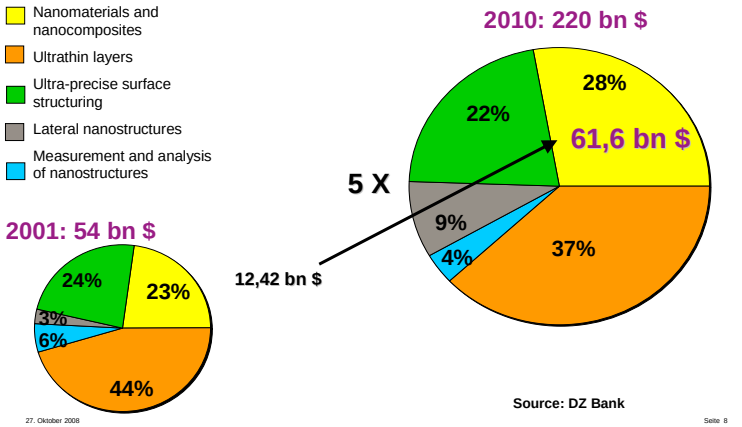
Technical segmentation of nanotechnology



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Business Expectations Nanotechnology

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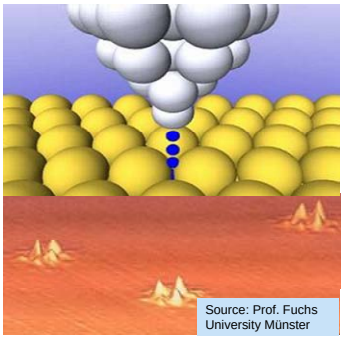
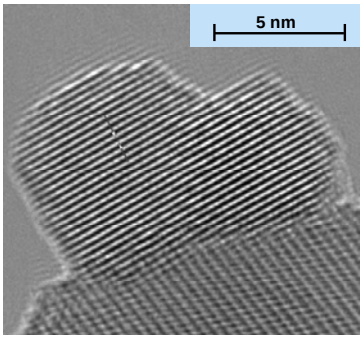
Scientific milestones initiate nanoscience and nanotechnology

Atomic Force Microscopy AFM



Electron Force Microscopy REM/TEM



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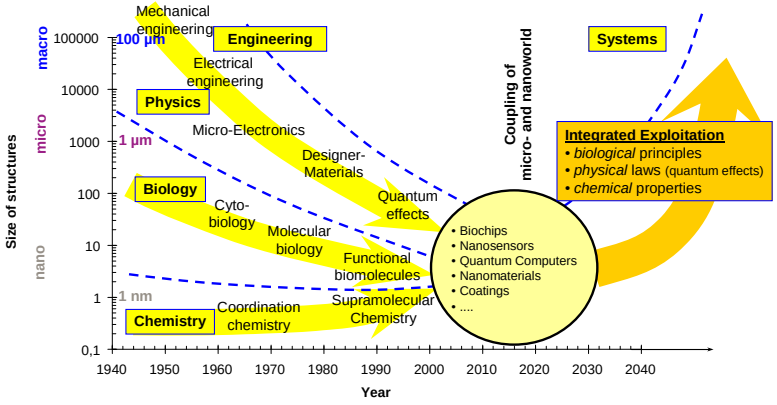
Right time for exploring nanotechnology



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… but not everything called *nano* is meant to be nanotechnology

Indian car Tata Nano

Apple´s i-pod nano

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What are nanomaterials?

Nanotechnology

Definitions 2

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ISO TC 229 – current draft of PG 5 Core Terms

nanomaterial
material having a geometric or structural feature in the nanoscale

NOTE Examples include nanocrystalline materials, nanoparticle powder, materials with nanoscale precipitates, nanoscale films, nanostructured objects, nano-porous objects, and materials with nanoscale textures on the surface.

EU Cosmetic Directive (25.3.2009)

nanomaterial

an insoluble or biopersistant and intentionally manufactured material with one or more external dimensions, or an internal structure, on the scale from 1 to 100 nm

Hierarchy and definitions
nanomaterial, nanoparticle, nanostructured

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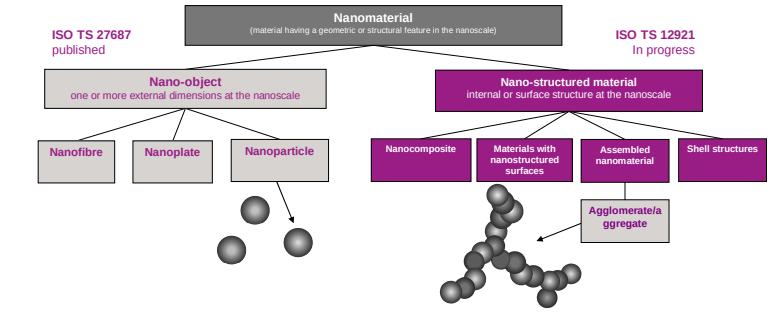
ISO



nanoscale
smaller than 100 nm

macroscale
larger than 100 nm

Selected terms and definitions 3
according to ISO TS 27687

Terms and definitions

2.1 **nanoscale**: size range from approximately 1 nm and 100 nm

2.2 **nano-object**: material with one, two or three external dimensions at the nanoscale

3.2 **nanoparticle**: particle with all three external dimensions at the nanoscale.

3.3 **nanoplate**: nano-object with one external dimension at the nanoscale and the two other external dimensions significantly larger.

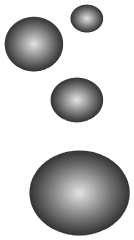
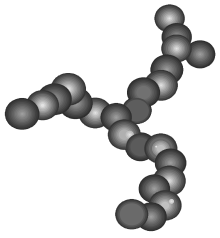
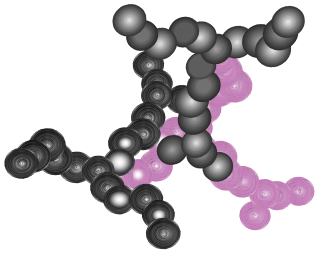
3.4 **nanofibre**: nano-object with two similar external dimensions at the nanoscale and the third dimension significantly larger.

3.5 **nanotube**: hollow nanofibre

4.1 **agglomerate**: collection of loosely bound particles or aggregates or mixtures of the two where the resulting external surface area is similar to the sum of the surface areas of the individual components

4.2 **aggregate**: particle comprising strongly bonded or fused particles where the resulting external surface area is significantly smaller than the sum of calculated surface areas of the individual components.

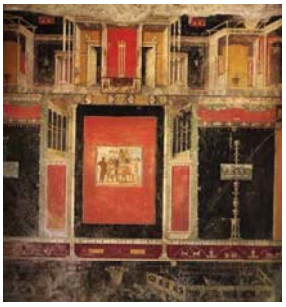
Nanomaterials

Nano-object	Nanostructured	
Nanoparticles	**Aggregate**	**Agglomerates**
	Chemically bonded	Van der Waals forces
		
100 nm	**Fused, tightly bonded primary particles**	**Particles or aggregates stick together**

Half life time of isolated 20 nm particles above 1 mg/m³ < 3,8 s

Preining (1998) The physical nature of very, very small particles and its impact on their behaviour. J. Aerosol Sci. 29, 481-495

Nanomaterials are not new



Early 1st century

Pompeji

Paintings with soot

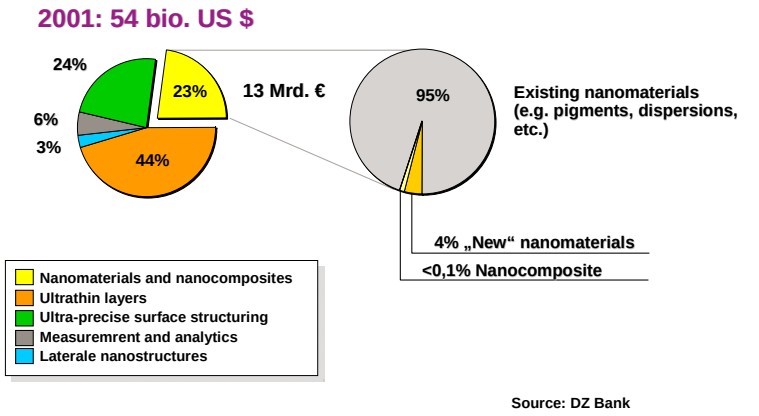
Quelle: Prof. Kreibig University Aachen

Early 18st century

Thurn & Taxis

Gold Rubin Glas (Gold Nano Cluster)

Manufactured nanomaterials are not new



Source: DZ Bank

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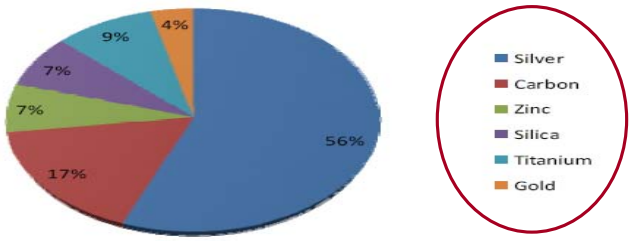
Nanomaterials on the market are mainly passive, nano-structured materials

Analysis of all entries of the Woodrow Wilson database according to materials (August 2008)



Active nanostructures (nano-devices) are still essentially at research level, though, sometimes, already at a very advanced phase of development, as in the case of medical products.

Source: EC, FramingNano-Project, E. Mantovani et al. (2009), Mapping Study on Regulation & Governance of Nanotechnologies; see: http://www.framingnano.eu

We are allways exposed to ultrafine particles (airborne particles < 100 nm)

II. Natural sources

- vulcanoes
- sea aerosols
- erosion
- Fire
- ….

II. Anthropogenic sources

- technical combustion
- candle lights
- cooking
- barbecue
- smoking
- traffic
- …..

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Effects

Nanotechnology

New properties at the nanoscale

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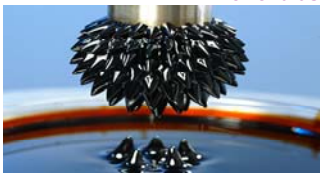
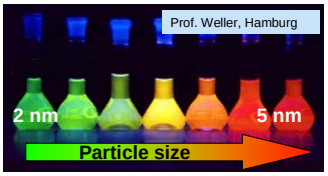
Advantages of nano ....

- Reinforcement (elastomers, polymers)
- Superparamagnetism (Fe_2O_3)
- Improved composites (CNT in polymers)
- Higher catalytic activity ($Pt@Al_2O_3$)
- Improved polishing properties (CeO_2 für CMP)
- Lowered sintering temperatures (ZrO_2)
- Increased luminescence (Si, GaAs)
- Transparent UV protection (ZnO,TiO_2)
- Transparent conductive electrodes (ITO)
- Nanotube transistors

Ferrofluids



Fluorescence of CdTe



Quantum Size Effect

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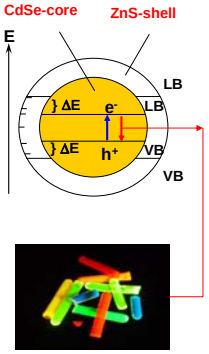
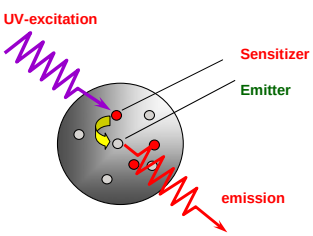
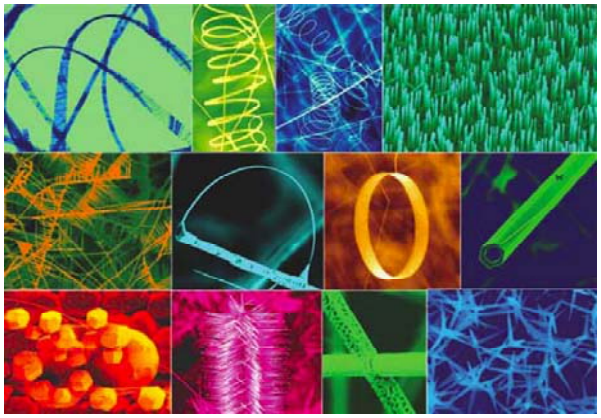


Picture: Prof. Weller, Univ. Hamburg



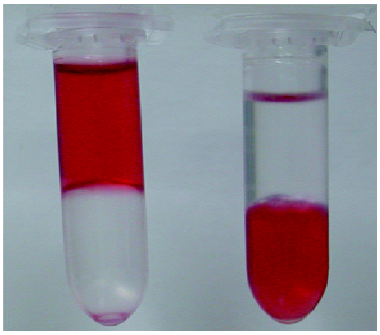
Picture: Nanosolutions

Chemistry, size and structure matter
Example: Zinc Oxide nanostructures



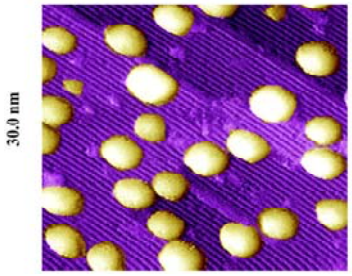
Materials Today June 2004. Zhong Lin Wang, Georgia Institute of Technology

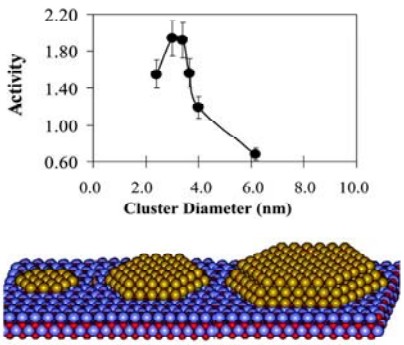
Example gold: Colour



Example gold: Catalysis
gold nanoclusters on TiO_2

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





From Valden et al. (1998) Science; Bell (2003) Science.

Technical applications

Nanotechnology

Nanomaterials in daily life









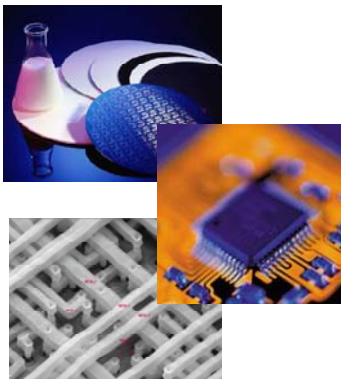
„Antique“ Carbon Black for reinforcement and pigmentation



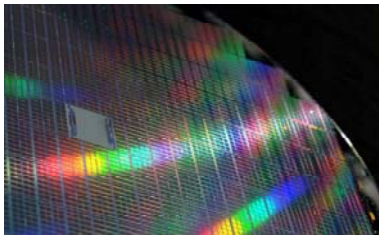


Nanomaterials for reinforcement of elastomers

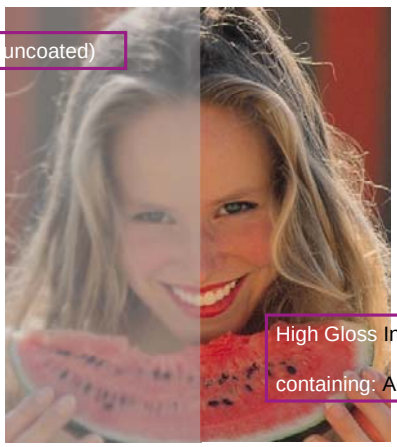
No computers without nanomaterials



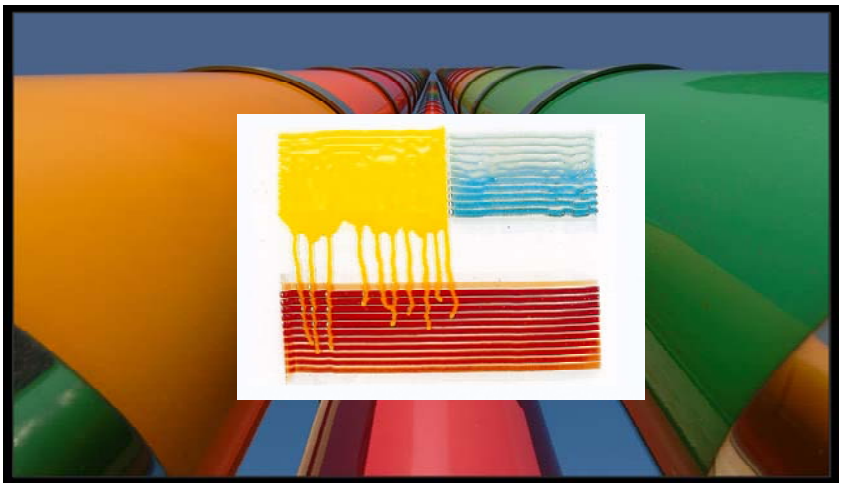
- **Polishing of wafers (CMP) in computer chip production**
- **Polishing lenses for photolithography**



Nanostructured surfaces for printing

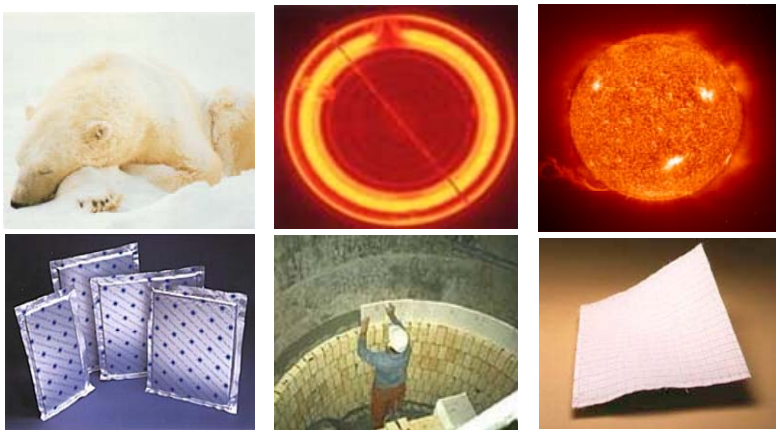


Nanomaterials for rheology control



Nanomaterials for scratch resistance coatings

Nanomaterials for thermal insulation



Nanomaterials for fluidizing powders

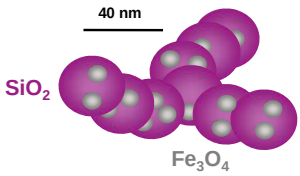
EVONIK INDUSTRIES

Nanotechnology saves ressources

EVONIK INDUSTRIES

Boosted adhesives

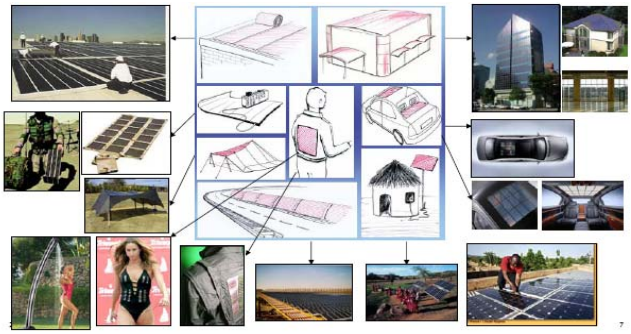
EVONIK INDUSTRIES



MagSilica® - Superparamagnetic essential

- Boosted bonding of non-metallic parts by heating of MagSilica® containing adhesive
- Faster processing by accelerated curing of elastomers, adhesives and other polymers
- Smart debonding

Organic photovoltaic



OLED-Technology

2006 2007

Small displays

2008

Medium and large displays

2010

Lighting

2012

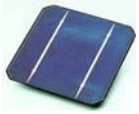
Flexible displays

Transparent Conductive Oxides as electrodes (indium tin oxide)

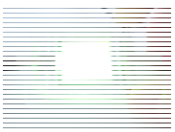
Many fast growing technologies depend on transparent conductive oxides:

Source: NEC.

Display-technology like LCD- and PDP-screens.



Photovoltaics



OLEDs

RE-Flex® Glass
Low E Glass solar control

Nanotechnology saves ressources and replaces toxic substances

Protection of light metals with sol gel coatings

- **Substitution of chrome (VI)**
- **Thinner coating, less material consumption**
- **Improved properties**

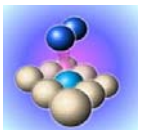


German award for material efficiency 2004
German ministry for economy

Catalysts relieve environment

Catalysts in the chemical industry

- About 80% of all chemical processes use at least one catalytic step
- Catalysts save energy, increase selectivity and productivity, reduce side products and waste

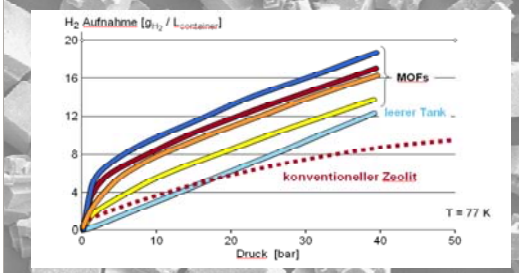


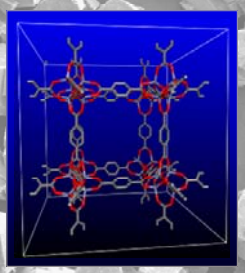
Automotive catalysts

- Nanoscale precious metals on ceramic supports (Pt, Rh, Pd)
- 90% less emission of hydrocarbons, carbon monoxide and nitrogen oxides
- Nanotechnology reduces catalyst consumption

Hydrogen storage for fuel cells

Metal Organic Frameworks



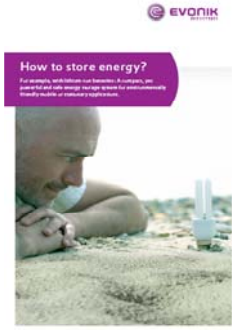


Source: BASF

Lithium batteries for hybrid cars and electric vehicles

Lithium batteries as buffers for regenerative energy sources

Nanomaterials addressing global challenges



Personal Care Products

- Skin care
- Sun protection
- Cleansing products
- Antiperspirants
- Hair care
- Color cosmetics

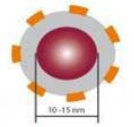
Nanomaterials for personal protection
Nanostructured TiO_2

Medical applications

Nanotechnology

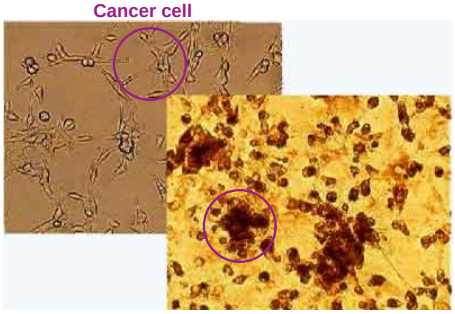
Engineered nanoparticles for cancer therapy (hyperthermia)

EVONIK INDUSTRIES



Fe_3O_4 core
coating
functionalization

Cancer cell

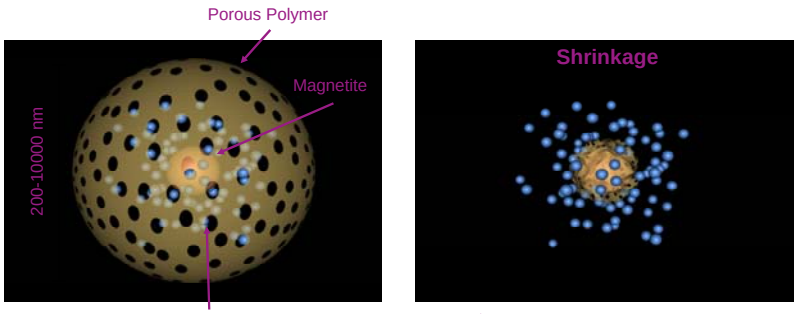


Cells after incorporating modified Fe_3O_4-particles

with courtesy **mag*force*® Nanotechnologies AG**

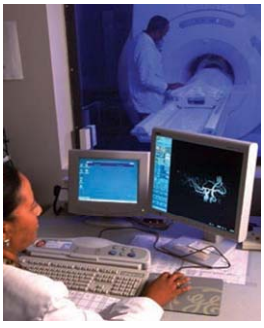
Engineered nanoparticle for inductive drug release

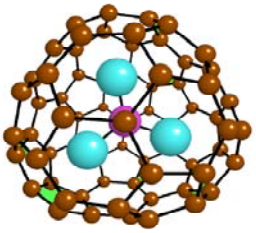
EVONIK INDUSTRIES

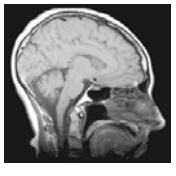


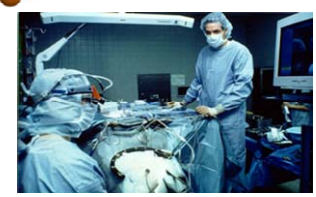
Metallofullerenes as contrast agents

EVONIK INDUSTRIES

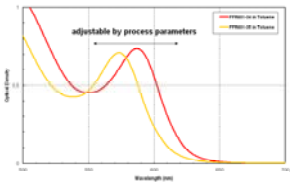




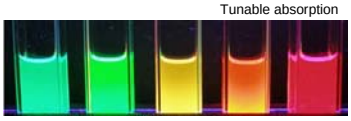




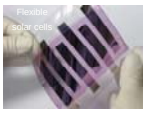
Quantum dots for biolabelling



Tunable absorption



- OLED's and flexible displays
- Functional polymer composites
- New flexible solar cells
- Biolabeling
- Security labels
- Printable electronics
- IR-emitting ink/pigments
- Information technology



Summary

Environment

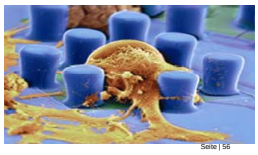
- Catalysts
- Solar cells
- Insulation/nanofoams
- Electrical vehicles
- Batteries and fuel cells
- Lighting
- Light weight construction
- Reinforcement
- Water/soil purification
- Thermoelectric efficiency

Personal benefit

- UV protections
- Cosmetics
- Self cleaning textiles
- Scratch resistant coatings
- Ink jet printing
- Printable electronics for displays
- Electronics

Health

- Cancer therapy
- Drug delivery
- Diagnostics
- Biocompatible implants
- Neuro-implantats



OECD Working Party on Manufactured Nanoma
Chemicals Committee

Objective

Nanotechnologies are likely to offer a wide range of economic benefits. However, unlocking this potential will require a responsible and co-coordinated approach to ensure that potential safety issues are being addressed at the same time as the technology is developing. As a part of the Chemical Programme, this programme focuses on the implications of the use of nanomaterials for human health and environment safety, focussing on testing and assessment methods.

Organization

- 8 strategic groups
  - SG1 Development of an OECD database on EHS research
  - SG2 EHS research strategies on manufactured nanomaterials
  - **SG3 Safety testing of a representative set of man. nanomaterials**
  - **SG4 Manufactured nanomaterials and test guidelines**
  - SG5 Cooperation on voluntary schemes and regulatory programs
  - SG6 Cooperation on risk assessment and exposure measurement
  - SG7 The Role of Alternative Methods in Nano Toxicology, founded 11-07, UK
  - **SG8 Exposure Measurements and Exposure Mitigation**
- Next meeting June 11-13th 2008, Paris

BackUp

Nanotechnology

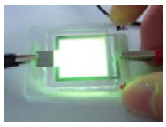
Transparent Conductive Oxides as electrodes (indium tin oxide)

Many fast growing technologies depend on transparent conductive oxides:

Source: NEC.

Display-technology like
LCD- and PDP-screens.

Photovoltaics



OLEDs

RE-Flex® Glass

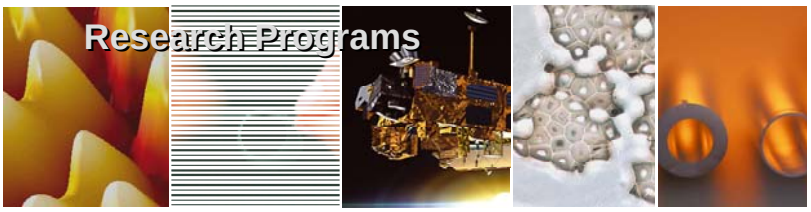
Low E Glass
solar control

The existing export control regimes (incl. dual-use and catch-all-clauses) are sufficient to avoid improper use of nanomaterials. There is no need for additional / special regulations.

Annex 3

PRESENTATION BY PROFESSOR HARALD KRUG

NANOMATERIALS AND HEALTH-RELATED EFFECTS: POSSIBLE USE AS CHEMICAL WEAPONS?



- Nanotechnology
- Adaptive Material Systems
- Natural Resources and Pollutants
- Materials for Health & Performance
- Materials for Energy Technologies

EMPA
Materials Science & Technology

2009
Den Hague

Materials-Biology Interactions Laboratory 3

Nanotechnology – A Lot of Hype Over Almost Nothing?

Charma Stang and Lorraine Sheremeta

Military uses of nanotechnology – It is predicted that the most significant early applications of nanotechnology will occur in the military. The large amount of nanotechnology research investment in the U.S. Department of Defense and the creation of new institutes reflect the suggestion that nanotechnology will be key in determining the balance of global power in the future. Examples of military applications include intelligent sensors, 'smart' munitions and missiles, and improved combat gear. There is concern that the technology may be used by rogue states or terrorist groups.

Health Law Review (2006) Vol. 15 (1) 53-55

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Limiting Military Uses of Nanotechnology and Converging Technologies

Jürgen Altmann, 2005

In conferences of the NNI, various goals were given for "National Defense" or "National Security" uses of NT and CT (Roco/Bainbridge 2001: ch. 2, Roco/Bainbridge 2003: section E). Among them are:

- **miniature sensors, high-speed processing and communication,**
- **sophisticated virtual reality systems for training,**
- **uninhabited combat vehicles,**
- **higher performance in military platforms,**
- **improved chemical/biological/nuclear sensing and casualty care,**
- **improved systems for nuclear non-proliferation monitoring and management,**
- **devices for control of nuclear systems,**
- **enhancement of human performance,**
- **a brain-machine interface.**

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Chemical Warfare

- Blood Agents (CN)
- Blister Agents (Arsine)
- Nerve Agents (Tabun)
- Pulmonary Agents (Phosgene)
- Incapacitating Agents (QNB)
- Riot Control Agents (CS Aerosol)

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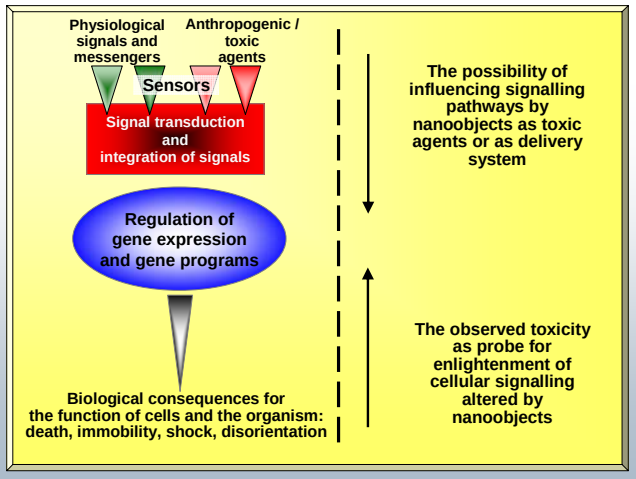
Effects and Consequences



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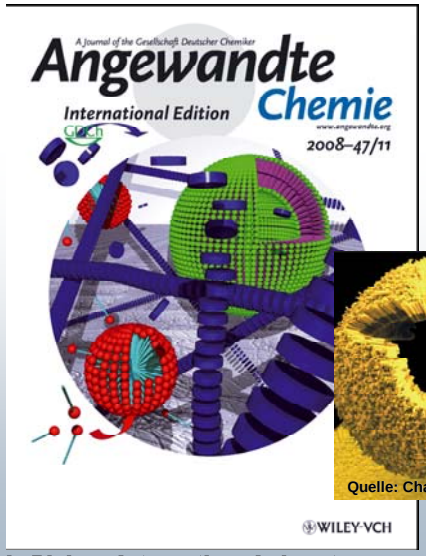

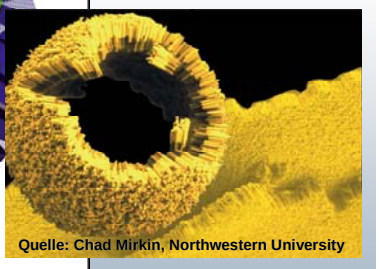

Quelle: Chad Mirkin, Northwestern University

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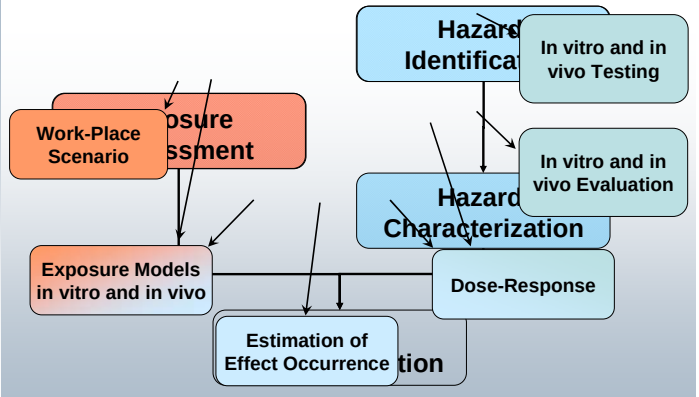
Risk Assessment



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Three Principles of Nanotoxicology

- The Transport-Principle
- The Surface-Principle
- The Material-Principle

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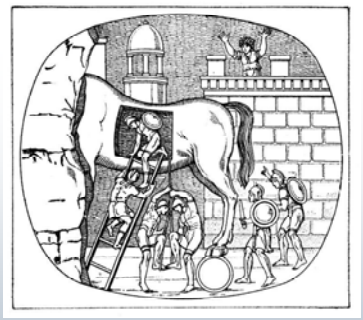
The Transport-Principle



The Trojan Horse like Uptake

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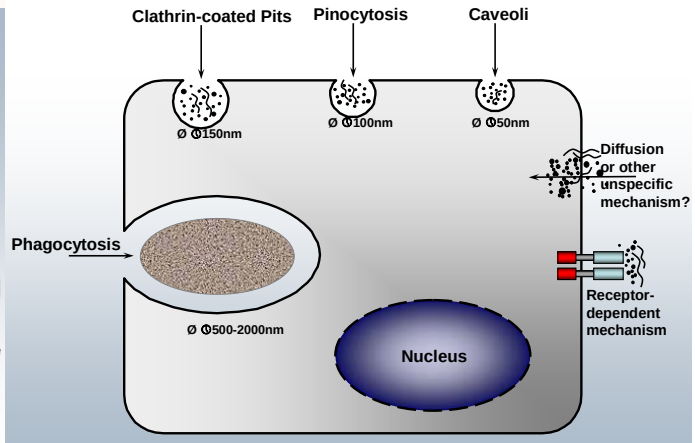
Principles of Particle Uptake



Krug et al. (2006) Toxicity of Nanomaterials – New Carbon Conformations and Metal Oxides. In: Nanomaterials – Toxicity, Health and Environmental Issues, Series title: Nanotechnology for the Life Sciences (Kumar, C., ed.) Wiley-VCh, Weinheim, pp. 153-185.

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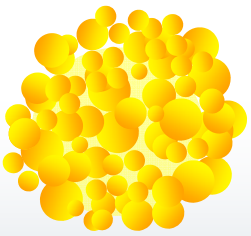
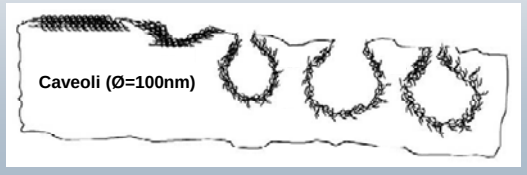
Size matters!





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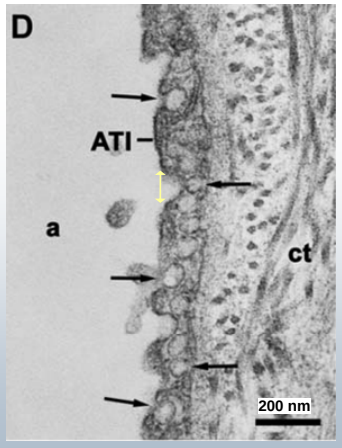
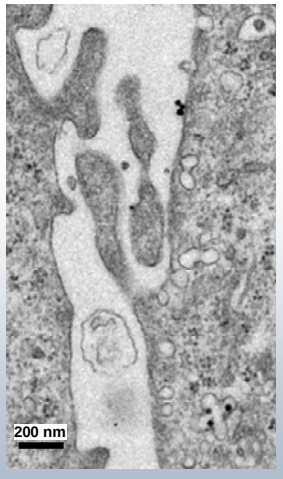
Caveoli – Nanoparticle as Shuttle



Steimer, A., Haltner, E., Lehr, C.M. (2005) J. Aerosol Med. 18, 137-182.



NanoMMUNE: A549-Lung Epithelial Cells exposed to Nanoparticles

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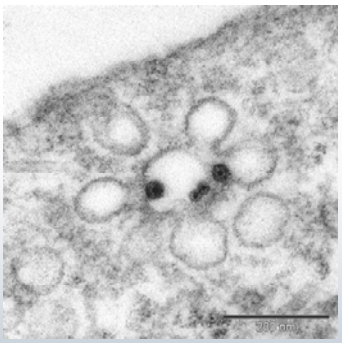
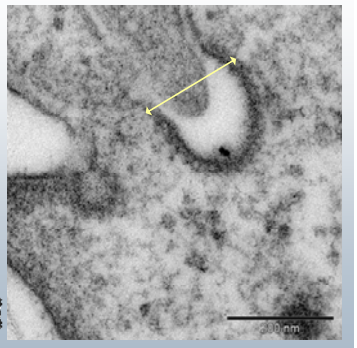
Materials-Biology Interactions Laboratory 14

Caveoli – Nanoparticle as Shuttle



↔ 10 nm Ironoxide Core
⟷ 22 nm SiO_2 Shell



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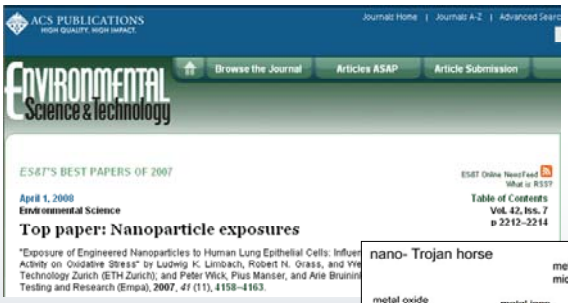
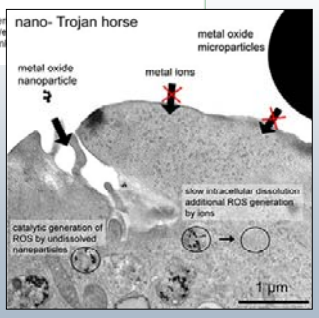
↔ 10 nm Ironoxide Core
⟷ 38 nm SiO_2 Shell

NANOMMUNE

Materials-Biology Interactions Laboratory 15





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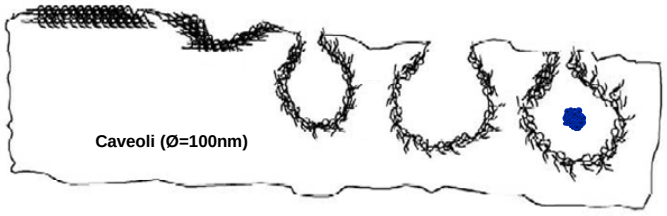
Size matters!



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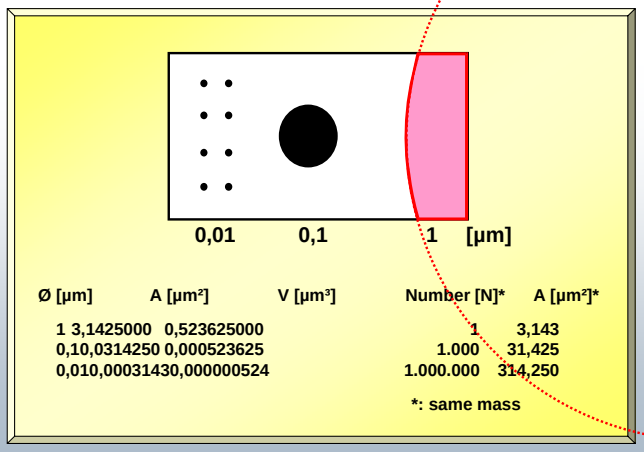
The Surface-Principle



Ø [µm]	A [µm²]	V [µm³]	Number [N]*	A [µm²]*
1	3,1425000	0,523625000	1	3,143
0,10,0314250		0,000523625	1.000	31,425
0,010,00031430		0,000000524	1.000.000	314,250

*: same mass

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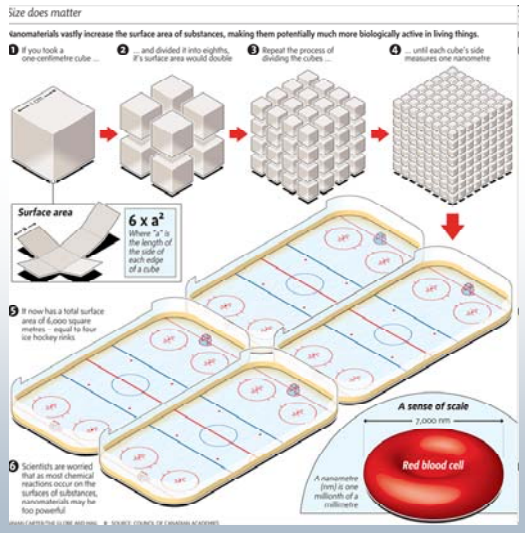

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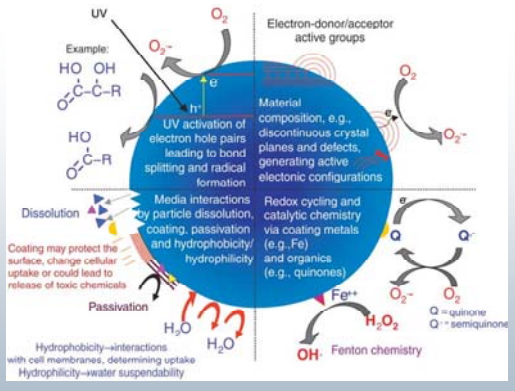
Surface Properties!



Nel et al. (2006) Science 311: 622-627

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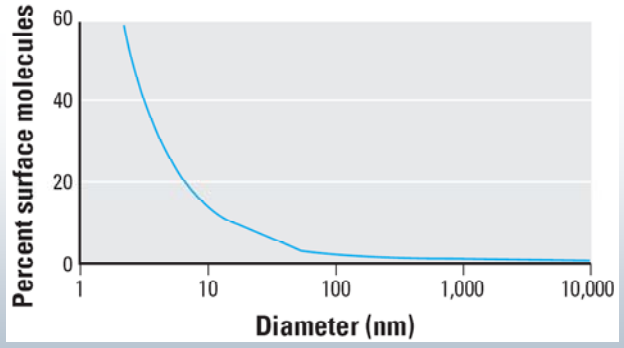
Surface to Volume Ratio



courtesy: H. Fissan, Duisburg)

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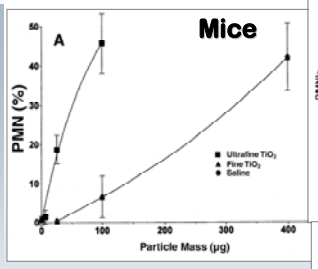
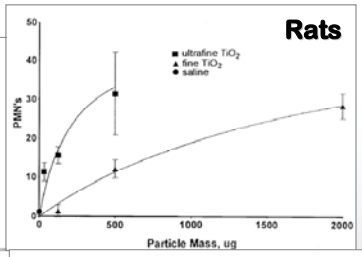
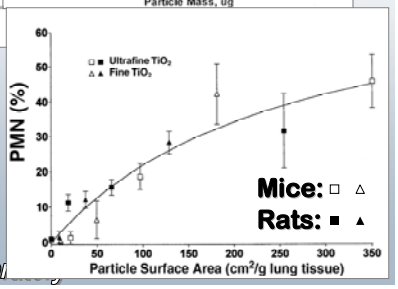
Acute Pulmonary Effects of Ultrafine Particles







Pulmonary inflammatory response (percentage of PMNs) in rats and mice 24 hours after intratracheal instillation of fine (~250 nm) and ultrafine (~20 nm) TiO_2 particles.

Oberdörster et al., 2000: HEI-Report 96
Oberdörster 2001: Int. Arch. Occup. Environ. Health, 74, 1-8

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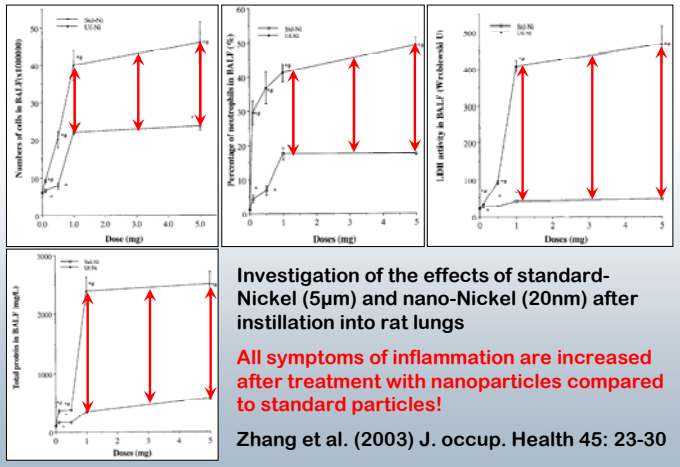
Nano versus Mikro

Nickel



Investigation of the effects of standard-Nickel (5µm) and nano-Nickel (20nm) after instillation into rat lungs

All symptoms of inflammation are increased after treatment with nanoparticles compared to standard particles!

Zhang et al. (2003) J. occup. Health 45: 23-30

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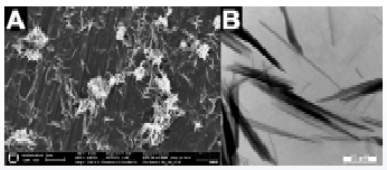
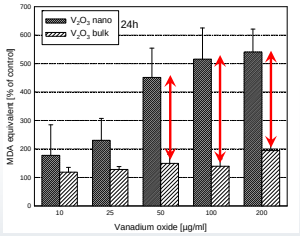
Nano versus Mikro

Vanadium



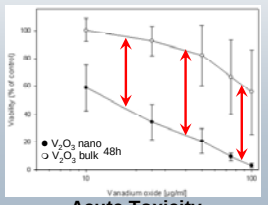


Vanadiumoxide (V_2O_3)
bulk versus nano
smaller diameter – larger surface
in comparison to bulkmaterial

higher lipid peroxidation

higher cytotoxicity

Oxidative Stress – Lipidperoxidation



Acute Toxicity

Wörle-Knirsch, J.M. et al. (2007) Environ. Sci & Technol. 41, 331-336.

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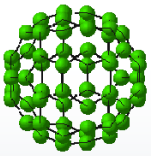
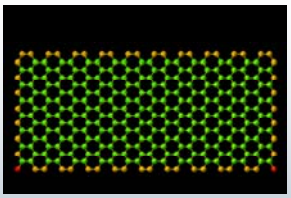
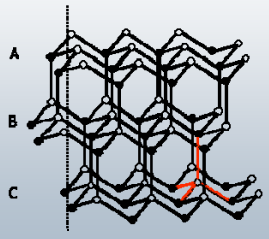
The Material-Principle







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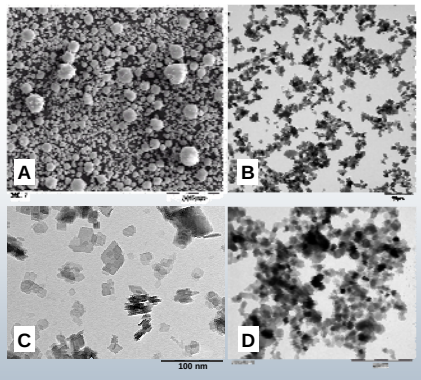
Nanoparticles

Examples from Electron Microscopy

nanoCare



A) $BaSO_4$

B) CeO_2

C) AlOOH

D) TiO_2 P25

Pictures: NanoCare Database

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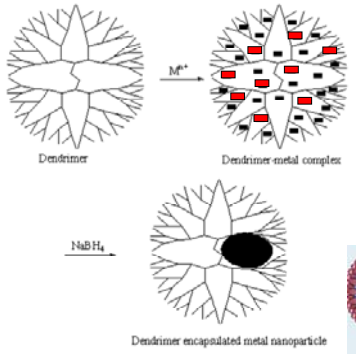
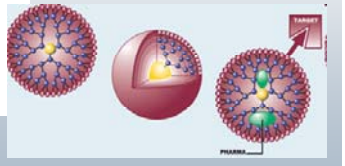
Possibilities for Nano-Weapons



Packages of toxic compounds for inhalation or distribution via the drinking water



http://jbc.kiku.dk/links/Research/Research.html

www.the-scientist.com/article/display/14895/

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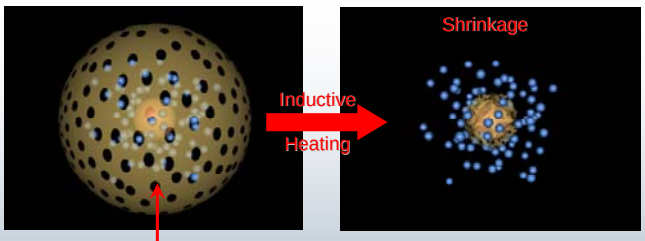
Drug Release ⊂ Toxin Release?



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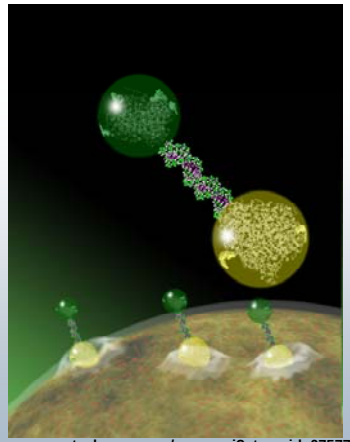
Possibilities for Nano-Weapons

Simple “Robot” systems or receptor coupling structures to alter cell behaviour – distributed via the air?

www.ediblecomputerchips.com/Applications.htm



www.nanotech-now.com/news.cgi?story_id=07577

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Recent Literature – rather Protection than Health Threat

Joshi, K.A., Prouza, M., Kum, M., Wang, J., Tang, J., Haddon, R., Chen, W., Mulchandani, A. (2006): V-type nerve agent detection using a carbon nanotube-based amperometric enzyme electrode. **Anal. Chem.** 78, 331-336.

Khan, M.A., Kerman, K., Petryk, M., Kraatz, H.B. (2008): Noncovalent modification of carbon nanotubes with ferrocene-amino acid conjugates for electrochemical sensing of chemical warfare agent mimics. **Anal. Chem.** 80, 2574-2582.

Liu, G., Lin, Y. (2006): Biosensor based on self-assembling acetylcholinesterase on carbon nanotubes for flow injection/amperometric detection of organophosphate pesticides and nerve agents. **Anal. Chem.** 78, 835-843.

Ma, X., Zhu, T., Xu, H., Li, G., Zheng, J., Liu, A., Zhang, J., Du, H. (2008): Rapid response behavior, at room temperature, of a nanofiber-structured TiO2 sensor to selected simulant chemical-warfare agents. **Anal. Bioanal. Chem.** 390, 1133-1137.

Pavlov, V., Xiao, Y., Willner, I. (2005): Inhibition of the acetycholine esterase-stimulated growth of Au nanoparticles: nanotechnology-based sensing of nerve gases. **Nano Lett.** 5, 649-653.

Robinson, J.T., Perkins, F.K., Snow, E.S., Wei, Z., Sheehan, P.E. (2008): Reduced graphene oxide molecular sensors. **Nano Lett.** 8, 3137-3140.

Virel, A., Saa, L., Pavlov, V. (2009): Modulated growth of nanoparticles. Application for sensing nerve gases. **Anal. Chem.** 81, 268-272.

Wang, F., Gu, H., Swager, T.M. (2008a): Carbon nanotube/polythiophene chemiresistive sensors for chemical warfare agents. **J. Am. Chem. Soc.** 130, 5392-5393.

Wang, J., Timchalk, C., Lin, Y. (2008b): Carbon nanotube-based electrochemical sensor for assay of salivary cholinesterase enzyme activity: an exposure biomarker of organophosphate pesticides and nerve agents. **Environ. Sci. Technol.** 42, 2688-2693.

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Conclusions I

- **Are nanoparticles intrinsic toxic?**

  No, but toxicity depends on material, surface chemistry, reactivity, uptake and transport, accumulation

- **Do nanomaterials have the potency to be a "chemical weapon"?**

  Yes, the chance to enclose drugs within a nanocapsule is the same as for a toxic compound, thus nanocontainer my be a Trojan Horse for toxins

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Conclusions II

- **Of course, every technology has the risk to be misused**
- **Particles may be toxic *per se* or function as transporter systems**
- **Most nanoparticular systems today have only low toxic potency**
- **Military use of nanomaterials/nanostructures described more often for devices like sensors or technical equipment or for human enhancement**
- **Research on health, environmental and societal side effects of nanomaterials has to be an essential part within all funding programs**

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„Dubious“ Nano-Application

12. September 2007
Russia tested the strongest conventional bomb ever in the world!!!

Blasting material: **3 Tons of Nanopowder !!!**

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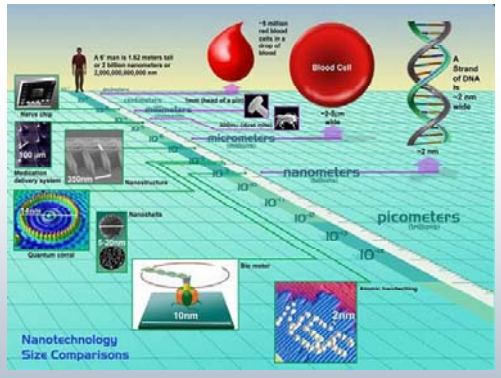

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Annex 4

PRESENTATION BY DR ROBERT MATHEWS ON SAXITOXIN

Saxitoxin and the CWC:

Personal Recollections and Reflections

Bob Mathews
Head, NBC Arms Control, DSTO.
Associate Professor, Law School, University of Melbourne.
Australia
OPCW SAB Meeting April 2009

Views presented do not necessarily reflect views of Australian Government.

Saxitoxin ??

- What is ‘Saxitoxin’ ??
- OR
- What do chemists mean when they refer to ‘Saxitoxin’ ??
- AND
- Which form(s) of Saxitoxin did CWC negotiators want covered in Schedule 1 ??
- AND
- What should SAB do about it??

Reality of CWC Negotiations

- Negotiation of Schedules was 'not a pretty picture'
  - many diverging views as indicated by many square brackets and footnotes in Rolling Text right to the 'end game' in 1992.
- Based on politics as well as risk assessment.
- A lot of 'horse-trading'
  - e.g. my delegation will accept chemical A on Schedule 1 if your delegation will accept chemical B on Schedule 2 and Chemical C is not listed at all.
- Resulting CWC Schedules not necessarily totally logical.

Development of CWC Schedules

- In early 1980s, agreement on three groups of chemicals to be covered by routine monitoring
  - Super toxic lethal chemicals
  - Other lethal chemicals
  - Other harmful chemicals.
- By late 1980s, three Schedules were being developed based on 'risk to the Convention' and 'industrial usage' rather than just 'toxicity'.
  - Guidelines for each Schedule were also being developed.

Development of CWC Schedules (cont)

- In 1985, draft lists of chemicals were being compiled
- Agreement that chemical names be in accordance with IUPAC Nomenclature
- A proposal by some delegations that the chemical structure also be included to avoid ambiguities

Salts of Saxitoxin

- As discussed at the SAB-8 meeting in February 2006, listing of CAS No of Saxitoxin dihydrate (free base) in CWC Text does not help.
  - especially as the CAS No for saxitoxin dihydrate was not added to the CWC 'Rolling Text' until after the understanding on the role of CAS Nos as an 'identification aid' rather then 'unique identifier' was reached.

Nomenclature of 'Saxitoxin

- It is useful to review the way that the name 'saxitoxin' has evolved in recent decades as the molecular structure of 'saxitoxin' has become better understood.

Saxitoxin

$C_{10}H_{17}O_4N_7 \cdot 2HCl$ MW 372

Paralytic poison from Alaska butter clams (*Saxidomus gianteus*), toxic mussels (*Mytilus californianus*), and the plankton *Gonyaulax catenella*. $[\alpha]_D$ $+130^\circ \pm 5^\circ$.

Schantz *et al.*, *J. Am. Chem. Soc.*, 1957, **79**, 5230, 5235; *Can. J. Chem.*, 1961, **39**, 2117.
Schuett, Rapoport, *J. Am. Chem. Soc.*, 1962, **84**, 2266.

From: Dictionary of Organic Compounds, 4th Ed, 1965

SAXITOXIN

Paralytic shellfish poisoning has been recognized as a clinical entity since the mid-nineteenth century; eating poisonous shellfish of various kinds has frequently caused mass-poisoning. The toxic principle involved was not isolated until World War II, when a programme for that purpose was initiated[15] within the US BW effort [30, 95].

While the structure of the active principle, called *saxitoxin* by some, has still not been definitely established—it has the empirical formula $C_{10}H_{17}N_7O_4 2HCl$, and seems to contain a novel pyrrole [1,2*c*]pyrimidine ring system [96]—

From: SIPRI 'CBW BLUE BOOKS', Vol. I, 1971

Table 1.1. Continued

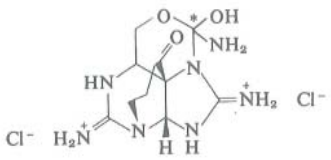
Chemical name	Common name[c]	Remarks
Lethal toxins		
Botulinal toxin A	*X*	Stockpiled after WWII
Ricin	*W*	Developmental WWII agent; about 1 700 kg produced in the USA
Saxitoxin (Shellfish poison)	*TZ*	Stockpiled in small quantities since WWII

Table 1.5. Some US CB weapons, 1940–1972[a]

Type and designation of weapon	Agent	Payload (kg)	Mechanism
Ground and naval weapons			
Weapons for the individual soldier			
Grenade, frangible, M1	AC	0.3	Impact
Grenade, riot, M6A1	CN-DM	0.11	Burning
Grenade, riot, M7A1	CN	0.17	Burning
Grenade, riot, M7A3	CS	0.12	Burning
Grenade, riot, M25A2	CS1	0.05	Bursting
Special munition, M1	TZ	..	Flechette

From: SIPRI 'CBW BLUE BOOKS', Vol. II, 1973.

In a further communication from Professor Rapoport's laboratory (Wong *et al.*, 1971b) determination of the complete structure of saxitoxin has been reported to be **107**. A remarkable feature of this unique molecule is a carbon (shown by asterisk) that is linked to two nitrogen and two oxygen atoms. This achievement ranks as one of the significant milestones in the chemistry of marine natural products and brings to successful conclusion a difficult structural investigation that had its beginnings some thirty years earlier.

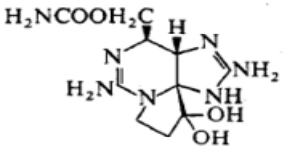


107

From: Paul J. Scheuer, Chemistry of Marine Natural Products, 1973

Saxitoxin **S-00132**

[35523-89-8]



Absolute configuration

$C_{10}H_{17}N_7O_4$ M 299

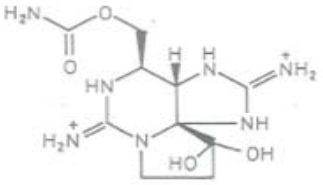
Paralytic poison from Alaska butter clams (*Saxidomus giganteus*), toxic mussels (*Mytilus californianus*) and the plankton *Gonyaulaux cantenella*. Noncryst. $[\alpha]_D$ +130°.

▷Extremely toxic, among the most toxic substances known. UY8708500.

Schantz, E.J. *et al*, *Biochemistry*, 1966, **5**, 1191
Bordner, J. *et al*, *J. Am. Chem. Soc.*, 1975, **97**, 6008 (*cryst struct*, *pmr*, *cmr*)
Tanino, H. *et al*, *J. Am. Chem. Soc.*, 1977, **99**, 2818 (*synth*)

From: Dictionary of Organic Compounds, 5th Ed, 1982

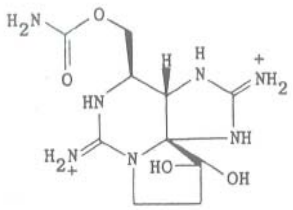
Saxitoxin: a neuromuscular blocking agent, which prevents nerve transmission by blocking sodium pores in postsynaptic membranes. S. is produced by dinoflagellates of the genus *Gonyaulax*, found in "red tides". S. accumulates in shellfish that ingest the dinoflagellates, hence cases of poisoning from eating the Californian sea mussel *(Mytilus californianus)*, the Alaskan butterclam *(Saxidomus giganteus)* and the scallop.



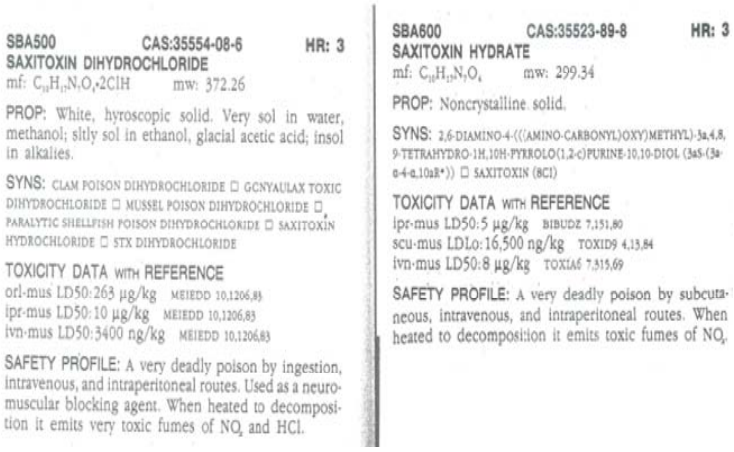
Saxitoxin

Concise Encyclopedia Biochemistry, 2nd Edition, 1988

8344. Saxitoxin. Mussel poison; clam poison; paralytic shellfish poison; gonyaulax toxin; STX. $[C_{10}H_{17}N_7O_4]^{2+}$; mol wt 299.30. Powerful neurotoxin produced by the dinoflagellates *Gonyaulax catenella*, or *G. tamarensis*, the consumption of which causes the California sea mussel *Mytilus californianus*, the Alaskan butterclam *Saxidomus giganteus* and the scallop to become poisonous:



Merck Index, 11th Edition, 1989
NB. CAS No. given as [35554-08-6]



SBA500 **CAS:35554-08-6** **HR: 3**
SAXITOXIN DIHYDROCHLORIDE
mf: $C_{10}H_{17}N_7O_4 \cdot 2ClH$ mw: 372.26

PROP: White, hyroscopic solid. Very sol in water, methanol; sltly sol in ethanol, glacial acetic acid; insol in alkalies.

SYNS: CLAM POISON DIHYDROCHLORIDE □ GONYAULAX TOXIC DIHYDROCHLORIDE □ MUSSEL POISON DIHYDROCHLORIDE □ PARALYTIC SHELLFISH POISON DIHYDROCHLORIDE □ SAXITOXIN HYDROCHLORIDE □ STX DIHYDROCHLORIDE

TOXICITY DATA WITH REFERENCE
orl-mus LD50:263 µg/kg MEIEDD 10,1206,83
ipr-mus LD50:10 µg/kg MEIEDD 10,1206,83
ivn-mus LD50:3400 ng/kg MEIEDD 10,1206,83

SAFETY PROFILE: A very deadly poison by ingestion, intravenous, and intraperitoneal routes. Used as a neuromuscular blocking agent. When heated to decomposition it emits very toxic fumes of NO_x and HCl.

SBA600 **CAS:35523-89-8** **HR: 3**
SAXITOXIN HYDRATE
mf: $C_{10}H_{17}N_7O_4$ mw: 299.34

PROP: Noncrystalline solid.

SYNS: 2,6-DIAMINO-4-(((AMINO-CARBONYL)OXY)METHYL)-3a,4,8,9-TETRAHYDRO-1H,10H-PYRROLO(1,2-c)PURINE-10,10-DIOL (3aS-(3a-α-4-α,10aR*)) □ SAXITOXIN (8CI)

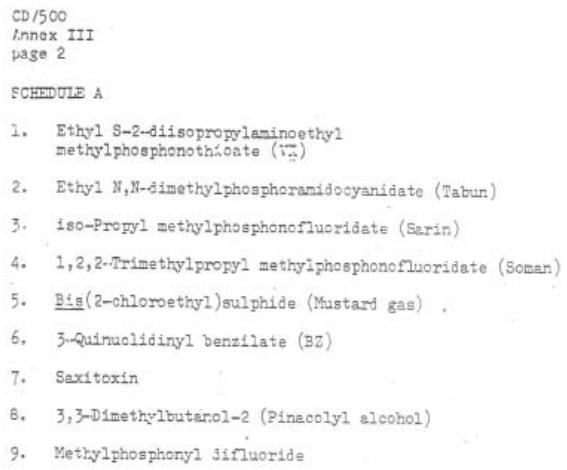
TOXICITY DATA WITH REFERENCE
ipr-mus LD50:5 µg/kg BIBUDZ 7,151,80
scu-mus LDLo:16,500 ng/kg TOXID9 4,13,84
ivn-mus LD50:8 µg/kg TOXIA6 7,515,69

SAFETY PROFILE: A very deadly poison by subcutaneous, intravenous, and intraperitoneal routes. When heated to decomposition it emits toxic fumes of NO_x

From: Richard J Sax Sr, Sax's Dangerous Properties of Industrial Materials, 9th Edition, 1995.

Saxitoxin - CWC

- Proposed by US in CD/500 in the 'STLC category'
- Understanding in 1984 was that US wanted the weaponised forms of Saxitoxin (including TZ) covered.
- Subsequent understanding (by me) was that other negotiators also wanted weaponised forms of Saxitoxin covered.
- There were different views where Saxitoxin should be placed (Schedule 1 or Schedule 2 with low threshold)



CD/500
Annex III
page 2

SCHEDULE A

1. Ethyl S-2-diisopropylaminoethyl methylphosphonothioate (VX)
2. Ethyl N,N-dimethylphosphoramidocyanidate (Tabun)
3. iso-Propyl methylphosphonofluoridate (Sarin)
4. 1,2,2-Trimethylpropyl methylphosphonofluoridate (Soman)
5. Bis(2-chloroethyl)sulphide (Mustard gas)
6. 3-Quinuclidinyl benzilate (BZ)
7. Saxitoxin
8. 3,3-Dimethylbutanol-2 (Pinacolyl alcohol)
9. Methylphosphonyl difluoride

From: CD/500 (US Draft Text), 18 April 1984

CD/952
page 52
Appendix I

[8. Saxitoxin 1/ [35523-89-8)]

[9. Ricin 1/]

1/ A view was expressed that, since toxins are covered by the Biological and Toxin Weapons Convention, they should not be covered by the Chemical Weapons Convention. Another view was expressed that since toxins are toxic chemicals, they would automatically be covered by the Chemical Weapons Convention. In addition, a view was expressed that relevant toxins should also be considered for inclusion in Schedule 2 part B. Another view was expressed that saxitoxin and ricin should only be considered examples of toxins that could be included in Schedule 1.

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8. Saxitoxin 1/ (35523-89-8)

9. Ricin 1/

1/ The placement of toxins on the Schedule requires further consideration. A view was expressed that relevant toxins should be considered for inclusion in Schedule 2 part B, for example, in a separate section with lower thresholds for declaration and verification compared with other chemicals on that Schedule. Another view was expressed that different toxins could be included in different Schedules in accordance with the guidelines for those Schedules.

From: Rolling Text, CD/1108, 27 August 1991

Concluding comments

- Salts of Saxitoxin' issue has caused considerable confusion.
- Part of problem is lack of clarity in nomenclature
  - At least a considerable number of negotiators considered that the name 'Saxitoxin' included all forms of saxitoxin suitable for chemical weapons (including TZ and other salts)
  - As discussed in 2006, the dihydrate CAS Number does not help.
- In my view, this issue should be revisited by the SAB.
- One possible solution: Saxitoxin, including all forms suitable for chemical weapons purposes, be relocated to Schedule 2A (with suitably low threshold) by amendment of CWC.